TAR PRODUCTION IN COAL PYROLYSIS - THE EFFECT OF CATALYSTS, PRESSURE AND EXTRACTION

by

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ABSTRACT

The pyrolysis of coal has been studied with specific interest in increasing the yield and improving the quality of the liquid product.

The results of experiments in two pyrolysis reactors are reported: a quartz fluidised bed reactor for flash pyrolysis at atmospheric pressure, and a fixed bed "hot-rod" reactor for pyrolysis at elevated pressure. The pyrolysis of Linby coal, a low rank, high volatile bituminous coal is studied as the base-case. A number of other British hard coals and a Turkish lignite are considered for comparison. The effect of three parameters on pyrolysis is considered: pressure, catalysts and extraction.

Increases of inert gas pressure on cause a decline in the tar yield from the pyrolysis of Linby coal. This decline is due to tar molecules undergoing secondary reactions which form char and gas, the extents of which are enhanced at elevated pressure due to the increased resistances to the mass transfer of volatiles.

The effect of elevated hydrogen pressure on the tar yield is dependent on the sweep gas velocity. At a high sweep gas velocity, increasing the hydrogen pressure from 1 bar to 50 bar increases the tar yield from the pyrolysis of Linby coal from 18% to 22.5%. When a low sweep gas velocity is used, the effect of increased hydrogen pressure is to diminish the tar yield. The higher gas velocity promotes mass transport from the particle surface to the gas bulk ie. the evaporation step. At low gas flowrates, the evaporation step is slow, and hence the volatiles are more liable to secondary reactions, which reduce the tar yield.

Impregnation with zinc chloride causes an increase in the flash pyrolysis tar yield from Linby coal at atmospheric pressure. This is a reversal of the trend observed in pyrolysis at low heating rate. Zinc bromide and iodide, and aluminium chloride have similar effects to zinc chloride. Other Lewis acids however, notably tin (II) chloride, cause the tar yield from flash pyrolysis to decrease. Impregnation with zinc chloride also causes an increase in the flash pyrolysis tar yield from other hard coals, however the effect on the flash pyrolysis of a lignite is to cause the tar yield to decline. In the flash pyrolysis of hard coals, zinc chloride appears to act as a hydrogenation catalyst, utilising hydrogen native to the coal to increase the yield and improve the quality of the tar.

In hydropyrolysis, impregnation with zinc chloride also causes a substantial increase in the tar yield for all hard coals studied. Zinc chloride also causes a small increase in the tar yield from the hydropyrolysis of the lignite.

Impregnation with tin chloride has a similar effect to zinc chloride in hydropyrolysis, causing a substantial increase in the tar yield. Furthermore, both catalysts have a similar effect on the tar structure, causing increases in both mean molecular weight and aromaticity.

Chloroform extraction prior to flash pyrolysis causes a substantial reduction in the tar yield, the size of which is substantially greater than the amount of extract removed. In the flash pyrolysis of Linby, 25 hour chloroform extraction, removing 2% extract, causes the tar yield to decline from 31% to 17%. A similar effect is noted for all the hard coals considered, and also for the lignite. In promoting tar formation in flash pyrolysis, it is proposed that the extractable material may be playing a role as a hydrogen donor/shuttler, or may be playing a physical solvating role, stabilising free-radicals.

In hydropyrolysis, chloroform extraction also as a significant effect on the tar yield. For Linby coal 25 hour chloroform extraction causes the tar yield to decline from 22.5% to 16% at 50 bar. A similar effect is observed for the of the other hard coals studied, however extraction has no discernable effect on the hydropyrolysis of the lignite. In the hydropyrolysis of hard coals, the chloroform extractable material appears to act as an intermediary in the action of the high pressure hydrogen. It is proposed that this action involves a hydrogen shuttling mechanism.

Chloroform extraction also has an effect on the action of zinc chloride in pyrolysis. Impregnation of chloroform extracted Linby coal with $ZnCl_2$ causes the tar yield from flash pyrolysis to decline, which suggests that the extractable material acts as an intermediary in the action of the catalyst. However in hydropyrolysis, no such effect is noted.

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CHAPTER 1 INTRODUCTION

1.1 COAL CONVERSION

The conversion of coal to liquid fuels has received considerable attention for many years. Liquefaction of coal was used to produce motor fuels on a large scale during World War II in Germany. Until recently however, interest in coal conversion to liquid fuels had diminished due to the cheaper and more easily available sources of crude oil. However the rapid rise in the price of crude oil in the early seventies, coupled with the increased awareness of the limited nature of oil resources, has led to increased research efforts into coal conversion to liquid fuels.

There are many processes by which coal can be converted to liquid fuels. These generally belong to one of the classes listed below in order of decreasing severity:

(1) Gasification/synthesis
(2) Pyrolysis/hydropyrolysis
(3) Liquefaction
(4) Extraction

Gasification/synthesis involves complete the gasificaton of coal producing carbon monoxide and hydrogen, followed by catalytic synthesis by, for example, the Fischer-Tropsch process producing hydrocarbons and the higher alcohols. Pyrolysis is the thermal degradation of

coal in an inert gas producing a volatile fraction, composed of tar and gas, and char. Hydropyrolysis involves pyrolysis under high pressure hydrogen. Liquefaction involves the thermal degradation of coal in the presence of a vehicle solvent at high pressure, and sometimes in the presence of the presence of high pressure hydrogen (or a CO/H_2O mixture) and also sometimes a catalyst. Extraction is carried out under high pressure using a solvent, which may be in a supercritical state, to remove a fraction of the coal. Many liquefaction processes are sometimes also termed extraction, though liquefaction processes are usually carried out at a higher temperature than extraction. In pyrolysis, liquefaction and extraction, subsequent catalytic hydrotreatment is required to upgrade the primary liquid product.

Currently, the sole commercial scale plant converting coal to liquid fuels is the SASOL plant in South Africa, which uses the gasification/ Fischer-Tropsch synthesis route. Recently, the National Coal Board has commenced the construction of a pilot plant at the Point of Ayr Colliery which will convert coal to liquid fuels using a liquefaction based process. Numerous other coal conversion pilot plants are also in existance.

All processes aim to increase the fraction of hydrogen present in the liquid compared to the amount present in the parent coal, and to improve the structure by diminishing the aromaticity, polarity and heteroatom

content. Typically the hydrogen to carbon atomic ratio of bituminous and lower rank coal is between 0.6-1.0. For liquid fuels the required value is between 1.7 and 2.2. In liquefaction, the H/C ratio is increased by hydrogen transfer to the coal from the solvent and/or the gaseous hydrogen, and during the upgrading step. In pyrolysis, the hydrogen present in the parent coal is concentrated in the volatile phase, with the solid product being depleted of hydrogen.

All the conversion processes listed above involve, to a varying extent, pyrolysis as the initial step. Pyrolysis is also the initial step in coal gasification and coal combustion. The study of pyrolysis is therefore not limited to its use as a conversion process per se, but also as a means to elucidate information about the initial stages of thermal decomposition of coal, in many conversion processes, and also information about coal structure.

The work described in this thesis is an investigation of coal pyrolysis with a primary interest in increasing the yield and improving the quality of the liquid product. However, the work is essentially fundamental in nature, and attempts to understand the mechanisms occurring in pyrolysis with respect to the effect of catalysts and high pressure hydrogen. The study therefore has applications in other aspects of coal conversion and utilisation.

1.2 NATURE OF THIS PROJECT

The objective of the work described in this thesis, was to investigate the effect of three parameters on coal pyrolysis. These parameters are:

(1) Gas Pressure
(2) Catalysts
(3) Extraction

The effect of gas pressure on pyrolysis, especially in a hydrogen atmosphere, is confusing. Although many workers have attempted to use high pressure hydrogen to increase liquid yields in pyrolysis, this effect has not consistently been observed (Howard, 1980). The effect of pressure on coal pyrolysis in both inert and hydrogen atmospheres is investigated in this project.

Many catalysts have been used in coal conversion processes. In this study the effect of Lewis acid type catalysts on coal pyrolysis and hydropyrolysis is examined. This aspect of the project follows up the work of Kandiyoti and co-workers (1984).

The effect of extraction of coal with an mild solvent has been shown to have a substantial effect on the behaviour of coal in several thermal processes (Brown and Waters, 1966a; Vahrman, 1970; Larsen and co-workers, 1980). In this project, the effect of extraction of coal with chloroform prior to pyrolysis and hydropyrolysis is

investigated.

The effect of these parameters on the pyrolysis of a number of different hard coals and a lignite is examined. Two pyrolysis reactors are used: a quartz fluidised bed reactor, of the type used by Tyler (1979), for flash pyrolysis experiments at atmospheric pressure; and a fixed bed reactor for pyrolysis at elevated pressure. An existing fluidised bed reactor (Weerasinghe, 1982) was modified for the experiments performed in this study, while the high pressure reactor used was designed and constructed as part of the project.

Structure of this thesis

The following three chapters (Chapters 2 to 5) of this thesis review the existing literature, examining various aspects of coal conversion. The remaining chapters (chapters 6-9) describe the experimental methods used, and present and discuss the results obtained.

Chapter 2 considers the nature and origin of coal and the fundamentals of coal pyrolysis. The nature of coal is considered on macroscopic and microscopic scales. The structure of coal on a molecular scale is discussed, examining the macromolecular nature of coal, and the chemical structures which make up that macromolecule. The fundamentals of coal pyrolysis are then considered. Firstly the primary pyrolytic reactions are examined,

together with the experimental parameters which affect the rate and extent of these reactions. The primary parameters considered are peak temperature, heating rate, nature of the ambient gas, and coal rank. The mass transfer of volatiles in pyrolysis is then discussed, in the context of the secondary reactions occurring during volatiles transport, and the parameters which affect these reactions. The secondary parameters considered are gas pressure, particle size and reactor geometry.

Chapter 3 is concerned with coal hydropyrolysis. The known effects of high pressure hydrogen on pyrolysis are discussed, with a primary interest in the effect of high pressure hydrogen on the tar yield.

Chapter 4 examines the known effects of catalysts on coal conversion processes. The influence of Lewis acid type catalysts on coal liquefation, carbonisation and flash pyrolysis is discussed. The mechanism by which Lewis acids act in these processes is then considered.

Chapter 5 is concerned with the known effects of coal extraction on the thermal degradation of coal. The influence of extractable material on the coking properties of coal, and on coal liquefaction and slow pyrolysis is discussed.

Chapters 6 describes the design of the fluidised bed reactor and its peripherals. The procedure used in pyrolysis experiments is also described, as are the

modifications made to this reactor in this study. The results of pyrolysis experiments performed in this apparatus are presented and discussed in Chapter 7. Experiments were performed to examine the effect of impregnation with Lewis acid catalysts, and extraction with chloroform on the flash pyrolysis of Linby coal. Experiments were also performed on Canakkale Can, a lignite, and on three other hard coals.

Chapter 8 describes the design of the high pressure reactor and the associated high pressure gas circuit. The experimental procedure used in pyrolysis experiments in the high pressure reactor is also described. Experiments were performed to examine the effect of elevated gas pressure on the pyrolysis of Linby coal under both helium and hydrogen. The effect of impregnation with Lewis acid catalysts and extraction with chloroform is also studied. The hydropyrolysis of two other hard coals and a lignite are also examined. The results of these experiments are presented and discussed in chapter 9.

The conclusions of this study are summarised in Chapter 10.

In addition, the techniques used in the analysis of coal derived liquids, and in studies of catalyst distribution in coals and chars are described in Appendix I, while detailed experimental results, which are not presented in Chapters 7 and 9, are tabulated in Appendices II and III.

CHAPTER 2 COAL PYROLYSIS

This chapter discusses firstly the origin and structure of coal. The pyrolysis of coal is then discussed. The nature of pyrolytic reactions and the experimental parameters which affect the rate and extent of these reactions in terms of the pyrolysis products is discussed. Following this, the mass transfer of volatiles is discussed, in the context of the secondary reactions occurring during the transport of volatiles, and the parameters which affect these reactions.

2.1 THE NATURE OF COAL

Coal is a generic term applied to a wide variety of sedimentary rocks, which consist primarily of organic material, together with a smaller quantity of inorganic mineral matter. The organic material is thought to originate from plants, which have decomposed and coalified to form coal. The inorganic material orginates from minerals and sediment deposited in the decomposing plant material. The nature of this mineral matter was discussed by Mraw and co-workers (1983).

2.1.1 THE ORIGIN OF COAL

Coal is considered to have been formed from plant material being deposited in swamps, subsequently undergoing bacterial decomposition to form peat. Peat

then underwent coalification which increased carbon content and aromaticity, and decreased the amount of oxygen present. The coalification process was a combination of the effects of high pressure (upto 1500 bar) and moderate temperature (200-250^{o}C) over a considerable period of time (up to 300 million years). The combination of conditions during coalification differed for coal from different seams, and has a great influence on the properties of the coal formed. The properties of the coal are also influenced by the nature of the plant life from which coal was formed. The rank of coal is a measure of the extent of coalification, higher rank coals being more aromatic, and containing more carbon, less oxygen, and above a certain level, less hydrogen. Coalification represents a transition to a more ordered, layered aromatic structure, ultimately towards graphite. The geochemical origin of coal was discussed in more detail by Given (1984).

Coal is highly heterogeneous, on a macroscopic scale, on a microscopic scale, and on a molecular scale. The nature of coal on both macroscopic and microscopic scales is discussed below, while the molecular structure of coal is discussed in the following section.

On a macroscopic scale, coal has a banded appearance. These bands consist of irregular alternating layers of differing appearance and composition, and represent successive layers of deposited matter. It has been

recognized for a considerable time that there are four components to this banded structure, these being vitrain, clarain, durain and fusain, according to terminology of Stopes (1919), which is now generally accepted. Vitrain is the bright shiny major constituent of Northern hemisphere coals, occurring in bands 2-10mm thick. Clarain is less shiny than vitrain, though still classified as bright. Durain is dull in appearance with a hard, granular texture. Fusain is also dull black. These components are usually refered to as lithotypes.

On a microscopic scale, these lithotypes are seen to be a complex aggregate of different constituents. These microscopic constituent are more commonly known as macerals, and have been internationally classified (International Handbook of Coal Petrography, 1963; 1971; 1975). Particular macerals and maceral groups tend to be associated with particular lithotypes. For example vitrinite is generally associated with vitrain, exinite (liptinite) with clarain, and inertinite with fusain and durain. Differing classifications are made for bituminous and brown coals. Table 2.1 presents a summary of macerals and maceral groups.

These macerals are thought to originate from different plants and parts of plants or from plants which have undergone a different degradation route. For example, resinite, a maceral of the Liptinite group, is thought to originate largely from plant resins; whereas fusinite, a maceral of the inertinite group, is thought

to originate from charred or charcoal-like plant material, formed during pre-historic forest fires.

Brown coals and lignites				Bituminous		
Maceral group	Maceral subgroup	Maceral	Maceral type	Maceral type	Maceral	Maceral group
HUMINITE	Humotelinite	Textinite	Texto-ulminite	Telinite 1	Telinite	VITRINITE
		Ulminite	Eu-ulminite	Telinite 2		
	Humodetrinite	Attrinite			Vitrodetrinite	
		Densinite				
		Gelinite	Levigelinite	Desmocollinite Telocollinite	Collinite	
	Humocollinite	Corpohuminite	Porigelinite Phlobaphenite Pseudo-phlobaphenite	Gelocollinite Corpocollinite		

Coals of all ranks

Maceral group	Maceral
Liptinite	Sporinite Cutinite Resinite Suberinite Alginite Liptodetrinite Bituminite Fluorinite Exudatinite
Inertinite	Fusinite Semifusinite Macrinite Micrinite Sclerotinite Inertodetrinite

Table 2.1 Summary of macerals and maceral groups for coal (Given, 1984).

Furthermore, these different maceral groups have distinctly different behaviour in thermal decomposition. For example, only vitrinite and liptinite (exinite) exhibit a tendency to coke, ie. develop plasticity and swell, while inertinite shows no tendency to develop plasticity. The properties of the individual maceral groups are dependent on rank, and hence not all vitrinite macerals demonstrate coking behaviour. The nature of coal macerals and their reactivity in coal liquefaction has been discussed by Given (1984).

2.1.2 MOLECULAR STRUCTURE OF COAL

It is widely thought that coal has a macromolecular structure, with a small fraction of free molecules of low molecular weight (<700 a.m.u) trapped in the structure. The following section will consider the molecular nature of coal with regard to the physical nature of the coal macromolecule, the chemical nature of the coal macromolecule, and the nature of the low molecular weight extractable material.

2.1.2.1 THE PHYSICAL NATURE OF THE COAL MACROMOLECULE

The agreed macromolecular type structure of coal can be considered to be polymeric in nature, consisting of a large number of different monomer units randomly distributed in the macromolecular structure (Wender and co-workers, 1980).

Recent studies of the physical nature of the coal macromolecule have used conventional polymer theory to explain the physical characteristics of coal, particularly the effect of polar solvents in causing coal to swell. Stress-strain measurements and solvent swelling studies have been used to model coal structure. Much of this work has been reviewed by Given (1984). The models developed in these studies describe the macromolecular structure of coal as either a cross-linked gel with rubbery charactersitics (Larsen, 1985), or as a macromolecular plastic (Brenner, 1985). The principal difference between these models is in the interpretation of solvent swelling measurements and observations.

Both models consider the coal macromolecule to consist of a series of aromatic clusters, joined together by linkages, with cross-links, ie locations where a cluster is bound to more than two others, further binding the structure together. Larsen estimated the molecular weight between cross links (M_c) from solvent swelling measurements in pyridine, using the Flory-Rehner equation developed from the theory of rubber elasticity (Larsen and Kovac, 1978; Larsen and Lee, 1983a; 1983b; Green, Kovac and Larsen, 1984). The value for M_c obtained from these studies was in the region of 1500.

However comparison with the value for M_c estimated from stress-strain measurements on dry coal showed a large discrepancy (Brenner, 1985). Brenner postulated that the

difference between the two estimates was due to the differing environments of the coal when the measurements were made, that is the presence of the solvent is thought to reduce the cross-link density in coal, by breaking weak interactions such as hydrogen bonds, and hence estimates of M_c in the swollen state measured only the molecular weight between covalent cross-links.

In extending his model of coal structure to take account of secondary, non-covalent crosslinks, which were not measured in the solvent swelling estimates, Larsen (1985) hypothesised that the number of cross-links due to hydrogen bonds exceeds covalent cross links by a factor of four. The modified model of coal structure derived by Larsen is shown in figure 2.1. Each pentagonal structure represents an aromatic clusters of mean molecular weight 300. Included in the structure is a free un-bound molecule representimg extractable material, in this model given a molecular weight of 900.

However, Given (1984) and Brenner (1985) have questioned whether it was appropriate to apply the Flory-Rehner equation to coal. Brenner (1985) considered that the Flory-Rehner equation could not be applied to a non-rubbery material such as coal unrigorously, since he considers dry coal to be a plastic. However swelling with a solvent renders the coal in a sufficiently "rubbery" state for the equation to be applied as a reasonable approximation. Hence the molecular weights between covalent crosslinks estimated by this method are

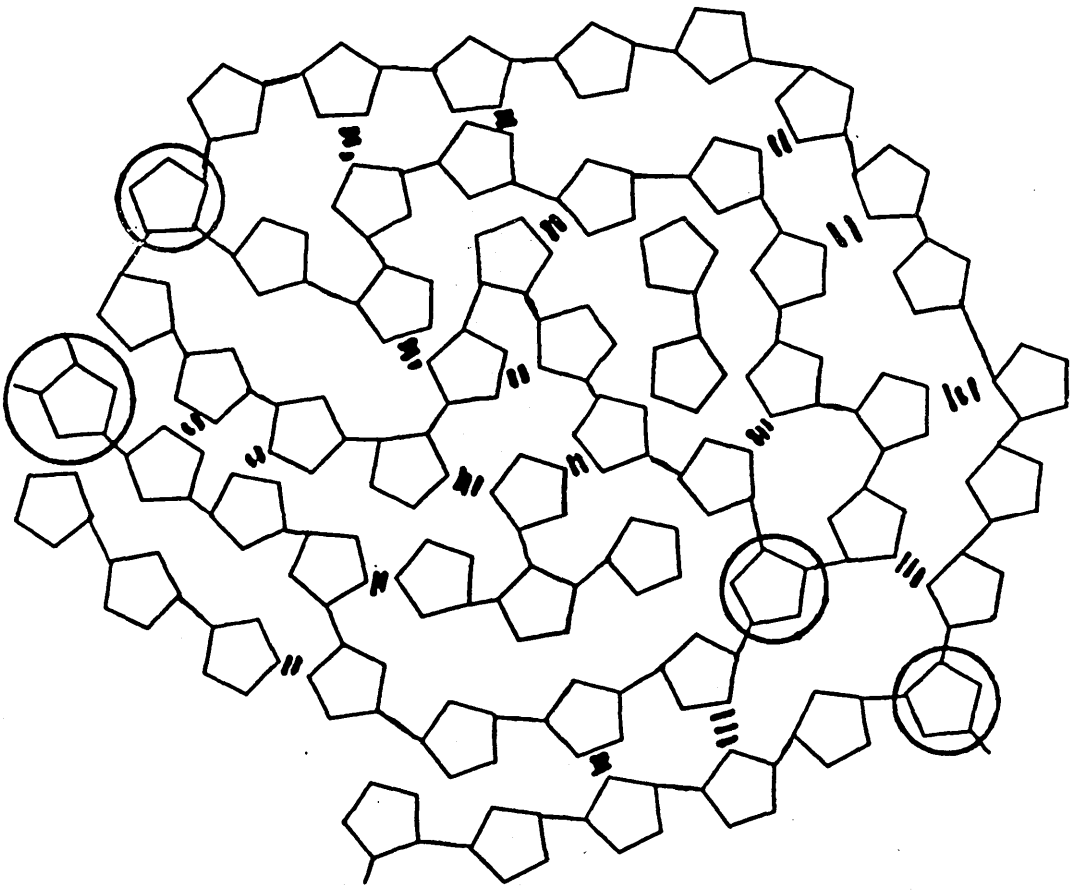


Figure 2.1 The Larsen model of the macromolecular structure of coal. The model is of Illinois No.6 coal, carbon content 78%. Pentagonal structures are aromatic clusters. Circled groups are attached directly to more than two other clusters. Hydrogen bond linkages are indicated by (⩘). (Larsen, 1985).

thought to be reasonably accurate.

2.1.2.1 CHEMICAL NATURE OF THE COAL MACROMOLECULE

The model for the macromolecular structure of coal, (see Figure 2.1) developed by Larsen (1985), does not make any assumptions about the nature of aromatic clusters, other than that their molecular weight is of the order of 300 a.m.u.. Many previous models of coal have attempted to draw an "average structure" for the coal molecule.An example is the structure drawn by Given (see Figure 2.2).

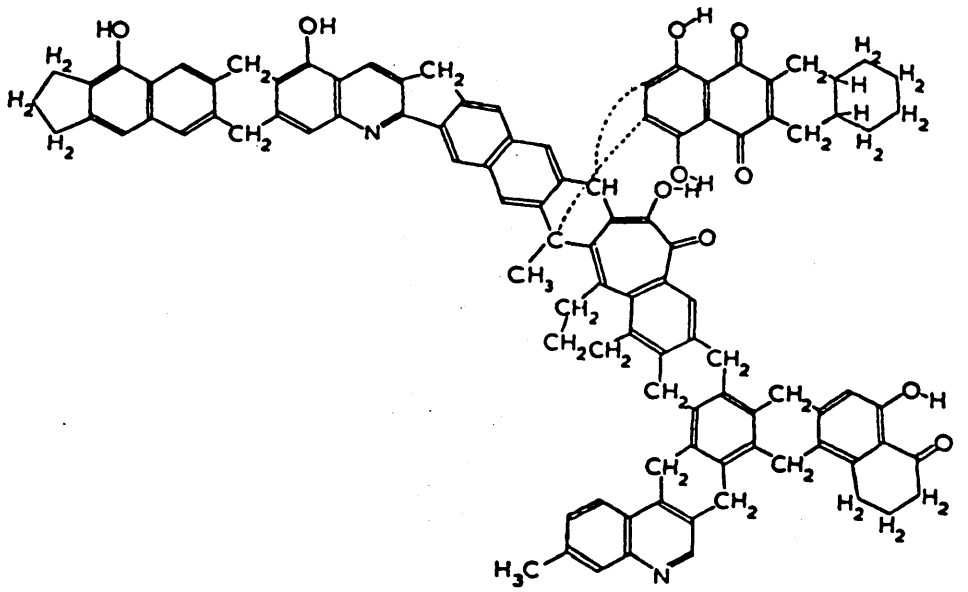


Figure 2.2 The Given model of the molecular structure of coal. The coal modelled is a vitrinite of 82% carbon content, formula $C_{102}H_{78}O_{10}N_2$ (Given, 1960).

The validity of "average" stuctures is always open to

question due to their nature as averages, which necessarily fail to describe the distribution of structures present in the coal.

This section attempts to describe the chemical nature of the macromolecular structure of coal. A number of functional groups and descriptive parameters will be considered, representing the major chemical species present in coal. The proportion and nature of these groups in different coals and macerals will be considered. The subjects considered are:

1) The molecular weight of clusters
2) Fractional carbon aromaticity
3) Nature of aromatic groups
4) Hydroaromatic groups
5) Aliphatic groups
6) Oxygen groups
7) Other heteroatoms
8) Nature of Linkages

1) <u>Molecular Weight of Clusters</u>

Wender and co-workers (1980) suggested that the average molecular weight of the basic unit of the coal macromolecule was around 400 amu for bituminous coals. For lignites the value would be smaller, while for anthracites the molecular weight would be larger. These estimates are based on the product of degradation of the coal structure, by chemical depolymerisation and thermal degradation.

Several studies have made direct measurement of the molecular weight of pyrolysis products, by in-situ pyrolysis in a mass-spectrometer (Evans and co-workers, 1984; Meuzelaar, 1986). Their results suggest that lower molecular weight groups predominate in coal, however the ionisation technique used in these studies renders the primary volatile fragments liable to fragmentation prior to the measurement of the mass-spectrum. When field ionisation, a "softer" ionisation technique, is used, the degree of fragmentation is reduced, and the molecular weight distribution shifts to a higher value, with a mean around 400 (Solomon and co-workers, 1984).

Furthermore, Solomon and co-workers (1985) have shown that the molecular weight distribution of tars from the pyrolysis of exinite is shifted to a higher value than that from vitrinite. The mean value from vitrinite falls around 400, while that from exinite falls around 500, suggesting that the cluster size in exinites is larger than in vitrinites, though these results may simply be a function of the differing pyrolytic behaviour of exinite and vitrinite due to other factors.

In conclusion, there is no direct evidence for the molecular weight of basic units, though there is strong secondary evidence suggetsing the value to be of the order of 400.

Carbon Aromaticity

Early estimates of the carbon aromaticity of coal used a variety of non-direct methods such as estimation from heat of combustion data. The variation in the values obtained was wide ranging from 0.5 to 0.9 for a bituminous coal of carbon content 82.6%. This early work was reviewed by Retcofsky (1982).

Recent developments pioneered by Retcofsky and Link (1978), and Maciel and co-workers (1979) have made it possible to determine the aromaticity of coal as a whole directly by solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. The use of this technique is made possible by the combination of magic angle spinning (MAS) to overcome magnetic anisotropy, and cross-polarisation (CP) to reduce aquistion times to reasonable levels during measurement of spectra. Retcofsky (1982) has claimed that use of cross polarisation produces results which correspond to results obtained by conventional high resolution ^{13}C NMR techniques. The results of numerous studies of coal aromaticity by this method have been reviewed by Retcofsky (1982) and by Given (1984). Data from the measurement of the aromaticity of some vitrains samples is shown in Figure 2.3. Furthermore, the technique has been extended to provide information about aspects of coal structure other than measurements of aromaticity (Yoshida and Maekawa,1986; Given, 1984).

However, use of cross-polarisation causes deficiencies

in the number of carbon atoms sampled during aquisition, such that the value of spectra obtained by this technique are open to doubt. The technique is thought to underestimate the carbon aromaticity by a few percent (Packer and co-workers, 1983; Snape, 1986).

Estimates of the carbon aromaticity of coal as a function of carbon content, based on values for coal depolymerisation products, and structural analysis schemes based on infra-red spectroscopy are shown in Table 2.2.

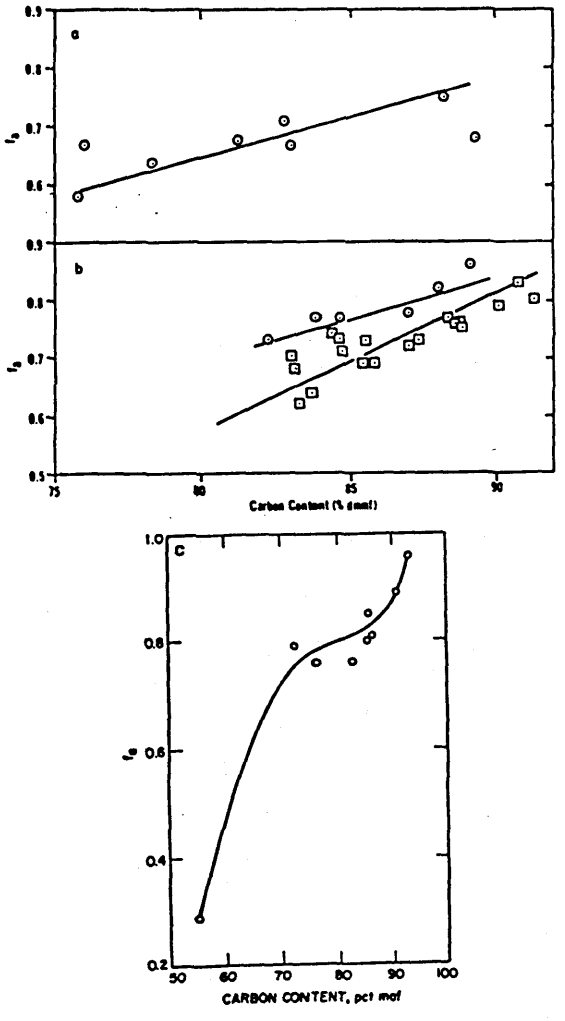


Figure 2.3 Carbon aromaticities for coal lithotypes and macerals. (a) Australian vitrains (Given, 1984); (b) USA vitrinite concentrates (Given, 1984); (c) USA vitrains (Retcofsky, 1982).

Table 2.2. Estimated coal carbon aromaticities (Wender and co-workers, 1980)

Substrate	Carbon content	Aromaticity
Vitrinite	82.5	0.665
Vitrinite	85.0	0.68
Vitrinite	87.5	0.705
Vitrinite	90.0	0.76
Vitrinite	92.5	0.88
CDP[a]	70.6	0.72
CDP	82.4	0.65
CDP	84.0	0.67
CE[b]	82.6	0.73
CE	86.1	0.73

CDP[a] - Coal depolymerisation product

CE[b] - Coal extract

Further to this data, the aromaticity of the exinite fractions were estimated to be lower than the corresponding vitrinite, while those of the inertinite were higher. The values shown in the above table are of the same order as those obtained by CP/MAS ^{13}C NMR, and the trend as carbon content increases is as expected.

The results from both this technique and CP/MAS ^{13}C-NMR are not precise values and can only be used as a guide.

Nature of Aromatic Groups

The principle interest in the aromatic groups is the number of rings per cluster and the degree of

condensation of the rings. Early studies of coal structure estimated that the number of aromatic rings per cluster to be 4 to 5. More recent studies have suggested that this value is an over-estimate. Studies utilising controlled oxidation techniques, as reviewed by Davidson (1982), as well as NMR based estimates, have suggested that for a high volatile bituminous coal (carbon content = 81%) the number of rings per cluster is 1-3. The suggested structures, where more than one ring is present, are the following types: naphthalene, phenanthrene, anthracene, dihydrophenanthrene, dihydroanthracene, diphenyl and diphenyl methane groups (Shinn, 1984). With increases in rank, the degree of condensation, and the proportion of larger number of rings is thought to increase (Davidson, 1982).

Hydroaromatic Groups

The number of hydroaromatic groups present in coal is considered to be of great importance due to their ability to provide donatable hydrogen during coal conversion processes. In the thermal decomposition of coal, these groups are thought to dehydrogenate, forming aromatic structures, and releasing hydrogen which is thought to be able to cap free radicals which are formed in the thermal degradation of coal. Studies to determine the fraction of the coals hydrogen and carbon in hydroaromatic groups have used catalytic dehydrogenation methods (Reggel and co-workers, 1964). This work has been reviewed by Wender and co-workers (1980)

The technique uses metallic catalysts (eg Palladium) in boiling phenanthrene (b.p. 330^{o}C) to dehydrogenate the hydroaromatic groups. The results have suggested that a bituminous coal of 82.5% carbon, with a carbon aromaticity of 73%, contains 25-30 hydroaromatic hydrogen atoms per 100 carbon atoms, corresponding to 40% of the total hydrogen present, this hydrogen being bonded to 15% of the total carbon.

Increases in rank show decreasing amounts of hydroaromatic hydrogen. For a coal with 89.5% carbon content, the estimated quantity is 15 hydroaromatic hydrogen atoms per 100 carbons. As might be expected, the distribution is not even in different maceral groups. Vitrinite from the 82.5% carbon coal was seen to yield 25 hydroaromatic hydrogen atoms per 100 carbons, while exinite gave 31. Fusinite produced only 5 hydroaromatic hydrogen atoms per 100 carbon atoms (Reggel and co-workers, 1970).

Snape (1986) however, has questioned some of the results obtained due to the differing results obtained with different catalysts, together with NMR data on British coal (82% Carbon) which suggested that a maximum of half the aliphatic carbon was present in hydroaromatic groups, that is 10% of the total carbon. Furthermore, Snape suggested that the hydroaromatic groups were present in one or two ring structures, with dihydro species predominating.

Aliphatic Groups

The nature and proportion of aliphatic groups present in coal is not clear. Early studies suggested that the greater proportion of non-aromatic hydrogen, and carbon in coal, was contained in hydroaromatic structures, some of which were thought to be of a highly condensed nature in adamantane type groups.

More recent work has suggested the presence of some long chain alkyl groups, substituted on aromatic rings, with higher concentrations present in lower rank coals (Snape and co-workers, 1985; Calkins, 1984; Calkins and co-workers, 1984a; 1984b; 1984c). Snape has estimated the carbon present in these groups to be up to 10% of the total carbon in coal. Calkins and co-workers (1984d) have further suggested that exinite contains a higher proportion of long chain aliphatics than vitrinite or inertinite.

The remainder of the aliphatic carbon and hydrogen is present in methyl substituents and in linking gouprs between aromatic clusters.

Oxygen groups

The amount of oxygen present in coal is a strong fuction of rank. For a bituminous coal, of carbon content 80%, the amount of oxygen is typically around 10-12%, while for low rank coals and lignites, this value can rise to greater than 25% coal. Oxygen is present in a number of

different functional groups. These are: phenolic groups (Ar-OH), diaryl ethers (Ar-O-Ar), alkyl aryl ethers (R-O-Ar), carboxylic acid groups(-COOH), carbonyl groups (C=O) and esters (-COOC). The proportion of these groups present has been studied by a number of workers (Blom and co-workers, 1957; Cronauer and Ruberto, 1979; Ruberto and Cronauer, 1978). The results originally published by Blom have recently been criticised by Given (1984) .However many of the major findings still hold true.

Blom showed that for coals with greater than 80% carbon, most of the oxygen was found in phenolic hydroxyl groups and in etheric groups (not CH_3-O-), while above 94% carbon, all the oxygen present was in ether groups. For coals with less than 75% carbon, significant quantities of carboxylic acids were shown to be present. Carbonyl groups were shown to present in measurable quantities for coals with less than 80% carbon.

For a coal with 78% carbon and 11% oxygen, the etheric groups accounted for 4% of the oxygen, and hydroxylic -OH the remainder. For coal of 65% carbon, with 28% oxygen, etheric groups accounted for 10% of the oxygen, while the remainder was composed of 7% hydoxylic -OH, 2% carbonyl, and 9% carboxylic acids. Given (1984) has questioned the measurements for the amount of carbonyl present, though results measuring the quantities of other groups present in Australian Brown coals, cited by Given, are similar to those of Blom.

Ruberto and Cronauer (1978) confirmed that for higher rank coals the oxygen was present almost exclusively in hydroxylic and etheric groups, with approximately equal proportions of each. For a lower rank subbituminuos coal (69.3% carbon), very little etheric oxygen was found in contradiction with the results of Blom and co-workers, with the bulk of the oxygen divided between hydroxylic and carboxylic groups.

Other Heteroatoms

The other major heteroatoms present in the organic structure of coal are nitrogen and sulphur. The quantity of sulphur present can be up to 3.5%, though typically it is approximately 1%. The amount of nitrogen present is usually 1-2%.

Sulphur has been shown to be present in the following groups: thiolic (R-SH), thiophenolic (Ar-SH), aliphatic sulphide (R-S-R), aryl sulphide (Ar-S-Ar), and thiophenes.

Davidson (1982) reported that in a study of five coals with a range of sulphur contents from 0.6% to 3.2%, the majority of the sulphur accounted for was presnt in thiophenes, aliphatic sulphides, and thiophenolic groups, with smaller quantities in the other functional groups.

It should be noted that Snape (1986) has drawn attention

to other labile sulphur groups which may be present, for example thioethers and disulphides, which are thought to play a significant role in coal liquefaction.

Nitrogen has been shown to be present in two principal forms: in strongly basic pyridine type groups, and in weakly basic pyrrole structures (Wender and co-workers, 1980; Bartle and co-workers, 1986). The comparatively unreactive nature of these groups makes them relatively unimportant in coal conversion, except for their tendency to interact with phenolic groups, modifying the properties of coal and coal derived liquids (Wender and co-workers, 1980).

The Nature of Inter-Cluster Linkages

The nature of inter-cluster linkages is of major importance as they are considered to be the most labile bond in the coal structure, and therfore have great relevance in coal conversion processes. The nature of the structures present in these linkages is dependent on coal rank and origin. The following groups have been shown to be presennt as linkages: thioethers and disulphides (Snape, 1986), ethoxy ethylenes and methoxy groups (Solomon, 1985), methylene and longer aliphatic chains (Wender and co-workers, 1980) and hydroaromatic groups (Shinn, 1985). Snape (1986) has questioned whether aliphatic bridges with more than one carbon atom exist in coal structures.

The proportion of each type of linkage depends on the

coal type, and the method used to quantify the linkages.

2.1.2.3 THE NATURE OF THE LOW MOLECULAR WEIGHT MATERIAL

It has been known for a long time that coals contains a certain amount of comparatively low molecular weight material that can be extracted from within it's structure by various solvents. Early work in this area has been reviewed by H.C.Howard (1963), and more recently by Wender and co-workers (1980). Some of the extractable material is thought to originate in the waxes, resins and fatty acids present in plants. Evidence for this can be seen in the presence of "biomarker" compounds (pristane, phytane) in extracts, together with a wide range of sesqui and diterpenoids and related (coalified) materials (Hayatsu and co-workers, 1978). It should be noted that Hayatsu and co-workers hypothesised that much of the material extractable from a bituminous coal was formed at a stage of coalification later than that of a lignite.

The proportion of coal present as low molecular weight potentially extractable material has been quantified by the long term extraction of coal with polar solvent such as pyridine. Up to 25% of bituminous coals can be extracted by this method. It has been shown that even after long term extraction of coal (>250 hours), measureable quantities of extractable material are produced (Spence and Vahrman, 1970; Rahman and Vahrman, 1971). Therefore the amount of material which can

ultimately be extracted from coal cannot be quantified directly.

However Marzec has attempted to use an NMR based approach to quantify the ultimate fraction of the coal structure which may be extracted, which was termed the mobile phase (Jurkiewicz and co-workers, 1982; Marzec and co-workers, 1983). The method used suggested that up to 40% of the coal is present in the mobile phase. However the technique used to obtain this figure has received considerable criticism, as much parts of the coal macromolecular structure, eg long aliphatic side chains, are thought to respond the NMR analysis in the same manner as the "mobile material" (Given and co-workers, 1986; Snape, 1986).

To confirm her data, Marzec cited the fact that long term (several months) extraction with a mixture of pyridine and ethylenediamine has been shown to produce up to 38% extract from a Polish bituminous coals (Bodzek and Marzec, 1981). However, Hombach (1982) has demonstrated that pyridine extracts from coal are liable to include substantial quantities of colloidal material of high molecular weight, suspended in the solution, which cannot be removed without ultra-filtration or centrifugation. Given (Given and co-workers, 1986) has suggested that the fraction of the material extracted by Bodzek and Marzec which cannot be distilled at 300^{o}C, may represent part of the macromolecular structure, which has presumably been extracted as a colloid. In

conclusion, there is substantial doubt of the validity of the data obtained by Marzec in its use to quantify the mobile phase. However, the amount of mobile material in coal probably lies between the amount which can be extracted, andd the amount indicated by the NMR analysis.

The chemical nature of low molecular weight extractable material has also received substantial attention, mainly as a result of its influence on the thermal properties of coal. This ability together with certain aspects of the structure of the mobile phase is discussed in Chapter 5.

The chemical structure of the extractable material depends on the solvent used in the extraction, and the extent to which the coal is extracted. Extraction of bituminous coals with chloroform produces a viscous liquid with a mean molecular weight 350-450, which is richer in hydrogen than the coal (Neuberg and co-workers, in press). Chloroform extraction of coking coals produces a glassy solid, which is also richer in hydrogen than the parent coal (Brown and Waters, 1966a). Several workers have suggested that the chloroform extractable material may possess hydrogen donating properties, which result from the presence of higher concentrations of hydroaromatic groups than are found in the parent coal (Brown and Waters, 1966a; 1966b; Neaval, 1980). Extraction with more polar solvents produces a higher molecular weight extract, whose analysis is close

to that of the parent coal (Wender and co-workers, 1980; Ouchi and co-workers, 1983; Grint and co-workers, 1984).

2.2 FUNDAMENTALS OF COAL PYROLYSIS - BASIC CONSIDERATIONS

Coal pyrolysis can be defined as the thermal degradation of coal in a non-oxidising atmosphere. This occurs when the temperature of the coal is raised above approximately 350^{o}C.

As the temperature of coal is raised, the weaker bonds in the coal structure undergo scission yielding free radical fragments. These free radicals are either capped by hydrogen or recombine with the coal mass. The hydrogen can either be derived from the coal itself or may be externally applied.

The fragments are then transported from the site at which they are formed, to the edge of the coal particle. Here they must "evaporate" into the bulk gas phase where they are transported out of the hot zone to a cold, quench zone, when they can be recovered as a volatile product, either tar or gas.

The inherent thermal instability of the volatile products at the temperature of formation means that they are liable to undergo secondary reaction at any stage following their formation. These secondary reactions can take the form of cracking to form smaller molecules,

repolymerisation to larger molecules, possibly char, or internal rearrangement.

The distribution of products from coal pyrolysis, and the nature of those products is highly dependent on a number of parameters. These parameters can be divided into two classes: the primary effects, ie. those affecting the rate of formation of primary volatile fragments, and the extent of those reactions, and secondary effects which manifest themselves during the transport of volatiles from the site of formation to the quench zone, affecting the rate and extent of secondary reactions. Due to the complexity of the pyrolytic process, it is difficult to isolate the effect of one parameter from the others, however a indication of the effects of the primary and secondary parameters is given in the following sections.

2.3 THE INFLUENCE OF PRIMARY EFFECTS ON COAL PYROLYSIS

2.3.1 THE NATURE OF PYROLYSIS REACTIONS

There are three principle types of chemical reaction occurring in coal pyrolysis. These are:
(i) Homolytic bond scission yielding free radical fragments of the coal structure,
(ii) Stabilisation of free radicals by hydrogen,
(iii) Charring of the coal macro molecular structure.

Other reaction may occur to lesser extents, such as radical combination. These processes occur either simultaneously or in close succession during coal pyrolysis, and result in the formation of the primary pyrolysis products. The nature of these three stages will be considered below:

Bond Scission

The nature of the bonds which are liable to undergo scission during coal pyrolysis has been examined by several workers. Given (1960) postulated that there existed a hierarchy of bond susceptibilities to scission, this being (in order of increasing stability):

(i) hydroxyl groups,
(ii) hydroaromatic group dehydrogenation,
(iii) methylene bridge scission,
(iv) alicyclic ring rupture.

Wiser and co-workers (1967) suggested that the more labile bonds in the coal structure are the linkages between aromatic cluster, the basic units of coal. The types of structures present in these linkages was discussed in a previous section (2.1). Their nature depends on the rank of coal, though in general ether structures, aliphatic groups, hydroaromatics and other heteroaromatic structures are thought to be present in varying quantities.

Solomon (1985) has concluded that there are two classes of initial bond scission: scission of inter-cluster linkages, and scission of side chains yielding small aliphatic groups which form gaseous products. These two reactions compete for the hydrogen which is native to the coal, to stabilise the radicals formed. Solomon has also hypothesised an ipso substitution reaction as being an important mode for, particularly, methane formation. This type of reaction involves substitution of a methyl side chain with free radical such as a tar precursor. Additionally Solomon concluded that the more labile inter-cluster linkages are aliphatic and etheric bridges. The nature of the weaker ether bridges was postulated to be ethylene oxyethylene ($-C_2H_4-O-C_2H_4-$) and oxymethylene ($-CH_2-O-$).

Radical Stabilisation

The nature of the chemical reactions stabilising free radicals is not well understood. Solomon has postulated that the hydrogen required to stabilise free radicals originates in the hydroaromatic groups in the coal structure, and that stabilisation involves dehydrogenation of these structures.

Van Heek and Jungten (1984) have suggested a number of mechanisms for fragment stabilisation. These are: Internal rearrangement, with and without dissociation, reaction with other radicals, and reaction with the coal structure abstracting another stabilising radical from

the macromolecule. The hydrogen donation mechanism proposed by Solomon is a variation of this last proposal.

Additionally the ipso substitution reaction involving a tar molecule would be a mode of release for stable gas molecules.

Char Formation

The last reaction suggested as part of the pyrolysis scheme has been less well studied. Suuberg and co-workers (1985) have studied the degree of cross linking in coal and its variation during pyrolysis. The temperature at which tar production ceases in pyrolysis (at high heating rate) corresponded to a rapid increase in cross-linking of the coal structure. This was shown to be the case for high volatile bituminous coals and for a lignite, where the commencement of cross-linking occurred at a lower temperature than in the bituminous coals. The temperature of cross-link formation corresponded to the temperature where repolymerisation of tar pre-cursors was observed, suggesting that increases in cross-link density corresponded to a repolymerisation of the coal structure, a char forming reaction.

Although Solomon has acknowledged the occurrence of cross-linking reactions (Solomon and Co-workers, 1985), he has also suggested that the production of tar in

pyrolysis ceases when the source of internally donatable hydrogen, ie the hydroaromatic structures has been used up (Solomon, 1985). Though this may be the case, considerable gas formation is observed in pyrolysis when tar formation has ceased, and as discussed above, small free radicals require a source of hydrogen to stabilise them in the same manner as tar precursors.

Summary

To summarise, the reactions occurring in pyrolysis are highly complex in nature. The initial step involves scission of weak linkages in the coal structure, which is followed by stabilisation of free-radicals. There is evidence suggesting that of char forming reactions occur in the pyrolysing coal structure.

The rate and extent of the reactions discussed above are affected by four primary experimental parameters. These are:

(i) Peak pyrolysis temperature and time at temperature
(ii) Heating rate
(iii) Reactivity of the ambient gas
(iv) Coal rank and type.

The observed effects of these parameters on the distribution of products from pyrolysis are discussed in the following sections.

2.3.2 PEAK PYROLYSIS TEMPERATURE

As the peak temperature employed in pyrolysis is increased the yield of total volatiles continues to increase, though above a certain temperature, this is at a decreasing rate.

The ultimate yield of volatiles obtainable from the pyrolysis of any coal cannot be defined, though its existence is implied in the proximate analysis terminology of "fixed carbon" and "volatile matter"(BS 1016 pt 3, 1973). In pyrolysis studies at progessively higher temperatures the yield of volatiles continues to increase, principally as gaseous products: hydrogen and methane, and at higher temperatures acetylene. Volatile matter yields exceeding proximate analysis results have been reported by numerous workers. Similarly increasing the time spent at temperature results in progressively increasing volatiles yields (Shapatina and co-workers, 1960)

Figure 2.4 (Howard, 1980) shows that as the temperature increased up to 1900^{o}C (at 1 bar in an inert atmosphere), the yield of total volatiles was still increasing for a number coals studied. There is no indication of an "ultimate char yield", even at these temperatures. The nature of volatile products at these temperatures is strongly influenced by secondary reactions which occur rapidly under these conditions. The most stable species with respect to secondary

reactions at high temperatures (>1200°C) are acetylene and hydrogen, which are the major volatile products.

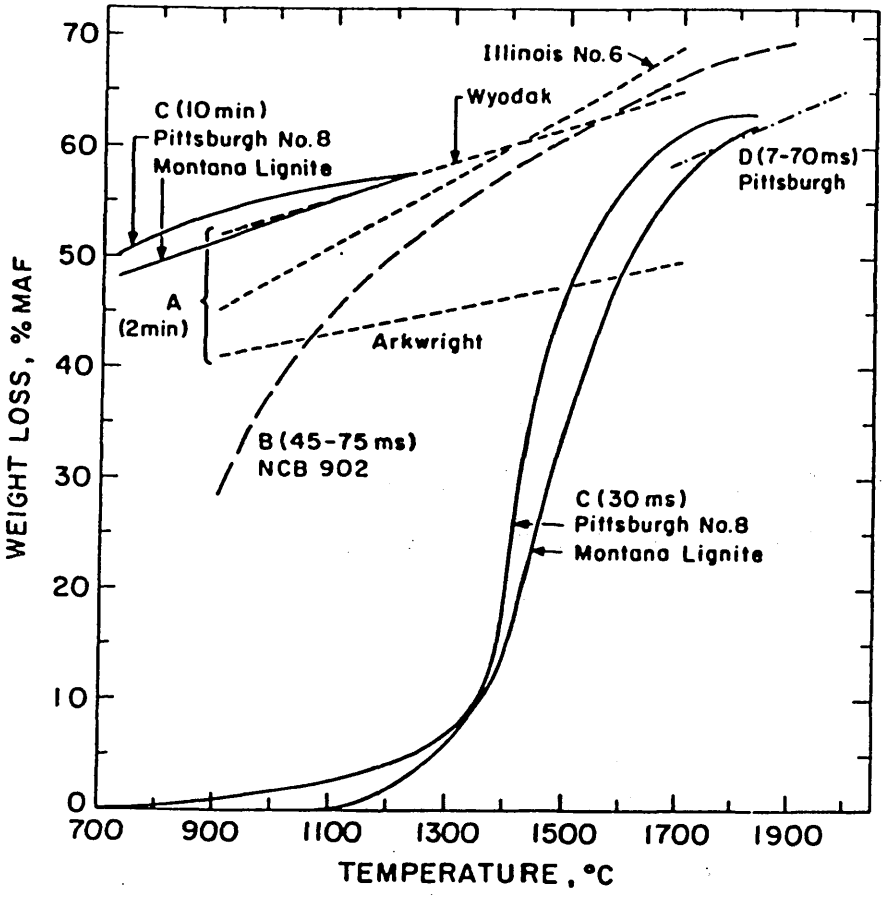


Figure 2.4 Effect of temperature on volatiles yield from coal pyrolysis (Howard, 1980).

Tar formation seems to come to an end at 600-800 °C though this is very much a function of heating rate and will be dealt with in the next sub-section.

2.3.3 HEATING RATE

It is now generally agreed that use of high heating rates in coal pyrolysis favours the formation of tar and other volatile products. It has been be argued that this is due to fine sample dispersion inherent to pyrolysis

at high heating rate, rather than changes in intrinsic reaction pathways (Howard, 1980). The absence of a reactor where the heating rate is continuously variable over the whole range used in coal conversion processes (from 5^{o}C/min to 1000^{o}C/s) in a single geometry, has made it impossible to confirm either hypothesis.

Anthony and co-workers (1975; 1976) varied the rate of heating from 10000^{o}C/s down to 650^{o}C/s in the pyrolysis of coal in a wire-mesh reactor and found this to have no apparent effect on the pyrolytic behaviour of either a caking or non-caking coal. Suuberg and co-workers (1978; 1980) extended this study over a wider range of heating rates, down to 270^{o}C/s and included a measurements on the yield of tar, and gas compositions. No significant changes were noted in either the yields of tar or gas, or the composition of the gas as a function of heating rate. Howard concluded that this indicated the occurrence of multiple parallel reactions rather than competitive reactions.

Stangeby and Sears (1981) performed a similar series of experiments to Suuberg, using a wire mesh reactor to study the effect of heating rate on the pyrolysis of Canadian coals. They showed that though the yield of total volatiles was unaffected when the heating rate was increased from 250^{o}C/s to 6000^{o}C/s there were substantial changes in the gas composition. These changes may have been due to increases in the residence time of the volatiles at high temperatures when the

higher heating rate was used, as is indicated by increases in the yields of ethylene.

In an earlier study, at the low end of the heating rate scale, Van Krevelen and co-workers (1956) showed the effect of changing the heating rate on the temperature of the maximum rate of volatiles formation. The results from this are given in Figure 2.5 and show clearly that as the heating rate is raised from 0.6 to 6.6°C/min the temperature of the maximum rate of devolatilization increased from 470°C to 525°C. Furthermore the maximum rate of devolatilization showed a ten fold increase when the heating rate was increased over this range.

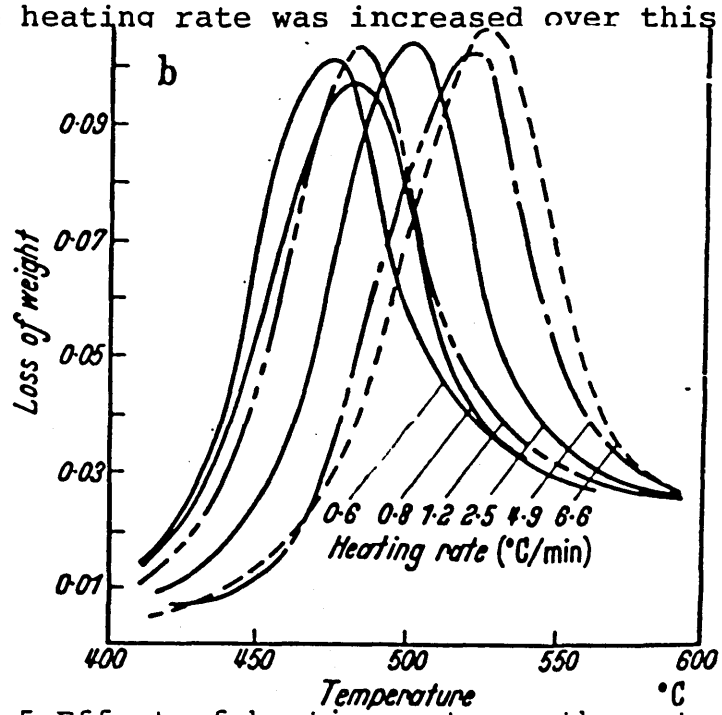


Figure 2.5 Effect of heating rate on the rate of weight loss in coal pyrolysis (Van Krevelen, 1956).

A similar trend was shown for experiments over a higher range of heating rates (1.5 to 10°C/min) by Brown (1957), though the temperatures at which the maximum weight loss rates occurred were at a consistently lower

level. This was due to the different rank of the coals studied.

The changes of heating rate employed in these studies were small, and at the low end of the range now used in pyrolysis studies. It is therefore difficult to extrapolate from this data to higher heating rates.

In a very recent study, Gibbins (in preparation) has extended the range of heating rates which can be obtained in a wire-mesh type reactor from 1000^{o}C/s down to 0.5^{o}C/s by using a feed-back control system and powering the mesh with a.c. Additionally a sweep gas is utilised to remove volatiles from the hot zone. Gibbins' results (Figure 2.6) show unequivocally that heating rate affects the yield of both tar and total volatiles in coal pyrolysis.

Below 50^{o}C/s the yield of tar is seen to rise slowly with increases in heating rate, while between 50^{o}C/s and 500^{o}C/s there is a substantial effect of the heating rate on tar and total volatiles. Above this level both tar and volatiles yields appear to reach a plateau. When these results are compared with those of Suuberg and co-workers (1978; 1980), Gibbins has shown that the yield of tar and volatiles is seen to be function of heating rate in a range where Suuberg showed that this was not the case. However it should be noted that Suuberg did not make use of a sweep gas in his version of the wire-mesh reactor.

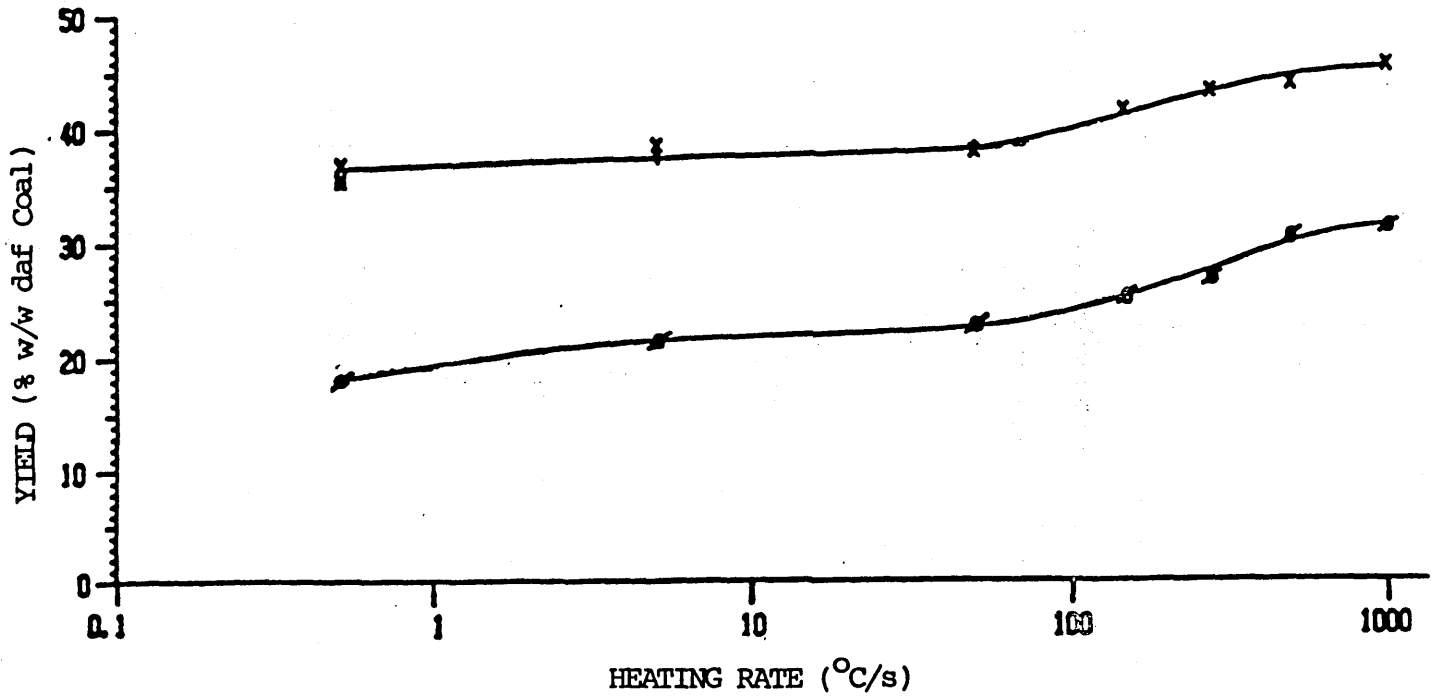


Figure 2.3 Effect of heating rate on the pyrolysis of Linby coal in a wire-mesh reactor. Coal heated to 700°C, with a 30 s hold at peak temperature: Total volatiles (x); tar (ø). (Gibbins, in preparation).

Suuberg has since hypothesised that (in the absence of a sweep gas) the evaporation of tar pre-cursors is the rate limiting step in the evolution of tar (Unger and Suuberg, 1981; 1983; 1984). Serio and co-workers (1984), in a separate study, have to some extent confirmed this theory. In Gibbins design evaporation ceases to be rate limiting, due to the sweep gas, and the changes in the heating rate in the same region as in Suuberg's study, are seen to manifest themselves in the product slate, although Gibbins has not yet performed experiments in the absence of a sweep gas. Gibbins' data, together with data on the effect of pressure on tar yields in pyrolysis presented later, confirm Suuberg's hypothesis that (in the absence of a sweep gas) tar evolution in coal pyrolysis is limited by mass transfer from particle to bulk, and shows the importance of this step in coal pyrolysis.

2.3.4 REACTIVITY OF THE AMBIENT GAS

In coal conversion studies where the aim is to produce a product richer in hydrogen than the original coal, either gas or liquid, the application of externally added hydrogen during the conversion process has been widely studied. During thermal degradation, hydrogen may be added directly from the gas phase, it may be formed *in situ* by chemical reaction of applied gases, or it may be added from a vehicle solvent.

The formation of hydrogen *in situ* from mixtures of

carbon monoxide and water has been the subject of many studies recently. (Ross and co-workers, 1985) Other methods of in-situ generation of hydrogen have also been studied (Mondragon and co-workers, 1984)

Use of vehicle solvents as sources of hydrogen has been widely examined in coal liquefaction studies. Solvents such as tetralin act as hydrogen donors, donating hydrogen to the coal. Non-donor solvents are effective as hydrogen shuttlers.

Gas-phase application of hydrogen, necessarily at elevated pressure (to achieve appreciable chemical activity), during pyrolysis and in the absence of a solvent, is more commonly known as hydropyrolysis. The effect is complicated as it represents the net product of two competing factors: the primary chemical effect of the added hydrogen, and the secondary effect due to the increased gas pressure. Gases other than hydrogen have also been studied as sources of hydrogen during pyrolysis (Sundaram and co-workers, 1984).

These effect of externally added hydrogen will be considered in more detail in chapter 3 while the effect of increases in pressure on secondary reactions will be considered in section 2.4.3.

2.3.5 COAL RANK AND TYPE

The effect of coal rank and structure on coal conversion

is not easy to quantify. The principal problem is how to classify coal in a meaningful manner, in order to be able to correlate some coal property with conversion.

Recently, Snape (1986) has reviewed the effect of coal rank and type on coal liquefaction. The concentration of reactive macerals in the coal structure was found to correlate well with conversion, the reactive macerals being vitrinite, exinite (or Liptinite) and semi-fusinite. Other properties which were found to correlate well with conversions were H/C ratio, carbon content, and sulphur content. However, the correlations tended to be limited to coals of a single geographical origin. Extending the correlations was of limited use due to the differing coalification processes occurring in coals of different geographical origin.

A systematic study of the pyrolysis of coals of different rank and geographical origin has not been performed. However a number of workers have performed studies of the pyrolysis of coals of differing ranks.

Tyler (1980) pyrolysed a series of different Australian coals in a small scale fluidised bed reactor. The heating rate in this reactor has been estimated at between 1000 and 10000^{o}C/s. The results of Tyler are shown in Figure 2.7. The yield of tar is seen to correlate reasonable well with vitrinite plus exinite content (Figure 2.7b), but a slightly better correlation is seen against coal H/C ratio (Figure 2.7a).

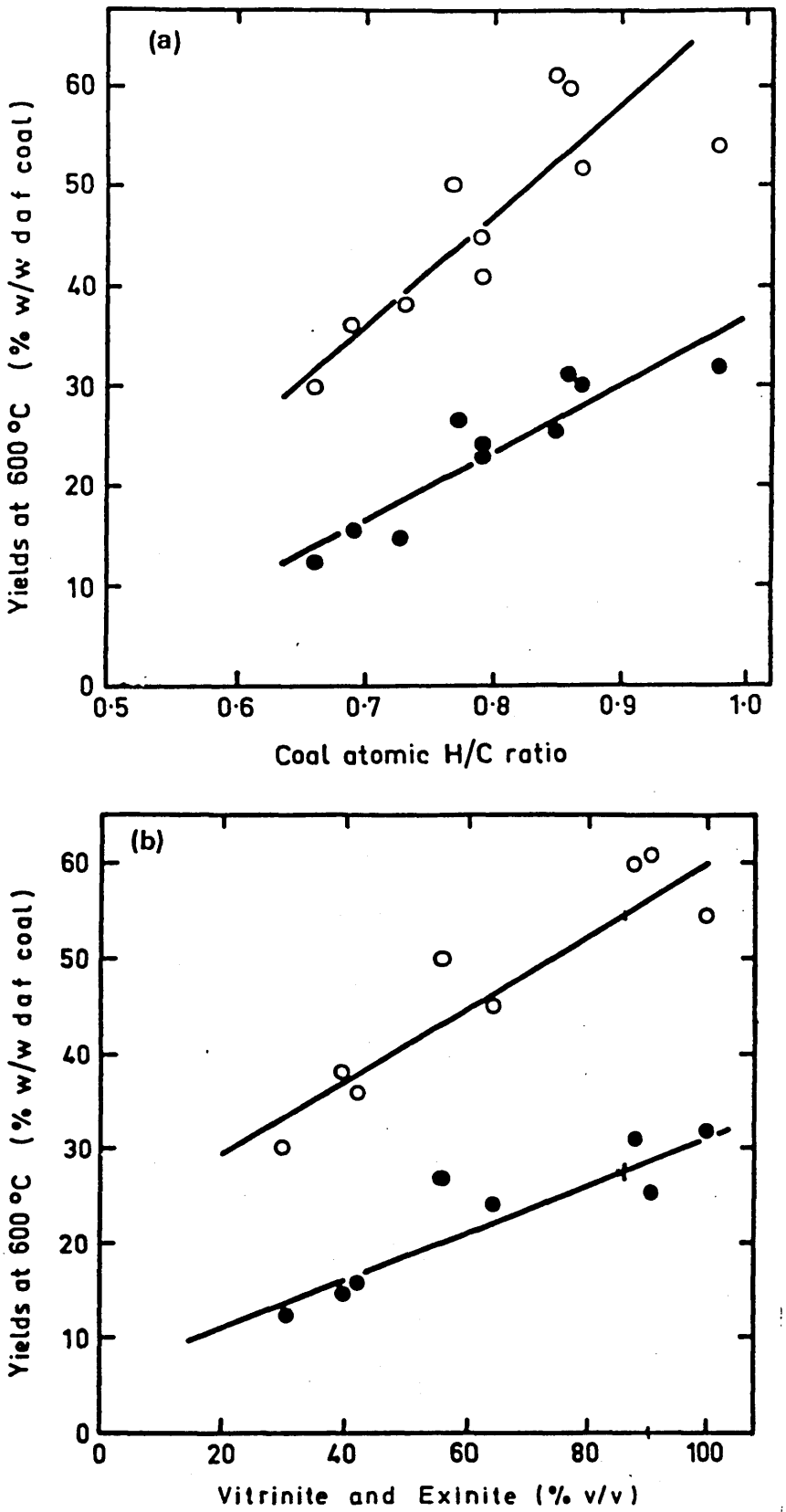


Figure 2.7 Tar and total volatile yields from flash pyrolysis experiments in a fluidised bed reactor: (a) as a function of coal H/C ratio; (b) as a function of coal maceral content. (Tyler, 1980).

The tar yield from a Victoria Brown coal (tar=23-24%, H/C ratio=0.82) also fits reasonably well on the correlation line for the H/C ratio.

Anthony and co-workers (1975; 1976), and Suuberg and co-workers (1978; 1980) have both studied the pyrolysis of a bituminous coal and a lignite in a wire mesh apparatus. The results are shown in Figure 2.8.

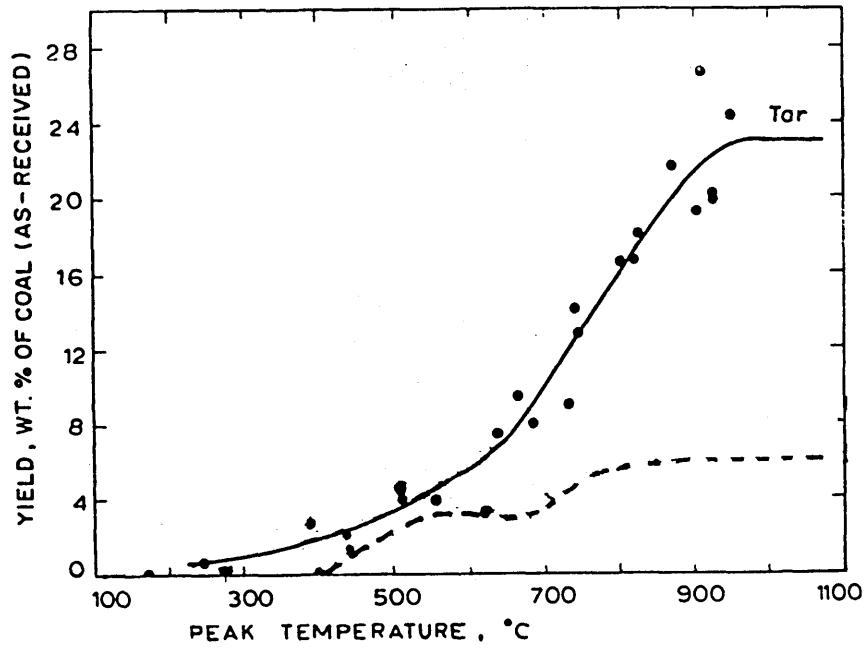


Figure 2.8 Tar yields from the pyrolysis of Pittsburg Seam coal (———) and Montana Lignite (- - -) (Howard, 1980)

The yield of tar produced from the bituminous coal was found to be considerably higher than that from the lignite. Furthermore the yield of tar from the lignite was seen to reach its plateau at a lower temperature than for the bituminous coal.

In a more recent study of the pyrolysis of a number of

coals, Suuberg has shown that the tar yield from another lignite (North Dakota) was much smaller than that obtained from high volatile bituminous coals or from a low volatile bituminous (semi-anthracitic) coal (Suuberg and Scelza, 1982; Unger and Suuberg, 1984). The molecular weight distributions of the tar from the pyrolysis of the different coals were seen to be similar.

In summary the effect of coal rank and structure on pyrolysis yields is not well documented. A good correlation of H/C ratio versus tar yield from flash pyrolysis has been obtained for coals from a single geographical location. It has also been shown that pyrolysis of lignites produces less tar than pyrolysis of bituminous coals.

2.4 SECONDARY EFFECTS

2.4.1 FUNDAMENTALS

The transport of volatile products in pyrolysis can be divided into two major stages:

(A) from the site of formation to the bulk gas phase

(B) in the bulk gas phase to the quench zone of the pyrolysis reactor.

The first major stage may be subdivided in two further stages:

(A1) transport from the site of formation to the external surface of the coal particle

(A2) "evaporation" into the bulk gas phase.

A diagrammatic representation of these divisions of volatiles transport is shown in Figure 2.9.

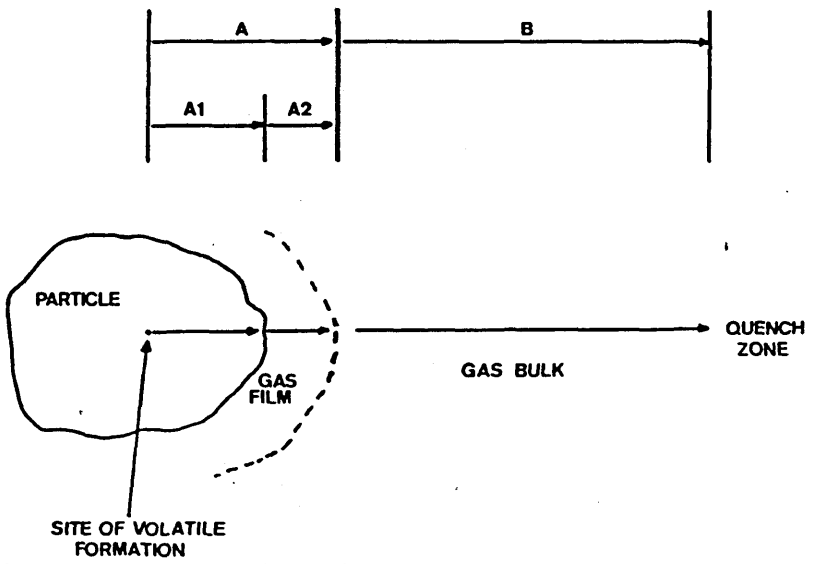


Figure 2.9 Stages during the mass transfer of volatiles in coal pyrolysis:

A - Transport in the vicinity of the coal particle:
A1 - transport from the site of formation to the surface of the coal particle.
A2 - transport from the surface of the particle though the gas film to the gas bulk, ie evaporation

B - Transport in the gas phase to the quench zone.

The primary volatiles produced in pyrolysis are largely unaltered fragments of the coal structure. The chemical bonds present in both the coal and volatiles are of the same type. Therefore at pyrolysis temperatures, where the bonds in the coal structure are liable to undergo scission, the bonds in the volatiles are also labile.

The result of this is that at the temperature of their formation, the volatile products of pyrolysis are inherently thermally unstable, and are liable to undergo secondary reactions at any of the transport stages discussed above. In a pyrolysis reactor, the secondary reactions often proceed to such an extent as to dominate the product slate, and the chemical nature of the products. From a fundamental point of view, this greatly complicates comparison of pyrolysis results from different reactor geometries, or those obtained under different conditions.

However, in assessing the distribution of products from pyrolysis and the nature of those products, it is as important to study the time-temperature history of the volatiles during their transport and the nature of the environment during that transport, as it is to study the time-temperature history of the parent coal.

There are three main types of secondary reaction: cracking to form smaller molecules often increasing gas yields at the expense of tar, repolymerisation forming larger molecules often increasing char yields, and molecular rearrangement. Any volatile molecule from methane upwards is liable to undergo secondary reaction.

The time-temperature history of the volatiles and therefore the nature and extent of secondary reactions in the first major stage of transport, stage (A), is affected by two experimental parameters:

(i) Particle size

(ii) External gas pressure.

In the second major stage, stage (B), it is solely affected by reactor geometry. A description of the effect of these experimental parameters on the distribution of products in pyrolysis, and the nature of those products is given in the following sub-sections.

2.4.2 PARTICLE SIZE

Particle size has its principle effect on the transport of volatiles from the site at which they are formed to the edge of the coal particle. The larger the particle size, the longer the residence time of the volatiles within the particle and the greater the likelihood that they will undergo secondary reactions. Particle size also has a parallel effect on heat transfer in the coal particle producing temperature profiles within the particle (Howard, 1980). Isolation of the two effects cannot been accomplished without resorting to techniques such as microwave heating.

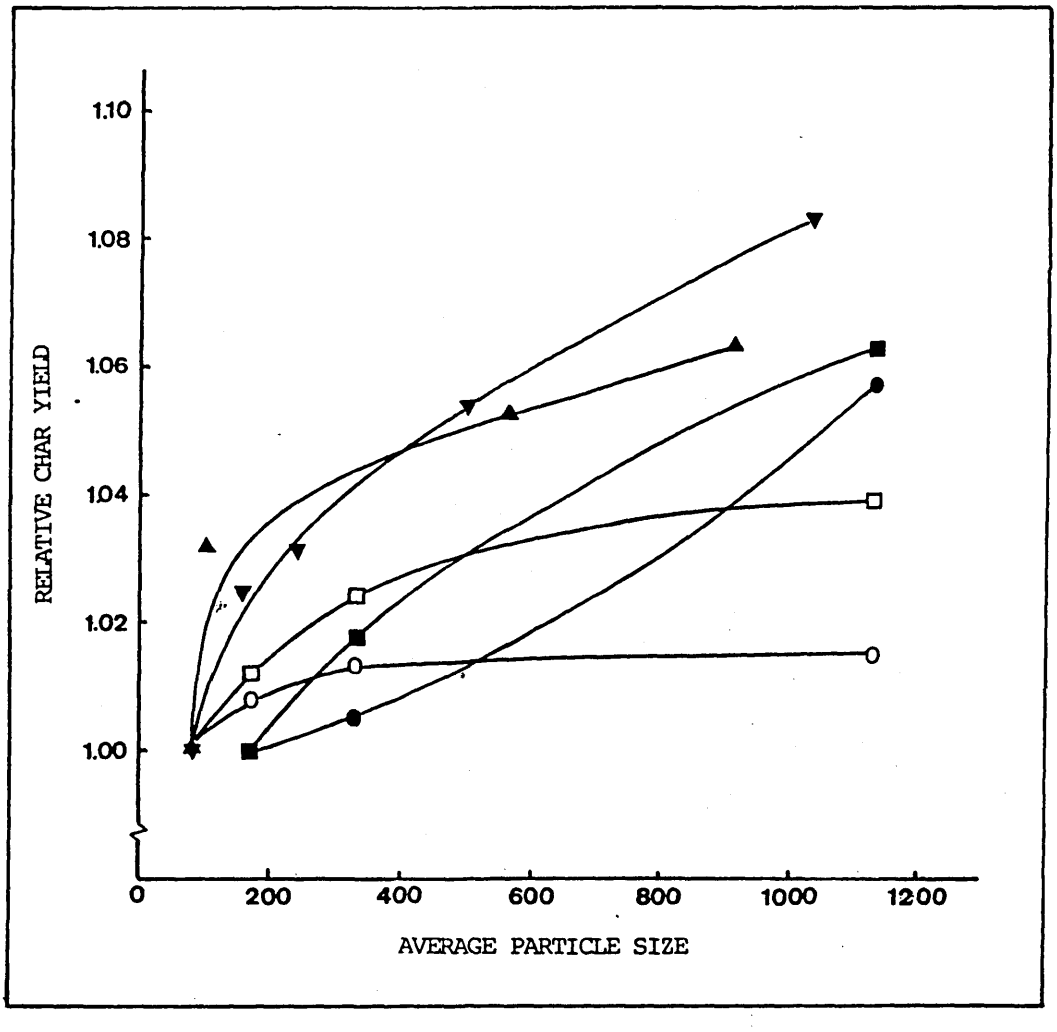
The transport of volatiles within the pyrolysing coal particle occurs by several mechanisms: pore diffusion, bubble transport, and diffusion through the plastic coal mass (Suuberg, 1985; Suuberg and Sezen, 1985). The extent to which each mechanism occurs depends on several factors, notably the rank of coal. In a plastic coal,

that is one which softens on heating, the volatiles are likely to be transported by all three mechanisms, while in a low rank coal, such as a lignite, or in a high rank coal, such as a semi anthracite, where melting does not occur except under high pressure hydrogen, and the major mechanism of volatiles transport is pore diffusion. Additionally for coals in which plasticity develops, cenosphere formation may play a significant role, where the coal balloons outward as a result of internal pressure.

Secondary reactions may occur during transport by any of the mechanisms and may take the form of any of the reactions described above. Several workers have hypothesised about critical particle size, above which the yield of volatile products is affected by mass transfer limitations within the coal particle (Anthony and co-workers, 1975; 1976; Suuberg and co-workers, 1978; 1980; Wagner and co-workers, 1985). Much of this work was reviewed by Howard (1980). This critical diameter represents a transition from the regime where volatiles production is chemical reaction rate controlled to one where transport is the limiting step.

Wagner showed this to be affected by the type of coal studied and the ambient pressure, while Howard and more recently Stiles (1986) showed the importance of heating rate. A summary of their findings is shown in Figure 2.10.

Figure 2.10 Effect of particle size on relative char yields from coal pyrolysis. Relative char yield = Char / Char at smallest particle size used. Flash Pyrolysis of Pittsburg NO.8: Data of Anthony and co-workers (1976) (▼); Data of Suuberg and co-workers (1980) (▲). Data of Stiles (1986): Flash pyrolysis of Linby (●), flash pyrolysis of Canakkale Can lignite (■), slow pyrolysis of Linby (O); slow pyrolysis of Canakkale Can (□).



Herskowitz (1985) has suggested that for low rank coals, the effect of increases in particle size (over the range studied) was much less than for bituminous coals. This conclusion was reached from data obtained at high heating rate, and is in contradiction to the data obtained by Stiles who showed that the effect of particle size on lower rank substrates and biomass was greater than that on coal for pyrolysis at low heating rate. This appears to be due to the more oxygenated nature of the volatiles from the lower rank substrate and hence there more labile nature.

The nature of the secondary reactions occurring within coal particles can be deduced by comparing the data of Suuberg with those of Anthony. Comparison shows that for coal particles larger than 300 um, the yield of tar from Pittsburg bituminous coal decreases with increasing particle size, while the total weight loss from the same coal is similarly affected by particle size. This suggests that the dominant secondary reaction occurring is repolymerisation within the particle to form char.

2.4.3 GAS PRESSURE

Changes in external gas pressure affects the tranport of volatiles during both substages of stage (A) of volatiles transport, ie. from the site of formation to the edge of the coal particle and during the "evaporation" of volatiles into the bulk gas phase. With inadequate experimental control, gas pressure may also

affect transport to the quench zone in the bulk gas phase further complicating the effect of pressure.

The effect of increases in inert gas pressure has been shown to be a decrease in the yield of tar and of total volatiles, while pyrolysis under vacuum has similarly been shown to result in increases in tar and volatiles release (Howard, 1980; Suuberg, 1985; Suuberg and co-workers, 1985). A summary of experimental results is shown in Figure 2.11.

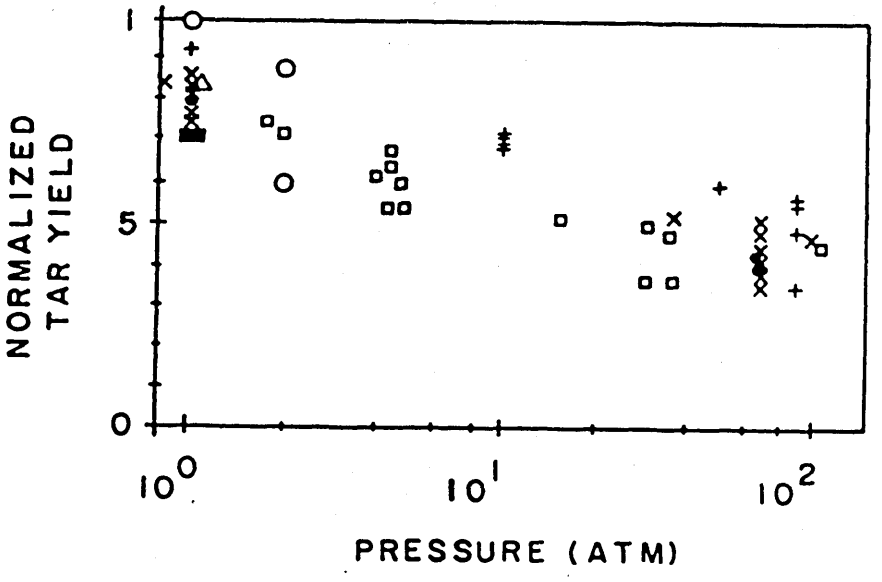


Figure 2.11 Summary of the effect of inert gas pressure on the tar yield from coal pyrolysis (Suuberg, 1985).

It should be noted much of the data pyrolysis plotted were obtained in the absence of a sweep gas. In the case of a reactive external gas such as hydrogen, the effect is complicated by the competition between the chemical effect of the reactive gas and the physical effects outlined below. Increases in gas pressure affect the transport of volatiles due to the resulting increases in

density and viscosity of the gas. These increases in density and viscosity manifest themselves in increasing the resistances to mass transfer in both subdivisions of the stage (A) of volatiles transport.

The influence of pressure on the critical particle size diameter, i.e. that representing the transition from chemical to transport control has been shown by Wagner and co-workers (1985). This represents the increased resistance to transport within the particle, resulting from, in plastic coal, the increased viscosity and density of the fluid coal particle in addition to enhanced resistance to cenosphere formation, and for coals in general, increased resistance to pore diffusion.

The effect on the evaporation step has been discussed by Suuberg (Suuberg and Sezen, 1985; Suuberg, 1985). In the pyrolysis of small coal particles, in a wire mesh reactor without a sweep gas, Suuberg has postulated that the evaporation is the rate limiting step in terms of tar formation. Correspondingly, as inert gas pressure is increased evaporation becomes progressively more difficult as a result of the increased density and viscosity of the film surrounding the coal particle, and the subsequent decrease in the gas phase diffusivity of the tar molecules.

The result of increases in pressure on the pyrolysis of bituminous coals, in the absence of a sweep gas, is

therefore a decline of collected tar yields with a corresponding decrease in total volatiles, suggesting that the dominant secondary reaction occurring is repolymerisation. In an earlier study however, Suuberg and co-workers (1980) showed that as the pressure of an inert gas increased, though the yield of total volatiles decreased, the yield of gas showed a small increase suggesting the occurence of some cracking reactions or repolymerisation and cracking reactions occurring simultaneously. Moreover yields of methane and other light hydrocarbons are seen to increase as a pressure increases suggesting that some cracking reactions probably occur.

The effect of increased pressure on the pyrolysis of low rank coal has also come into question. Herskowitz (1985) has questioned whether increases in pressure have any effect on the pyrolysis of subbituminous coals and lignites, though Suuberg has shown that for lignites, increases in pressure causes decreases in tar yields.

It should be noted that Howard (1980) has reported that in the case of the wire-mesh reactor, pressure was not seen to have any effect on volatile formation below a certain critical temperature, this temperature being a function of heating rate, and time at peak temperature. This temperature presumably represents a critical temperature for the occurrence of secondary reactions.

2.4.4 REACTOR GEOMETRY

The secondary reactions occurring during the transport of volatiles through the bulk gas phase to the quench zone is entirely dependent on reactor geometry. Secondary reactions may occur either in the gas phase or as a result of contact with hot solid surfaces.

2.4.4.1 GAS PHASE SECONDARY REACTIONS

Gas phase secondary reactions are usually limited to cracking and rearrangement, though Cypres (1986) has suggested that at high temperatures (800^{o}C) gas phase recombination reactions may occur, producing aromatic species from light alkanes and alkenes.

The extent of gas phase cracking reactions is dependent on the time-temperature history of volatile products. It is generally accepted that "in-flight" cracking for the volatiles from bituminous coals does not occur at temperatures below 580-600^{o}C, though for more lower rank substrates this secondary reactions occur below this temperature. The most common types of cracking reactions are as follows: cracking of high molecular weight aliphatics to light alkenes (ethylene and propylene), dealkylation of aromatics with subsequent cracking of the aliphatic side chain, dehydroxylation of phenols, dehydrogenation of hydroaromatics, ring closure reactions,intramolecular condensation. At higher temperatures (>900^{o}C) smaller molecules such as

methane, acetylene and hydrogen are the only stable species.

The most obvious manifestation of secondary reactions in terms of product yields from pyrolysis reactors is the tar production trends from a fluidised bed reactor, especially when compared to the results from a wire-mesh apparatus. The tar yield as a function of temperature, from a fluidised bed reactor, has a characteristic "bell shape", reaching a maximum between 580-600 for a bituminous coal. At higher temperatures, the tar yield falls as a result of secondary reactions (Tyler 1979; 1980; Kandiyoti and co-workers, 1984).

Tyler (1980) compared the results from the fluidised bed pyrolysis of Pittsburg No.8 with those obtained by Suuberg and co-workers (1980) for the same coal in a wire-mesh apparatus. A comparison of the two sets of results is shown in Figure 2.12. In the wire-mesh apparatus the amount of "in-flight" cracking is generally assumed to be negligible so the tar yield reaches a plateau with temperature and does not subsequently fall.

The effect of cracking on the structures of the tar and the nature of the gas was also studied by Tyler (Tyler, 1980; Collin and co-workers, 1980a; 1980b) and more recently by Calkins (1984).

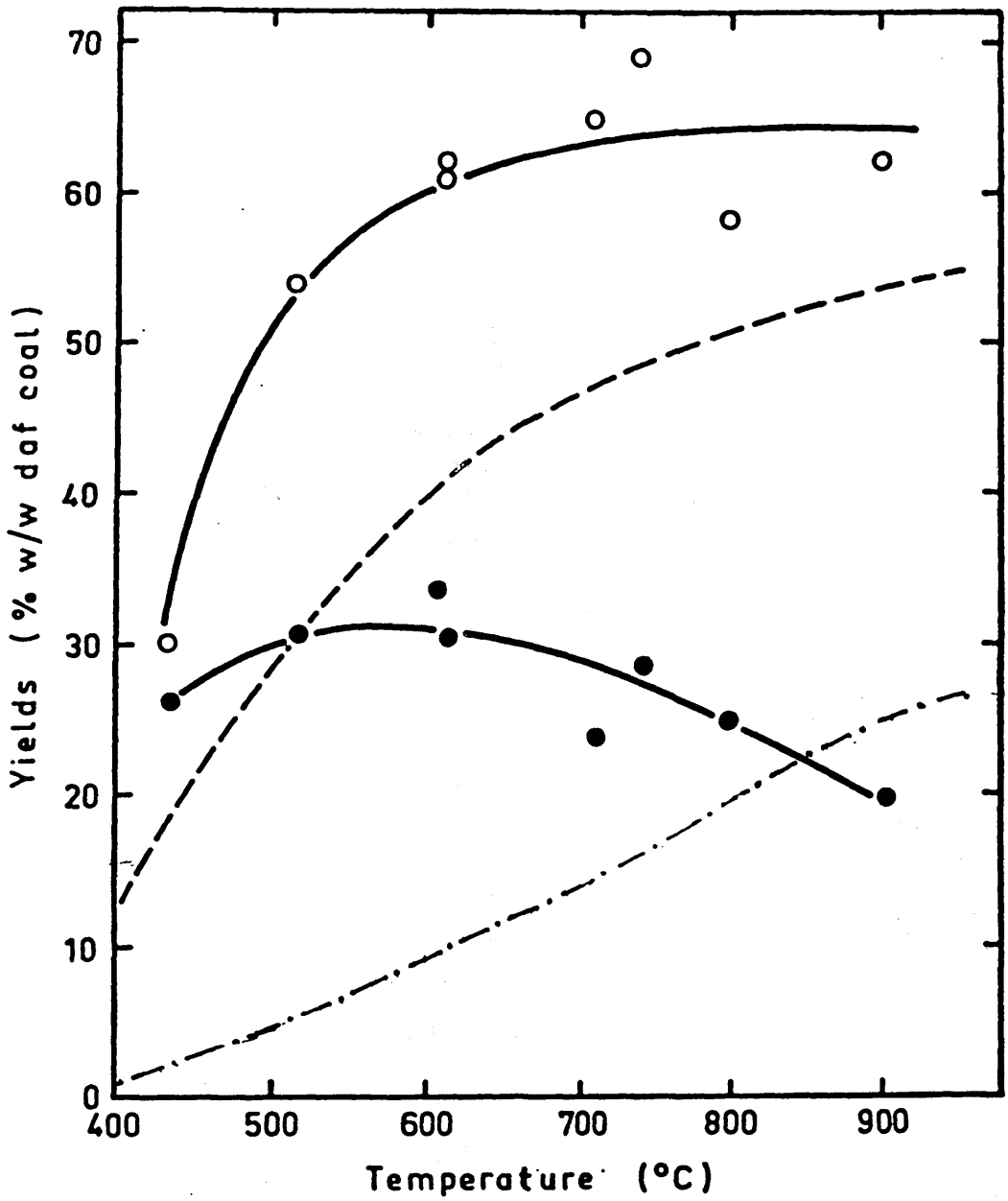


Figure 2.12 Comparison of the results of flash pyrolysis of Pittsburg No. 8 coal in a fluidised bed reactor and in a wire mesh reactor. Fluidised bed data: Tar yield (●); Total volatiles (O) (Tyler, 1980). Wire-mesh data: Tar yield (-·-·-·-); Total volatiles (— — —) (Suuberg and co-workers, 1980).

In both reactors the heating rate was in the range 10^3-10^4°C/s.

The most noticeable changes in the gas composition above 600°C were increases in alkene yields, particularly ethylene and propylene, together with increases in methane formation. Yields of benzene were also seen to rise. At higher temperatures, above 950°C ethylene and methane yields fell, with a parallel increase in the formation of acetylene.

Collin and co-workers (1980a) showed that this increase in gas yields was paralleled by major structural changes in the tar. These included increases in the hydrogen and carbon aromaticities, together with decreases in the degree of substitution of aromatic rings. The quantity of aromatic hydrogen expressed as a fraction of the hydrogen originally present in the coal did not change as a function of temperature suggesting that the dominant secondary reactions occurring to the tar molecules were dealkylation, with bond scission at the beta (benzyl) position, and dehydroxylation. Calkins and co-workers (1984a; 1984b; 1984c; Calkins, 1984) have suggested that the majority of the alkenes formed by secondary cracking during pyrolysis originates in long aliphatic "poly-methylene" chains, which are either physically trapped in the coal structure or chemically bound to aromatic clusters. Above 700°C the alpha sustituents were also seen to decrease. As the temperature increased above 600°C, the mean molecular weight of the tar decreased.

To summarise, "in-flight" cracking of the volatiles

produced in pyrolysis results in major changes in the distribution of volatiles between gas and tar, and in the chemical structure of those volatiles. In-flight cracking causes gas yields to increase at the expense of tar, while the average size of tar molecules falls and their aromaticity rises.

2.4.4.2 REACTIONS ON SOLID SURFACES

There are several different types of solid surface which volatiles might come into contact with once they have cleared the parent particle: other coal/char particles, reactor walls, or in the case of a fluidised bed, the fluidised medium, eg. sand particles. The nature, surface area and temperature of those solids surfaces has been shown to have a critical influence on the extent and type of secondary reactions occurring on them.

Mazumdar and Chaterjee (1973) measured changes in char yield in volatile matter crucibles as a result of increases in the depth of the coal bed. Heating slowly ($5^{o}C$/min.)to $900^{o}C$ the yield of char was shown to increase from 72.5% to 78% as a result of increasing the depth of the bed from a few millimetres to 10 cm.A similar trend was noted at $600^{o}C$. This suggests that a substantial amount of repolymerisation of volatiles occurred as a result of contact with other coal particles. Pyrolysis of a 1:1 mixture of coal with coconut char yielded very little tar, again suggesting a

great extent of repolymerisation reactions.

Griffiths and Mainhood (1967) examined secondary reactions of coal pyrolysis vapours in a small scale tubular cracking reactor at temperatures between 350°C and 900°C. When the volatile products were passed over activated carbon, the yield of tar was seen to decline rapidly with increasing temperature above 500-600°C. The dominant type of secondary reaction was cracking to lighter molecules, though some repolymerisation was noted. Yields of benzene, toluene and xylene passed through maxima at around 500-600°C. This temperature was much lower than that recorded in the absence of packing in the cracking reactor. In the case of the slow pyrolysis of a swept bed of coal, the maximum for BTX formation occurs at around 700°C (Cambell, 1976a; 1976b).

Serio and co-workers (1983, 1984) performed a similar experiment to study the kinetics of secondary reactions of tar produced from the slow pyrolysis of coal, comparing the results from a cracking stage packed with various solids with those from cracking in the absence of solids. The results are shown in Figure 2.13.

As can be seen, below 700°C the presence of active carbon in the cracking section produced large increases in the extent of secondary reactions. A smaller increase was noted in the presence of coal char, while quartz showed no substantial change from "in-flight" cracking

yields. Above 700°C secondary reactions in the absence of solids occur to approximately the same extent as in the presence of solids no matter what the nature of the solid surface. The authors did not report the nature of secondary reactions in terms of discrimination between repolymerisation and cracking.

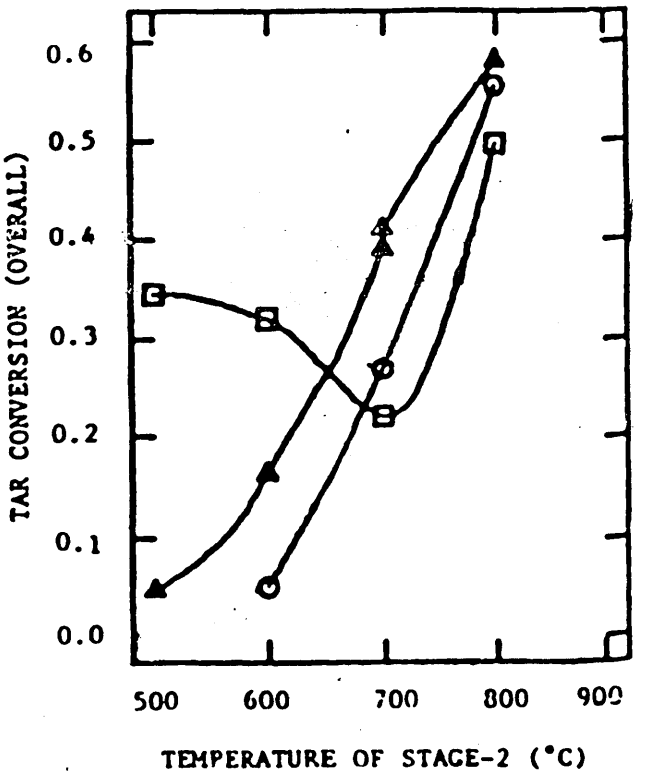


Figure 2.13 Effect of temperature on the secondary cracking of tar in the presence of various surfaces: Active carbon (□); Coal char (Δ); Quartz (○) (Serio and co-workers, 1983).

Tyler (1980) performed a series of experiments to demonstrate the effect of various bed materials in a small scale fluidised bed reactor as described in the previous section. Standard experiments on flash pyrolysis used sand as the fluidised medium with a specific surface area of 0.01 m^2/g, and produced a maximum in the tar yield of 29% at 580°C. When the sand

was replaced by petroleum coke with an active surface area of 1.6 m^2/g the tar yield at 580^oC declined to 25% though the total yield of volatiles remained substantially constant suggesting that secondary cracking was the dominant secondary reaction occurring. Above 700^oC however, substantial decreases in both tar and total volatiles occurred, a symptom of repolymerisation reactions taking place to a noticeable extent on the petroleum coke.

A single experiment utilising activated carbon as the bed material (specific surface area 800 m^2/g) yielded only 3% tar while the yield of light hydrocarbons (C_1-C_3) showed no corresponding increase. Increases in C_1-C_3 hydrocarbons yields are seen to represent the presence of cracking type reactions. In this case, repolymerisation is the dominant secondary reaction occurring.

In summary, the extent and nature of secondary reactions on solid surfaces is highly dependent on the temperature and relative reactivity of the surface. Surface area appears to play an important role. At lower temperatures and on surfaces with lower surface areas, cracking type reactions predominate, while on surfaces with a higher surface area, or at higher temperature (>700^oC), repolymerisation reactions occur to an increasing extent. It also should be noted that the structure of the tar molecules is altered by the same secondary reactions occurring on the solid surfaces.

CHAPTER 3 PYROLYSIS OF COAL AT ELEVATED HYDROGEN PRESSURE - HYDROPYROLYSIS

3.1 BACKGROUND

The underlying principle of pyrolysis at elevated hydrogen pressure is to add external hydrogen during the pyrolysis process, that hydrogen being taken up by the volatile products. The objective of this is to increase the conversion to the desired volatile product. Hydrogen can be added either directly from the gas phase, as in hydropyrolysis, or can be added indirectly, either via a solvent, or by in-situ generation during a chemical reaction.

When a vehicle solvent is used to add hydrogen the process is usually referred to as liquefaction. This is usually performed at moderate temperatures 350-480^{o}C in the presence of a hydrogen-donor under pressures between 100-200 bar. Additional gas-phase hydrogen is sometimes used, as are catalysts, depending on the severity of the process. High conversions to volatiles of up to 100% can be obtained with distillable liquid yields of up to 60%. The nature of the reactions occurring in coal liquefaction, and the influence of reaction conditions and coal type have been reviewed by Neavel (1976; 1981) and by Snape (1986).

In-situ generation of hydrogen has been studied to an increasing extent recently. The most common chemical

reaction used to generate hydrogen is the CO/H_2O shift reaction, though other reactions have also been studied such as Zn/H_2O. In the case of the CO/H_2O shift reaction, it is not clear whether any hydrogen is actually generated by the shift reaction during the liquefaction, though the net effect corresponds to significant hydrogenation.

Hydropyrolysis is pyrolysis in the presence of gas phase hydrogen, usually at elevated pressures, in the absence of solvents. The effect of catalysts is not considered in this chapter. Hydropyrolysis has been studied as a potentially commercial process more many years. The desired product from processes has either been high btu pipeline gas, coal derived liquids as a source of fuel, or as a source of light aromatics. Additionally in order to aid commercial viability, a secondary objective is to modify the nature of the solid char product to render it useful as a low-sulphur solid fuel.

Early hydropyrolysis and hydrogenation studies in Germany and the U.S.A used very high hydrogen pressures of up to 700 bar at comparatively low temperatures (400-500^{o}C). Lower pressures were used for bituminous coals than for Brown coals. Conversions to volatile products of up to 100% were achieved for low rank coals. However, many processes included the use of process derived vehicle solvents and catalysts. This early work has been reviewed by Donath (1963). More recently,

commercial hydropyrolysis has again been investigated in the U.S.A. Several pilot-plant studies have been performed using a variety of reactor types.

Despite this commercial interest, the effect of high pressure hydrogen in pyrolysis is not clear cut. The effect of high pressure hydrogen in enhancing volatiles formation, is complicated by increased resistances to the mass transfer of volatiles at higher pressure. The observed effect of hydrogen in pyrolysis and its implications in the pyrolysis are discussed in the following sections.

3.2 HYDROPYROLYSIS

The effect of high pressure hydrogen in pyrolysis is complicated as it represents the summation of two effects: the increased resistances to mass transfer as a result of increased gas pressure (see section 2.3.3), and the chemical effect of the hydrogen on the pyrolysis reactions. Additionally hydrogen would appear to modify the pathways of secondary reactions.

Attempts to assess the fundamental effects of hydrogen in pyrolysis by reviewing the existing literature, is further complicated by the emphasis of different workers on different products and different classes of products. Much early work was performed on hydropyrolysis as a means to hydrogasification, ie production of methane. Several workers have studied hydropyrolysis with a

primary interest in yields of benzene, toluene and xylene (BTX) and other light aromatics.

Much of this work has been reviewed by Howard (1980), and by Fynes, Ladner and Newman (1980).

The first major study of dry coal hydrogenation (ie. in the absence of a solvent), that is hydropyrolysis, was undertaken by the U.S Bureau of Mines (Clark and co-workers, 1950; Hiteshue and co-workers, 1957; 1960; 1964; Friedman, 1964) following up unpublished data obtained by Donath (1947). A study by Clarke and co-workers (1950) used a fluidised bed of coal heated slowly ($8^{o}C$/min.) to $600^{o}C$. The yield of "oil", equivalent to tar, increased from 10% to 27% as a result of increasing the hydrogen pressure from 1 bar to 69 bar. A substantial increase in hydrocarbon gas yield was also noted, rising from 8% to 28% over the same pressure range. When the peak temperature was limited to $500^{o}C$, though the tar yield was again seen to increase as a result of increases in hydrogen pressure, no parallel increase in gas yield was noted.

A follow up study at the Bureau of Mines by Hiteshue and co-workers (1957; 1960; 1964; Friedman, 1964) used a "hot-rod" reactor to obtain higher heating rates ($10^{o}C/s$) than could be obtained in the fluidised bed, or in autoclaves. The major interest of this study was the production of high btu pipeline gas, so high peak temperatures ($800^{o}C$) and hydrogen pressures (410 bar)

were used. Conversions of Rock Springs, Wyoming Coal to gaseous products of up to 69% were obtained, 90% of which was methane. The yield of tar were comparatively small (20%).

A secondary study of the effect of the velocity of the hydrogen sweep gas on the hydropyrolysis of New Mexico coal showed the tar yield to be highly dependent on this parameter. A summary of the results is given in Table 3.1. As can be seen, when the superficial gas velocity was increased from 0.03 m/s to 0.15 m/s the yield of tar, increased from 12% to 41%. The data examining the effect of coal/hydrogen ratio show the observed effect on tar yields to be a result of increases in gas velocity alone.

Table 3.1 The effect of hydrogen flowrate in the hydropyrolysis of New Mexico coal. (800^{o}C, 410 bar) Yields as % w/w daf coal. Results are means of numerous experiments. (Friedman and co-workers, 1964)

Hydrogen/ Coal ratio l/hr/gram	Gas Velocity m/s	Residence Time s	Conversion %	Tar Yield %
71	0.03	25.0	72.2	11.6
170	0.09	10.0	82.8	23.0
354	0.15	5.0	89.2	41.1
807	0.33	2.3	95.0	39.1
707	0.15	5.0	87.9	41.5
353	0.15	5.0	90.1	41.5
190	0.15	5.0	86.6	37.6

More recently Graff and co-workers (1975; 1976; Dobner and co-workers, 1976; Chen and co-workers, 1983), and Stangeby and Sears (1980) used similar types of hydropyrolysis reactors to study the formation of benzene, toluene and xylene (BTX). The reactor used by Squires and co-workers was of a smaller scale than that used by Hiteshue, and could therefore be heated at a higher rate (1400^{o}C/s) though whether the coal itself was heated at that rate is open to some doubt. Maximum yields of benzene of up to 12% were obtained at 800^{o}C, with a hydrogen pressure of 100 bar, while the methane yield was 21%. When the residence time of the volatiles in the hot zone was increased from the optimum level for benzene of 0.6s to 23s, the yield of benzene fell to 2.3%, while that for methane rose to 44.7%. Similar results were obtained by Stangeby and Sears.
Both these studies were essentially concerned with the secondary cracking of coal pyrolysis products in a hydrogen atmosphere, superimposed on the hydropyrolysis.

Workers at the National Coal Board, Coal Research Establishment have also used a "hot-rod" type reactor to study the fundamentals of coal hydropyrolysis and also the cracking of hydropyrolysis volatiles in an attempt to maximise yields of BTX (Finn and co-workers, 1979; 1980; Fynes and co-workers, 1981; 1984). Under conditions where the residence time of the volatiles remains constant as the pressure is increased, the yield of tar from Linby coal is seen to increase from 18% to

40% as a result of increasing the hydrogen pressure from 1 bar to 300 bar. More complete results are given in Table 3.2.

Table 3.2 Hydropyrolysis of Coal. Yields as % w/w daf coal (Fynes and co-workers, 1984)

Coal	Pressure (bar)	Tar Yield	Char Yield	Gas Yield
Linby[a]	1	18	70	6
	50	24	63	12
	300	40	35	22
Abernant[b]	1	2	97	3
	50	n.d	94	2
	300	6	81	8
Brown Coal[c]	1	22	59	8
	50	31	45	15
	300	32	39	20

a - Linby high volatile bituminous coal

b - Abernant anthracite

c - Australian brown coal

The coal were heated at 5^{o}C/s to 575^{o}C. Large yields of methane were also obtained when the temperature was raised above 500^{o}C. Use of a cracking section placed above the "hot-rod" produced yields of benzene of 13%, ethane of 16% and methane of 20% (NCB-Unpublished data, 1982).

The effect of high pressure hydrogen on the structure of the tar was also studied by workers at the NCB (Fynes

and co-workers, 1984). They found that as the pressure of hydrogen increased from 1 bar to 300 bar, the hydrogen aromaticity rose from 0.26 to 0.4, the H/C atomic ratio fell from 1.16 to 0.97, the amount of oxygen present fell from 8.6% to 4.5% and the amount of phenolic OH fell from 7.3% to 3.2%.

Cypres and Furfari (1980; 1981; 1982a; 1982b; 1985; Furfari and Cypres, 1982; 1985) performed a series of studies on the hydropyrolysis of a number of different coal at low heating rates ($10^{o}C$/min). The size of the coal sample pyrolysed was large (100g) producing a high estimated residence time of volatiles within the coal mass (60 sec). As the pressure was increased, the yield of oil (tar) appeared to increase up to a maximum at 10 bar, falling as the pressure was further increased. Overall the trend was inconclusive. The hot-zone vapour residence times in this reactor was long when compared with the residence times of workers at the NCB, and of Graff in studying secondary reactions. It can be seen from this, and from the tar production trend, that the yield and nature of volatile products formed in this reactor are likely to be dominated by secondary reactions. High yields of light aromatics have been noted corresponding to the secondary cracking results of Finn and co-workers (1979; 1980).

Noor and co-workers (1985) have studied the hydropyrolysis of a coking coal in a batch autoclave, heated slowly ($4^{o}C$/min) to $500^{o}C$. The results of this

study showed that the yield of liquids was seen to fall as a function of hydrogen pressure, while the yield of gas rose substantially. The absence of a sweep gas suggests that the initial pyrolytic reactions are again dominated by secondary processes, in this case, cracking of the tar to gas.

Several workers have studied the effect of high pressure hydrogen on pyrolysis at high heating rate in a wire-mesh type reactor. Anthony and co-workers (1976) studied the effect of hydrogen with respect to coal hydrogasification. The effect of high pressure hydrogen was to increase the total weight loss when compared to results at atmospheric pressure. High pressure helium decreased the total volatiles yield from 54% under vacuum to 37% at 69 atm. The weight loss under hydrogen increased to 60% at 69 atm, with no difference between the results with helium and hydrogen below 10 bar. As the holding time at peak temperature increased the weight loss from hydrogen continued albeit slowly, while for helium the weight was approximately constant.

Suuberg and co-workers (1980) extended this study to examine the effect of pressure on tar yields. The effect of high pressure (69 atm) hydrogen on the tar yield was essentially the same as high pressure helium. As can be seen from the results which are shown in Figure 3.1 the tar yield at atmospheric pressure, from a Pittsburg seam coal heated at 1000^{o}C/s to 1000^{o}C, was 22%. Under hydrogen pressure the tar yield fell to 10%, with a

similar result for helium. Above 500°C substantial increases in the yield of methane and other light hydrocarbons were noted under hydrogen from the bituminous coal and also from a lignite.

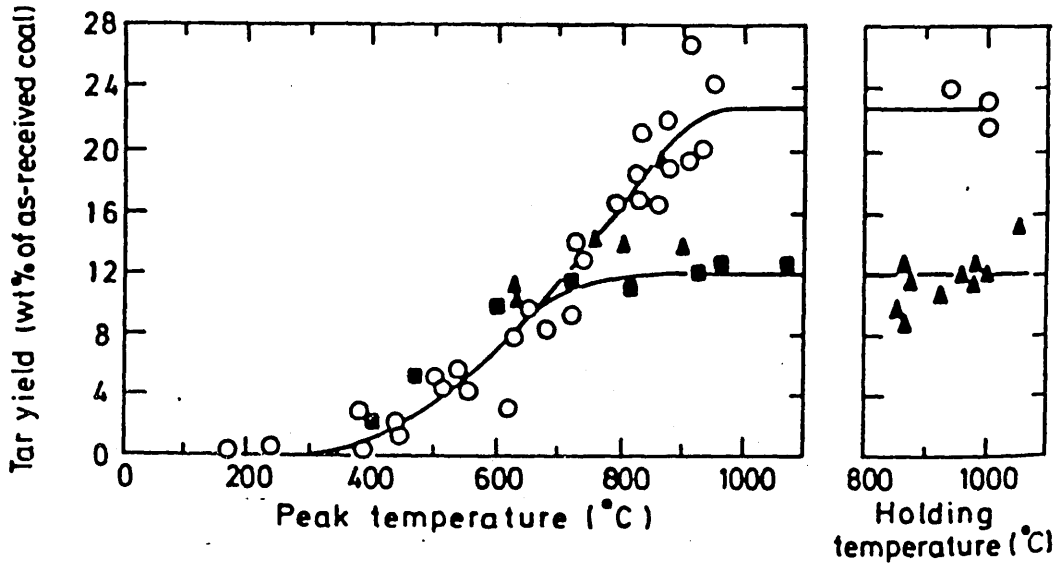


Figure 3.1 Comparison of Tar yield from the hydropyrolysis and pyrolysis of Pittsburg Seam Coal: 1 atm He (O); 69 atm H_2 (▲); 69 atm He (■). (Suuberg and co-workers, 1980)

Similar results to those obtained by Suuberg were found by workers at Bergbau-Forschung for a range of coals (Arendt and Van Heek, 1981). Experiments in a wire mesh reactor using high heating rates (210°C/s) the effect of high pressure hydrogen was to cause the tar yield of tar to fall for all the coals studied. Similar trends were found using inert gas, though the magnitudes of the falls in tar yields were larger. In a more recent study, Kaiser and co-workers (1985) showed that at larger particle sizes, the decrease in the tar yield for hydrogen was greater than that for inert gas. In experiments at low heating rates in a thermobalance, the

trend for inert gas was as for high heating rates, but under hydrogen, the tar yield was seen to increase as the pressure was increased.

Other workers have studied coal hydropyrolysis using high heating rate coal flow type reactors such as fluidised beds, and entrained flow tubular reactors (Sheehan and co-workers, 1973; Steinberg and Fallon, 1975; Fallon and Steinberg, 1977; Steinberg and co-workers, 1978; Oberg and co-workers, 1978). The nature of these reactors means that heating rates, residence times of volatiles and coal particles, together with local gas velocities are ill-defined. The tar production trends as a function of pressure from these reactor were inconclusive. The imprecision of these reactors renders the data produced in these studies of little use in a fundamental assessment coal hydropyrolysis.

3.3 FUNDAMENTALS OF HYDROPYROLYSIS

Howard (1980) has suggested that high pressure hydrogen has two principle effects on the primary reactions occurring in coal pyrolysis:

(i) It stabilises free radicals following their formation in the vicinity of the coal particle.

(ii) It can react with the coal/char during pyrolysis to to produce methane; this stage being hydrogasification.

These effects are further complicated by the additional resistance to volatiles mass transfer introduced by the increased gas pressure. In addition the effects on the primary reactions, hydrogen appears to modify the pathways of secondary reactions, specifically cracking. This can be seen by comparing the data of the "in-flight" cracking of tar vapours at atmospheric pressure (Tyler, 1980, Serio and co-workers, 1984; Calkins and co-workers, 1984a; 1984b; 1984c), with those obtained by Finn and co-workers (1979; 1980) under hydrogen pressure. In many hydropyrolysis studies secondary reactions dominate the product slate. For several workers the yield of the desired product has been maximised by manipulating the conditions for hydrocracking of the tar to the desired product. The nature of these cracking reactions was examined by Cypres (1986).

However fundamental questions remain about the effect of high pressure hydrogen in pyrolysis especially with respect to the effect on the tar yield. Dryden and Sparham (1963), reviewing some Russian papers, concluded that the effect of high pressure hydrogen in pyrolysis could be resolved by consideration of the hot-zone volatiles residence time. If, in the process of increasing the hydrogen pressure in pyrolysis, the residence time of the volatiles is maintained at a constant level, below a certain critical value, the the tar yield will increase as the pressure rises. This

hypothesis has been, in part at least, confirmed by the data of Friedman and co-workers (1964) and that of the NCB (Fynes and co-workers, 1981; 1984; Unpublished data, 1981).

The data obtained by Suuberg and co-workers (1980) and by Arendt and Van Heek (1981) show the tar yield to fall as a function of hydrogen pressure in a wire-mesh reactor where the residence time of the volatiles was assumed to be negligible. As has been discussed in previous sections (2.3.2 and 2.3.3), Suuberg has since suggested that the tar evolution in the wire-mesh reactor is evaporation controlled, and that as the external pressure is increased whether inert gas or hydrogen, the rate of evaporation is lower due to increased resistances to mass transfer. The tar production trend still represents the competition between mass transfer increases and the chemical effect of hydrogen, though in this case, the former dominates.

In the case of a swept wire-mesh reactor Gibbins (in preparation) has hypothesised that evaporation is no longer the rate limiting step in tar formation, and therefore the effect of high pressure hydrogen may be the same as at lower heating rates ie. it may result in an increase in tar yield.

It remains unclear as to the location at which the hydrogen acts to stabilise free radicals or the mechanism by which the hydrogen acts. These stabilising

reactions may occur in the film surrounding the coal particle, in the pores and bubbles formed in pyrolysis, or within the coal mass itself.

The effect of hydrogen in gasifying the coal/char to methane is better characterised. Hydrogasification reactions occur at temperatures above approximately $500^{o}C$ (Clark and co-workers, 1950; Fynes and Newman, Unpublished data, 1982). The temperature above which this commences is a function of the type of coal hydropyrolysed, and has been studied recently by Gorbaty and co-workers (1986).

CHAPTER 4 CATALYTIC COAL PYROLYSIS

4.1 SCOPE

The catalysts considered in this study are all of the Lewis acid type, which are defined as electron pair acceptors. This class of compounds is used widely in organic chemistry as catalysts for Friedel-Crafts type reactions (Olah, 1964).

In coal conversion processes this class of compounds has also been used extensively as a catalyst. Lewis acids have been shown to be capable of catalysing coal liquefaction processes under high pressure hydrogen, and also of catalysing various carbonisation reactions (formation of char/coke by slow pyrolysis) of coal and other organic substances. A recent study has shown $ZnCl_2$ to be capable of catalysing the formation of tar in flash pyrolysis at atmospheric pressure.

This chapter reviews the existing literature on the effect these catalysts on the coal conversion processes described above, and the proposed mechanisms by which these catalyst are thought to act.

4.2 CATALYTIC COAL LIQUEFACTION

Catalysts of the Lewis acid type have been used extensively in coal liquefaction, using a range of conditions aimed to maximise yields of coal derived

liquids. The range of heating rates that have been used is wide from 5°C/min to 1000°C/s, up to temperatures between 400 and 650°C, and hydrogen pressures up to 410 bar, with and without solvents.

It has been known for many years that tin and tin based compounds are active as coal hydrogenation catalysts. Moreover, addition of chlorine as NH_4Cl increased catalytic activity. This early work was reviewed by Donath (1963). The first major systematic study of the activity of a range of catalysts was performed by the US Bureau of Mines. Weller and co-workers (1950a; 1950b; 1951; Pelipetz and co-workers, 1948) studied the effect of various catalysts on the dry hydrogenation of coal in a batch autoclave. The heating rate used was low (5°C/min) up to 450°C, with a cold hydrogen pressure up to 250 bar. The level of catalyst loading was small, less than 1% of the coal. A summary of their results is given in Table 4.1.

The most effective catalyst, in terms of conversion to liquids, was tin (II) chloride, impregnated onto the coal. Of the other catalysts studied, zinc chloride was not so effective as tin (II) chloride, while use of ferric chloride, known as a strong Lewis acid, caused the conversion to fall when compared to the uncatalysed coal. Weller considered that the active species were the metal and HCl gas formed by the degradation of the catalyst at reaction temperature, though when the results obtained with the metal and gas (from NH_4Cl)

used as catalysts individually, were compared with those obtained using mixtures, some synergism was seen to be occurring.

Table 4.1 Effect of various metal halide catalysts on the liquefaction of Bruceton Coal (Weller and co-workers, 1950). Yields on % w/w daf basis.

Catalyst	Liquefaction	Asphaltene	Gas
None	55.0	15.4	14.0
0.5% $SnCl_2$	88.8	50.0	13.7
1.0% $SnCl_2$	84.6	31.3	12.7
1.0% $ZnCl_2$	80.3	22.5	--
1.0% $FeCl_3$	37.0	5.6	11.4
1.0% $FeSO_4$	44.8	15.2	13.6
1.0% MoO_3	70.0	26.6	13.6

The activity of some metal sulphates as liquefaction catalysts, together with the inactivity of the corresponding chloride (eg. the case of iron), also casts doubt on this conclusion. However, tin sulphate has been shown to have little catalytic activity. It seems likely that the active species is the metal halide. In a secondary study (Weller and co-workers, 1951), the increase of catalyst activity as a result of impregnation onto the coal was also reported, with ball-milling of the catalyst with the coal being in turn better than simple admixing.

A study by workers at the Consolidation Coal Co. (Zielke and co-workers, 1966a; Zielke and co-workers, 1966b)

used substantially similar conditions to those used by Weller and co-workers, but utilised much higher loadings of catalyst in their coal liquefaction experiments. The ability of Lewis acids to act as hydrocracking catalysts for coal extracts was also shown. In hydrocracking experiments, a 50% loading of zinc chloride as a "melt" was shown to be more active than the same loading of tin (II) chloride with respect to the formation of light hydrocarbon liquids from perylene. Use of aluminium bromide resulted in high gas yields. In coal liquefaction experiments, heated to 385^{o}C at low heating rates, using 140 bar H_2, 75 % conversions were obtained, with light distillate yields of up to 50%. In this study, the authors reported that the most stable catalytic species under reaction were the metal halides themselves.

A further study at the US Bureau of Mines compared the effect of catalyst loading and also a further variety of catalysts in coal and coal derived asphaltene liquefaction (Kawa and co-workers, 1970). The conditions used were similar to those of Weller: a batch autoclave heated at 7^{o}C/min to 425^{o}C with a hydrogen pressure of 280 bar. As can be seen from the results give in Table 4.2 under conditions of high catalyst loading (50%) the total conversion of the coal with zinc chloride was 88%, while with tin chloride the conversion was 82%. At lower loadings (1%), tin (II) chloride gave a higher conversion (88%) than zinc chloride (67%), though at both loadings zinc chloride was more specific to the

production of lighter liquid products. The most effective catalyst was found to be zinc bromide.

Table 4.2 Effect of various catalysts and loading levels in the hydrogenation of Pittsburg-seam Coal (Kawa and co-workers, 1970); 50 g coal, 275 bar H_2, 425°C, 1 hour. Yields on % w/w daf basis.

Catalyst	Conversion	Light Oil	Heavy Oil	Gases
none	63.0	6.0	13.0	6.0
50% $ZnCl_2$	88.0	45.0	16.0	14.0
50% $SnCl_2$	82.0	29.0	40.0	6.0
50% $ZnBr_2$	90.0	56.0	8.0	14.0
50% ZnI_2	90.0	55.0	5.0	17.0
50% SnI_2	92.0	20.0	42.0	6.0
1% $ZnCl_2$	67.0	8.0	18.0	8.0
1% $SnCl_2$	88.0	7.0	34.0	4.0

Workers at the University of Utah (Wood and co-workers, 1970; Wood and Hill, 1972; Anderson and co-workers, 1975; Wood and Wiser, 1976) utilised an entrained coal flow type, coiled tube reactor to generate high heating rates (approx. 1000°C/s) in their catalytic liquefaction experiments. Coal impregnated with moderate loadings of Lewis acid catalysts were heated in the tubular reactor to temperatures between 500°C and 650°C at hydrogen pressures between 125 and 140 bar. A range of catalysts were compared at a 10% loading with the catalyst being impregnated. A summary of their results is given in Table 4.3. The most effective catalyst found was again found to be zinc bromide with 58.5% conversion, while

zinc chloride was found to be more active than tin (II) chloride. Attempts to recover zinc chloride from the char showed that this was difficult to accomplish completely, even using acid washing.

Table 4.3 The effect of various catalysts on hydrogenation of Last Chance Coal in an entrained flow reactor (Wood and Wiser, 1976); 125 bar, 650°C, 10% catalyst loading.

Catalyst	Percentage Conversion
$ZnBr_2$	58.5
ZnI_2	46.3
$ZnCl_2$	41.1
$SnCl_2$	40.5
$FeCl_3$	7.2
$CdCl_2$	7.9

More recently Yoshida and Bodily (1979), and Yokoyama and co-workers (1983) have characterised the liquid product derived in this process as an attempt to gain some insight into the mechanisms of the action of these catalyst and specifically zinc chloride. This will be dealt with in greater depth in section 4.5.

Kershaw and Barrass (1979) examined the effect of tin chloride as a catalyst in the hydropyrolysis of coal in a "hot-rod" reactor. The heating rate used here was 100°C/s up to 450°C at 150 bar hydrogen. As the loading of tin chloride was increased, though no change in the structure of the liquid products could be identified by

either ^{1}H or ^{13}C NMR spectroscopy, the viscosity of the oil fraction decreased and the fraction of acid and basic compounds fell. These two findings are probably linked and suggest that the effect of the catalyst may principally be on the heteroatoms.

A more recent study by Kershaw (Kershaw and Bagnall, 1984) examined the effect of the presence of various liquefaction solvents on catalytic coal hydrogenation. The hydrogenation experiments were carried out in a batch autoclave heated at 7°C/min to 400 or 450°C, with a cold hydrogen pressure of 105 bar. Kershaw showed that at 400°C, the presence of the solvent, whether hydrogen donor or not, increased the conversion to liquids, though a similar increase was seen when sand was added, the effect of the sand being to inhibit coal agglomeration. At 450°C the presence of a solvent increased the yield of liquid over experiments without solvent even when sand was added. Indeed the yield of liquids at 450°C without solvent was lower than the yield at 400°C suggesting that retrograde reactions are occurring at the higher temperature. At the higher temperature the yield of liquids formed during the liquefaction was very similar whether the solvent used was a hydrogen donor or a non-hydrogen donor. This is different to the trends observed in the absence of a catalyst (Neavel, 1976) and suggests that at least part of the action of the catalyst involves interaction with the solvent or part of the coal resulting in the formation of hydroaromatic type hydrogen-donor

structures.

Other work involving the use of Lewis acids as coal liquefaction solvents includes liquefaction of coal in supercritical water using tin (II) chloride as a catalyst (Barton, 1983), liquefaction of coal using a melt of zinc chloride and methanol (Shinn and Vermeulen, 1979) and an extensive study on the liquefaction of coal using melts containing zinc chloride and tin (II) chloride, together with a variety of other metal salts, mainly chlorides (Nomura and co-workers, 1982a; 1982b; 1983; 1984; 1985). In this latter study, both low and high concentrations of catalysts were used (5%) under dry liquefaction conditions. In general, addition of other metal chlorides to either zinc or tin chloride resulting in higher yields of liquids. The reasons for these increases in activity are unclear.

In conclusion it can be seen that under a variety of liquefaction conditions, many Lewis acids catalyse coal conversion to liquids. The relative activity of the various catalysts especially tin (II) chloride and zinc chloride is highly dependent on the reaction conditions employed. Under conditions of high catalyst loading or high heating rate, zinc chloride seem to be more active towards liquid formation, whereas at low loadings and low heating rates, tin (II) chloride is the more active catalyst. Stronger Lewis acids such as aluminium halides or iron (III) chloride produce differing results; aluminium bromide was seen to be a very powerful

hydrocracking catalyst by Zieldke and co-workers (1966a), producing high gas yields, while ferric chloride acts to reduce liquid yields in coal liquefaction.

4.3 CATALYTIC CARBONISATION

A substantial amount of work has been performed using Lewis acids to increase the yield of coke/char in the carbonisation (slow pyrolysis) of coal, heavy organic liquids and model compounds, and to modify the structure and texture of the coke.

Two independent studies of the slow pyrolysis of coal have used a variety of catalysts (Georgiadis and Gaillard, 1956; Bodily and co-workers, 1975). The results are shown in Table 4.4.

Georgiadis and Gaillard (1956) performed Fisher Assays ($3^{o}C$/min to $525^{o}C$) on coal samples impregnated with a variety of inorganic compounds, including aluminium chloride and zinc chloride, with a catalyst loading of 2-3%. The effect of the catalysts was to increase the yields of char, and to decrease the yield of tar. Additionally, increased yields of molecular hydrogen were noted.

The more recent study by Bodily and co-workers (1975) showed similar results for American coals. Reduced yields of total volatiles were noted when coal samples

were impregnated with low concentrations (12%) zinc halides and tin (II) chloride prior to slow pyrolysis ($5^{o}C$/min) in a nitrogen swept thermo-balance.

Table 4.4 Effect of catalysts on the carbonisation of coal. Yields on % w/w daf basis.

Coal	Catalyst	Loading	Char	Tar
Br 3	none	-	77.0	14.0
Br 3	$ZnCl_2$	3%	82.0	12.1
Br 3	$AlCl_3$	2%	78.5	13.2
B 3	none	-	86.0	6.5
B 3	$ZnCl_2$	3%	93.0	4.1
B 10	none	-	78.5	9.3
B 10	$ZnCl_2$	3%	92.0	6.3
B 10	$AlCl_3$	2%	84.0	7.5
Hiawatha	none	-	72.5	--
Hiawatha	$ZnCl_2$	12%	85.7	--
Hiawatha	$SnCl_2$	20%	89.6	--

In another study, (Bodily and co-workers, 1974), increased yields of molecular hydrogen were noted, with the initial hydrogen release being at a lower temperature ($200^{o}C$) than in the absence of the catalyst ($300^{o}C$). Use of Palladium as a catalyst for dehydrogenating hydro-aromatics in the residues (chars) from the pyrolysis, both catalysed and uncatalysed, suggested that a substantial amount of the hydrogen released originated in the hydro-aromatic structures in the coal.

Mochida and co-workers (1975; 1978; 1982) performed a study on the carbonisation of heavy organic liquids and polycyclic aromatics in the presence of aluminium chloride. In all carbonisations low heating rates were used.

Carbonisation of a range of polycyclic aromatic hydrocarbons in the presence of 10% aluminium chloride resulted in the formation of a mesophase, and subsequent formation of anisotropic coke, for aromatics heavier than benzene, whereas in the absence of the catalyst the substrate would merely sublime (Mochida and co-workers, 1975). Increased loadings of aluminium chloride resulted in increased coke yields. Other Lewis acids investigated ($FeCl_3$, $CuCl_2$) did not result in a mesophase being formed. Similar results were noted for nitrogen containing aromatics (Mochida and co-workers, 1978).

The action of aluminium chloride on the carbonisation of a vacuum residue from Orinoco Tar Sands was studied by the same authors (Mochida and co-workers, 1982). The effect of the catalyst was to decrease the yield of oil and to increase the coke yield. As the catalyst loading increased up to 30%, the amount of hydrogen released in the carbonisation was seen to increase greatly, while the initial temperature at which hydrogen production occurred decreased. The yields of C_2, C_3 and C_4 hydrocarbons were similarly affected, though the effect on methane was smaller.

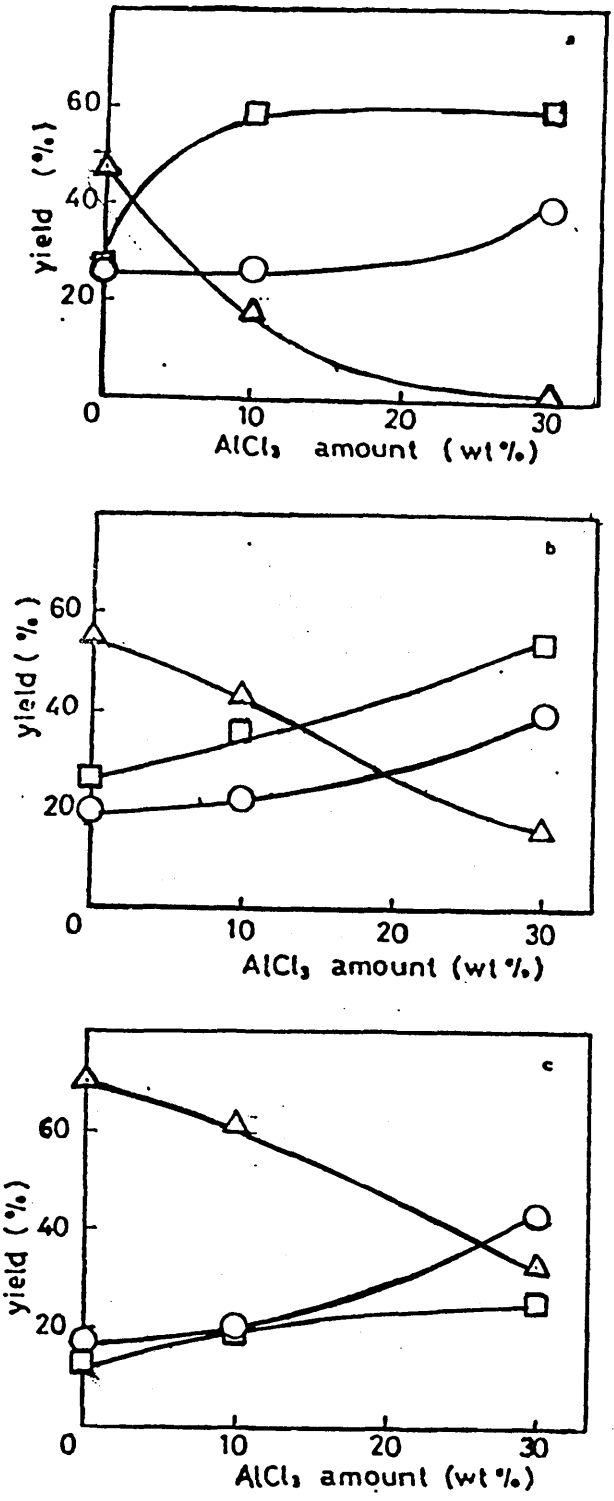


Figure 4.1 Effect of heating rate on the products from the catalytic carbonisation of Orinoco Vacuum Residue: oil yield (Δ); gas yield (O); coke yield (□); (a) 50°C/hr; (b) 600°C/hr; (c) 1200°C/hr.

The changes in the product slate occurring as a result of the presence of the catalyst were seen to be a function of the heating rate used as can be seen from Figure 4.1. When the heating rate is increased from $0.83^{o}C/min$ to $20^{o}C/min$, the effect of the presence of the catalyst in diminishing the yield of oil is substantially reduced, while the yield of char is not similarly affected.

Similar results were noted by Rey Boero and Wargon (1981a; 1981b) for the catalytic carbonisation of naphthalene. In the presence of the catalyst, mesophase formation was again noted, while in its absence the naphthalene sublimed. Substantial releases of hydrogen were also noted. Studies of the fractions of the mesophase soluble in toluene and quinoline suggest that these fractions contain aliphatic groups which are produced as a result of disproportionation reactions hydrogenating some aromatics with hydrogen formed in the carbonisation of other aromatic molecules.

To summarise, it can be seen that Lewis acids and particularly aluminium chloride catalyse the carbonisation of coal, aromatic model compounds and heavy hydrocarbon liquids. The evolution of molecular hydrogen is reported in many cases and may be associated with condensation reactions, though other types of dehydrogenation and hydrogen transfer have also been reported. There is also an indication that heating rate may have a significant influence on catalytic effect.

4.4 CATALYTIC FLASH PYROLYSIS

A recent study by Kandiyoti and co-workers (1984; Weerasinghe, 1981; Dyrvold, 1982; Lazarides, 1983) has examined the effect of zinc chloride as a catalyst in coal flash pyrolysis, using an atmospheric pressure fluidised bed, of the type used by Tyler (1979). The heating rate of the coal in this reactor has been calculated to be greater than $1000^{o}C/s$. The zinc chloride was impregnated onto the coal from aqueous solution prior to pyrolysis.

Results at lower heating rates using a Gray-King Assay ($5^{o}C$/min to $600^{o}C$) showed similar trends to those obtained by Georgiadis and Gaillard (1956), and by Bodily and co-workers (1975). The tar yield was seen to fall as a result of the presence of the catalyst, while the char yield increased.

At high heating rates, this trend was reversed. As can be seen from Figure 4.2, the maximum tar yield of 22% from a British bituminous coal was obtained at $580^{o}C$. When zinc chloride impregnated coal was flash pyrolysed, the maximum tar yield was again obtained at $580^{o}C$, and was seen to increase to 29%. The changes in the product slate occurring as a result of the presence of the catalyst were seen to be a function of the heating rate used as can be seen from Figure 4.1.

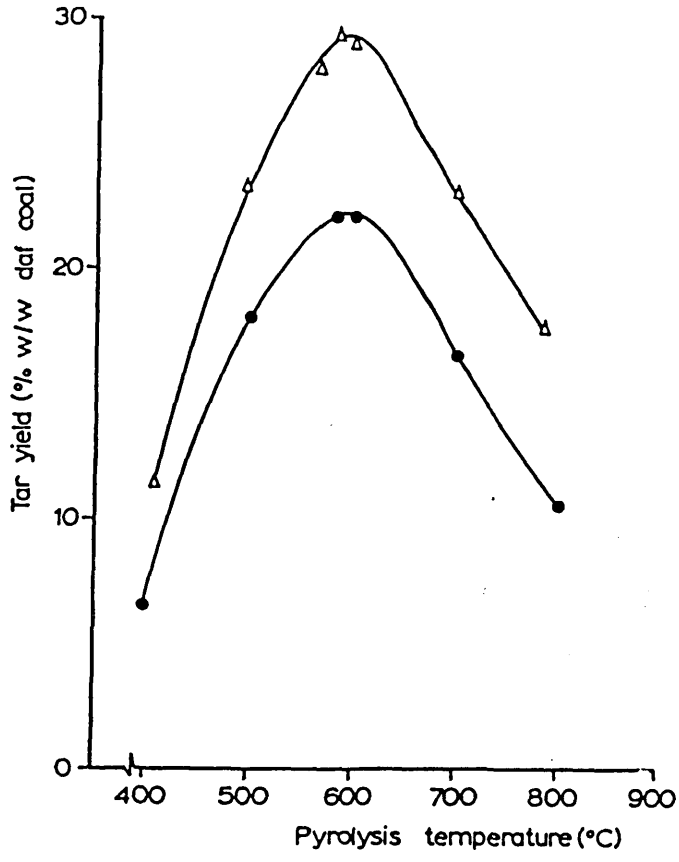


Figure 4.2. Tar yields from the flash pyrolysis of zinc chloride impregnated (Δ), and untreated Linby coal (●) as a function of pyrolysis temperature (Kandiyoti and co-workers, 1984)

As the catalyst loading was increased to 10%, the tar yield continued to rise to 36%. Analysis of the tar by ^{1}H NMR spectroscopy and elemental micro-analysis, showed no noticeable difference between the tars from the catalyst impregnated coal and those from the untreated coal, though significant changes were noted in both tars as a function of pyrolysis temperature, of the type already reported by Collin and co-workers (1980a) and discussed in section 2.3.4.1.

Kandiyoti concluded that the observed reversal of catalytic activity occurred solely a result of the use of higher heating rates. They hypothesised that zinc chloride could catalyse either condensation char forming reactions, or hydrocracking type reactions involving catalysed hydride abstraction from the coal mass resulting in an increase in the yield of volatiles. The proposed mechanisms were thought to involve Friedel-Crafts chemistry. The relative rates of each reaction type were thought to be dependent on heating rates. It was also noted that in the low heating rate experiments, significant quantities of the catalyst had been converted to zinc sulphide.

4.5 CATALYST DISTRIBUTION

In order to assess the mechanism by which zinc chloride and other Lewis acids act in coal pyrolysis, it is necessary to have knowledge about the location of the catalyst during the pyrolytic process, and also about the nature of the chemical species present at that location. There have been several studies examining catalyst distribution and its importance particularly in liquefaction. These will be discussed below, together with several methods used to examine catalyst distributions and chemical nature.

The first study of the importance of catalyst dispersal was performed by Weller and co-workers (1951), as mentioned in section 4.2. The results as shown in Table

4.5, suggest that for all the catalysts studied, the more intimate the initial contact between the coal and catalyst, the better the conversion in coal liquefaction.

Table 4.5 Effect of catalyst distribution on the dry liquefaction of Rock Springs Coal (Weller and co-workers, 1951). Yields % w/w daf coal.

Catalyst	Mode of distb.	Liquefaction	Oil
1% $FeSO_4$	Impregn.[a]	84.9	21.7
1% $FeSO_4$	B.M.[b]	66.2	21.2
1% $FeSO_4$	Powder[c]	38.9	8.1
1% $NiCl_2$	Impregn.	88.2	45.3
1% $NiCl_2$	B.M.	56.9	19.3
1% $NiCl_2$	Powder	44.2	13.2
1% $SnCl_2$	Impregn.	88.3	41.4
1% $SnCl_2$	Powder	82.3	29.2
1% A.M.[d]	Impregn.	92.7	41.4
1% A.M.	Powder	33.7	13.8
1% $PbBr_2$	B.M.	80.7	28.5
1% $PbBr_2$	Powder	71.1	20.7

a - Catalyst impregnated from aqueous solution

b - Catalyst ball-milled with the coal for 6 hours

c - Catalyst added as a dry powder to the liquefaction

d - Ammonium Molybdate

More recently Wood and Wiser (1976) have claimed that catalyst dispersion is unimportant in coal hydrogenation though the data showing this were not published. The

hydrogenation in this case was catalysed by zinc chloride, and was performed using higher heating rates and temperatures, where presumably the catalyst is more mobile.

The mobility of tin (II) chloride and its chemical form during coal hydrogenation was studied by Shibaoka and co-workers (1980) using electron and optical microscopy and utilising a microprobe analyser.

Impregnation of coal with tin chloride from ethanolic solution resulted in the coating of the coal surface with the catalyst with no apparent migration inwards. During hydrogenation at comparatively low temperatures ($< 400^{o}C$), the catalyst was observed to diffuse inwards into the coal particle, its diffusion limiting the rate of hydrogenation. The active form of the catalyst was seen to be the tin chloride itself, though following hydrogenation, significant quantities of catalyst were converted to tin sulphide.

A more recent study (Shabtai and co-workers, 1985) of catalyst distribution in coal using a microprobe analyser, has shown that the distribution of zinc chloride is highly dependent on the solvent used in the impregnation procedure. Impregnation of zinc chloride from aqueous solution does not result in the catalyst migrating into the coal particle, while use of acetone as a solvent produces an even distribution across the coal particle, producing what the authors described as

an coal-catalyst intercalate. Presumably the nature of the solvent and its ability to "wet" the coal is the limiting factor in the impregnation process.

Mossbauer spectroscopy studies of Australian brown coal impregnated with tin (II) chloride from aqueous solution has shown that the tin was present as hydrated tin (IV) oxide ($SnO_2.xH_2O$) (Cook and co-workers, 1985). The authors concluded that the tin chloride had been both hydrolysed and oxidised during the impregnation procedure. Microprobe studies of the same impregnated coal suggested that the catalyst was finely dispersed throughout the coal particle. This is in contradiction of the work of Shibaoka and co-workers (1981), though the impregnation method is significantly different. Furthermore, Cook and co-workers concluded that high a concentration of tin sulphide was present at 350^{o}C (40% of tin), with the sulphide and metallic tin being the catalytic species. This is also in contradiction to the work of Shibaoka and co-workers (1981).

X-ray diffraction studies of coal samples impregnated with zinc chloride and other Lewis acids by a variety of methods, has shown that the catalysts are incorporated into the coal structure in a similar manner to graphite intercalation compounds (Beall and Wadja, 1984; Lazarov and co-workers, 1984). The condition employed to obtain intercalation typically more extreme than are used in catalyst impregnation, for example using higher temperatures or ultra-violet radiation. Additionally,

the coals studied were of a high rank where the macromolecular structure is thought to be more ordered, in terms of its similarity to graphite.

The effect of impregnation processes on catalyst dispersion remains largely unclear. However, the importance of catalyst dispersion under certain condition has been clearly shown. It also remains unclear as to what the active forms of the Lewis acid catalysts are in coal pyrolysis and hydrogenation reactions.

4.6 THE MECHANISM OF THE ACTION OF LEWIS ACIDS IN COAL CONVERSION

It has been assumed by most of the workers, whose studies of catalytic coal conversion have been reported in this chapter, that Lewis acids act as catalyst for Friedel-Crafts reactions involving heterolytic bond scission, and carbonium ion formation. Mechanisms have been suggested to explain most of the phenomena reported involving this type of reaction. The ionic mechanism involved in these theories is different to the usually accepted theory of pyrolysis which is exclusively a free radical based process initiated by homolytic bond scission. Liquefaction is also not thought to involve heterolytic bond scission, though recently Ross (1985) has suggested that this may be in error.

The nature of the mechanisms by which the Lewis acids

may act have been investigated by numerous workers. Work by Bell and co-workers (Mobley and Bell, 1979; 1980; Taylor and Bell, 1980; Bell and co-workers, 1981) on the effect of catalyst on model compounds under hydrogenation conditions, has shown that Lewis acids are capable of catalysing the scission of linkages between aromatic nucleii whether these are sulphur linkages, oxygen (ether) linkages or aliphatic bridges. Bell proposed carbonium ion based mechanisms as the mode of the catalyst action involving hydride ion abstraction. Bell also proposed that the major source of hydride ions may be Lewis acid catalysed Scholl condensation reactions.

Yoshida and Bodily (1979), and Yokoyama and co-workers (1983) have suggested that the dominant reaction catalysed by zinc chloride during hydrogenation was scission of ether linkages. Bodily also concluded that zinc chloride catalysed dealkylation reactions. This has also been noted more recently in catalytic carbonisation of coal by Neuberg and co-workers (in print).

Mastral and co-workers (1984; 1985a; 1985b) investigating the Lewis acid catalysed solubilization of Spanish lignite, suggested that under the conditions employed, carbonium ions may be formed by the catalytic scission on methylene and ether bridges.

The nature of the action of catalysts in carbonisation is thought to be better understood, again involving

carbonium ion formation, under these circumstances as a precursor to condensation reactions (Mochida, 1982). The occurrence of these reactions is accompanied by the production of molecular hydrogen, which has been observed in many of the catalytic carbonisation studies.

However, Bodily and co-workers (1974) have shown that at least some of the hydrogen released may have originated in the hydroaromatic structures in coal, and may be evolved due to catalytic dehydrogenation reactions. It should be noted that the loss of this hydrogen may be expected to have the effect of reducing tar production in pyrolysis due to the non-availability of some of the hydrogen used to stabilise free radicals, which would subsequently repolymerise increasing char yields.

Studies at low temperature on model compounds suggest that some hydrogenation may occur utilising the hydrogenation formed in the condensation reaction. A significant yield of tetralin, together with a polymerised "tar" was noted, when naphthalene was treated at 70^{o}C with aluminium chloride in heptane solution (Stobart and Zaworotko, 1985). Similar results were found by Mochida under carbonisation conditions.

The hypothesis that the action of zinc chloride and other Lewis acids is via a carbonium ion mechanism has been considered by several different workers under hydrogenation and carbonisation conditions.

Bodily and co-workers (1975) used nitric oxide as the gaseous environment during the slow pyrolysis (5°C/min) of coal impregnated with tin (II)chloride and zinc chloride. Nitric oxide is known to be a free radical scavenger and so would not interfere with the action of the catalysts, if this was via an ionic mechanism. The results of the study are shown in Table 4.6. They demonstrate that the decrease in weight loss as a result of the presence of nitric oxide is not affected by the presence of the catalyst and that the presence of nitric oxide does not interfere with the action of the Lewis acid in reducing total weight loss. This implies that the action of both tin (II) chloride and zinc chloride is not via a free-radical mechanism or more correctly is not via a free radical mechanism which nitric oxide can interfere with.

Table 4.6 Effect of Nitric Oxide as an atmosphere in catalytic slow pyrolysis. (Bodily and co-workers, 1975)

Sample	Atmosphere	Weight Loss
Coal	N_2	27.5
Coal	N_2/NO	23.0
Effect of NO		4.5
Coal/12% $ZnCl_2$	N_2	14.3
Coal/12% $ZnCl_2$	N_2/NO	10.1
Effect of NO		4.2
Coal/20% $SnCl_2$	N_2	10.4
Coal/20% $SnCl_2$	N_2/NO	5.0
Effect of NO		5.4

Larsen and Earnest (1979), in a study of isotope scrambling in zinc chloride catalysed coal hydrogenation, concluded that carbonium ion mechanisms were an inadequate explanation of the action of zinc chloride.

Direct measurements of the concentration of free radicals in coal is possible using electron spin resonance (e.s.r). In-situ e.s.r. spectra of coal during pyrolysis have given measurements of free radical concentrations during the pyrolysis process (Sprecher and Retcofsky, 1983). In-situ measurements of the pyrolysis of coals in the presence of Lewis acids have been recorded in two different studies.

Sakawa and co-workers (1983) recorded the e.s.r. spectra of the carbonisation of coal and coal derivatives in the presence of aluminium chloride. Significant changes in the concentrations of free-radicals were noted as a result of the presence of the catalyst. Changes of free radical concentrations were also noted due to the presence of aluminium chloride in the carbonisation of aromatic model compounds. In the case of the carbonisation of the quinoline insoluble fraction of coal the free radical concentration was seen to fall as a result of the presence of the catalyst, while for carbonisation of a quinoline extract from the same coal, the presence of the catalyst caused the free radical

level to rise.

A more recent study by Yokono and co-workers (1985a; 1985b; 1985d) made in-situ measurements of free-radical concentrations during the pyrolysis of coal at high pressure and at low pressure. The effect of a number of Lewis acid catalysts on the free radical concentration was examined. In the atmospheric pressure pyrolysis (heating rate = $1^{o}C/s$) the presence of the Lewis acids had little effect on spin concentrations at $390^{o}C$, but at $420^{o}C$ the presence of all Lewis acids caused an increased in the concentration of free-radicals. The results are shown in Figure 4.3. It should be noted that the smallest increase was noted with aluminium chloride. At high pressure as the temperature was increased above $350^{o}C$, in the absence of a catalyst under hydrogen, or under helium, the free radical concentration rose rapidly. Under hydrogen, in the presence of both tin (II) chloride and zinc chloride, no such rise in the level was noted.

Both these studies, but especially the more recent one suggests that the action of certainly zinc chloride and tin chloride involves the formation of free radicals, under the reaction conditions employed, that is in slow pyrolysis under atmospheric pressure. Under high pressure hydrogen, the presence of the catalyst seems to reduce the concentration of free radicals, implying interaction with the externally applied hydrogen.

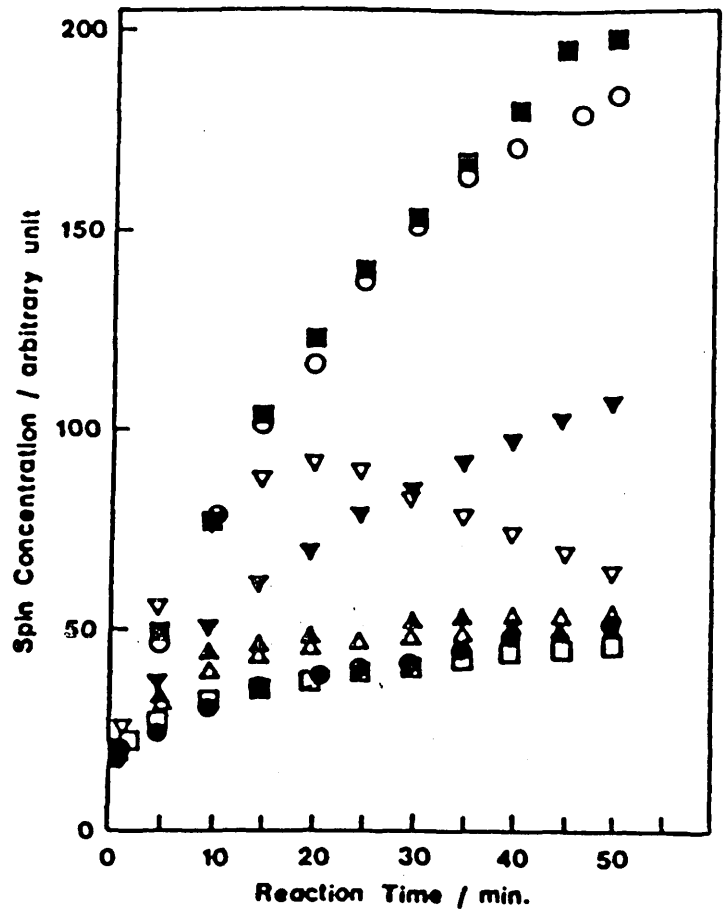


Figure 4.3 Spin concentration as a function of time for the pyrolysis of Taiheyo coal + catalyst: Untreated coal (□); Coal + $ZnCl_2$ (impregnated) (■); Coal + $ZnCl_2$ (dispersed) (○); Coal + $ZnCl_2$/KCl (▼); Coal + $SnCl_2$ (▽); Coal + $AlCl_3$ (▲); Coal + $SbCl_3$ (△); Coal + $CaCl_2$ (●).

It is clear from these e.s.r. results that simple Friedel-Crafts chemistry is inadequate to explain all the observed phenomena, though free radical mechanism cannot be invoked as an automatic replacement. Olah (1964) has suggested the possible existence of radical ions, which would participate in Lewis acids catalysed processes accompanied by changes in e.s.r. spin concentrations. Recently Camaioni (1985) has suggested the existence of radical cations in the copper

peroxydisulphate (CuS_2O_8) catalysed degradation of coal model compounds. Though the chemistry of this process is greatly different from that involving Lewis acid catalysts, the suggested existence of radical ions in a coal conversion process is of significance.

It is difficult to apply this chemistry directly to the heterogeneous nature of coal. However it is clear that Lewis acids catalyse two principle types of reaction: condensation and hydrocracking/hydrogenation. The extent of each of these reaction in coal conversion is governed by the reaction conditions. The hydrogenation of model compounds utilising hydrogen produced in condensation of the same compounds is of great significance showing the ability of Lewis acids to catalyse both types of reaction under the same conditions. In all catalysed coal degradation there exists a similar competition, the net result of which is dependent on the catalyst, the coal, and the reactor conditions including the heating rate.

5. THE INFLUENCE OF LOW MOLECULAR WEIGHT EXTRACTABLE MATERIAL ON COAL CONVERSION PROCESSES.

5.1 BACKGROUND

The presence of low molecular weight material as part of the structure coal was discussed in section 1.2. As was described the amount of this material and its nature is highly dependent on the means used to isolate the material or quantify it.

The ability of this extractable material to influence the thermal decomposition behaviour of coal has been widely studied for a number of different conversion processes. This chapter discusses the influence of extractable, low molecular weight material present in the coal, on a number of coal conversion processes. These are coking, liquefaction and pyrolysis. Additionally, the nature of the role played by the low molecular weight material will be discussed.

5.2 THE INFLUENCE OF THE LOW MOLECULAR WEIGHT EXTRACTABLE MATERIAL ON COKING BEHAVIOUR

When coking coals are heated to pre-pyrolysis temperatures the amount of material which can be extracted by solvents is greater than can be extracted without pre-treatment. Such a trend is not observed for non-coking coals (Illingworth, 1922).

These initial findings were followed up by a number of workers in an attempt to derive information on the fundamentals of coal coking behaviour. (Dryden and Pankhurst, 1955; Dryden and Joy, 1961; Brown and Waters, 1966a; 1966b; Lazarov and co-workers, 1971).

Dryden and Pankhurst (1955) confirmed the trends observed by Illingworth for two British coals, a coking coal and a non-coking coal. The coal were pre-heated in a "shock tube" at about 60°C/s to temperatures between 100°C and 450°C. The yields of chloroform extract following exhaustive soxhlet extraction are shown in Figure 5.1. The extraction residue of the coking coal, following pre-heating to the temperature of maximum extract yield (400°C), showed no coking behaviour, while the unextracted, pre-heated coal demonstrated considerable swelling ability. Admixing the extract from the coking coal with the non-coking coal imparted considerable coking properties to the latter.

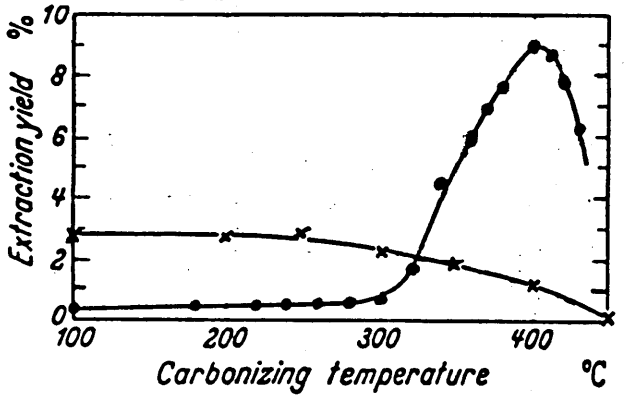


Figure 5.1 Yield of chloroform extract from a Coking coal (•) and a non- coking coal (×) as a function of pre-heating temperature (Dryden and Pankhurst, 1955).

Brown and Waters (1966a; 1966b) performed a very

detailed study on a range of Australian coals. The results obtained were similar to those observed by Illingworth and Dryden. The yield of chloroform extract was again seen to be function of pre-heat temperature, with maximum yields around 400°C. Additionally the yield of extractable material was seen to be highly dependent on a coal's coking properties. The maximum yield of extract obtained was seen to correlate well with the Gieseler fluidity of the parent coal.

Furthermore, separation of the "gamma-fraction" (the fraction of the pyridine extract of the unheated coal, which was also soluble in chloroform) showed that the quantity of material present in this fraction was substantially similar to the amount of extract obtained by heating to 400°C, the temperature of maximum extract yield for the coking coals. Comparison of the extract and gamma fraction from the same coal using an NMR based analysis scheme, showed that the structure of the gamma fraction was very similar to that of the chloroform extract. This finding was confirmed for a number of coking coals, suggesting that the material extracted from the coal following the preheating, was present in the original coal matrix.

It was therefore hypothesised that coking behaviour was influenced strongly by low molecular weight material present in the original coal. The release of extractables as a result of pre-heating was assumed to be due to a relaxation of the forces physical trapping

the extractables. The accessibilty of the internal surface of coking coals, as measured by porosity and vapour sorption techniques, has also been shown to increase as a result of pre-heating. Brown and Waters (1966b) suggested that the extractable material played a physico-chemical role in the coking process, involving hydrogen transfer from the extractable material to free radicals formed in the pyrolysis, in addition to playing a role as a solvating agent.

Neavel (1982) proposed that the development of plasticity in coal pyrolysis is "essentially a transient, hydrogen donor liquefaction process in which the solvating and hydrogen-donating vehicle is supplied by the coal itself", that is the extractable material. Neaval's proposals, and their implications in coal liquefaction, are further discussed in the following section.

The proposed hydrogen donation mechanism has been called into doubt by several authors. Ouchi and co-workers (1983) questioned whether the extractable material had any hydrogen donating properties, while Chen and co-workers (1985) have suggested that the hydroaromatic groups present in coal exist predominantly in the rigid immobile macromolecular structure.

A study by Grint and co-workers (1985) examined the role of the mobile phase in coal plasticity, with particular reference to proposed hydrogen donor mechanisms. They

showed that extraction of coking coal with tetrahydrofuran (THF), a polar solvent, without preheating resulted in the loss of plasticity in the coal.

Analysis of the THF extract suggested that the structure of the extract was similar to that of the original coal. Significant quantities of the long chain aliphatics were noted though large concentrations of hydroaromatic hydrogen donor groups were not found. Impregnation of the extracted coal with model compounds succeeded in restoring the coking properties. The most effective compound in this was found to be decacyclene, a ten ring aromatic compound. Grint therefore suggested that the principle role of the extractables in coking was as a hydrogen shuttler and radical stabiliser, with direct hydrogen donation not being the dominant process. Other workers have come to similar conclusions (Ouchi and co-workers, 1983; Chen and co-workers, 1985)

It can be concluded that the extractable material present in coking coal plays a critical role in the development of coal plasticity. The precise nature of that role is not fully understood, in parallel to the lack of understanding of the development of coal plasticity in general. Hydrogen transfer to free radicals involving the extractable material is a crucial step. This may include hydrogen shuttling or hydrogen donation.

5.3 INFLUENCE OF THE LOW MOLECULAR WEIGHT EXTRACTBLE MATERIAL ON COAL LIQUEFACTION

Neavel (1982) has suggested that the initial chemical reactions occurring in the development of coal plasticity and in coal liquefaction are fundamentally the same. The implications of this hypothesis in terms of coal plasticity mechanisms were discussed in the previous section. Both liquefaction and plasticity development involve the stabilisation of pyrolytically formed free radicals as a major step. In coal liquefaction, Neavel hypothesised that the solvent employed in the process plays a similar role to the extractable material in the development of plasticity. However, under liquefaction conditions, the extractable low molecular weight material remains free to fulfill a role similar to that played in plasticity development and can therefore influence the liquefaction process. It can therefore be concluded from Neavel, that removal of extractable material from coal should have an effect on susequent liquefaction.

Larsen and co-workers (1980) tested this hypothesis by performing liquefaction experiments on two coals using non-hydrogen donor solvent. The results of the study are shown in Table 5.1.

It can be seen that removal of chloroform extractable material results in a large decrease in the conversion to pyridine solubles. This corresponds to Neavel's

hypothesis. The nature of the role played by the extractable material remains unclear.

Table 5.1. Conversion of extracted and unextracted coal in liquefaction at 482°C for 15 minutes. Yields on a % w/w daf basis of the original coal. (Larsen and co-workers, 1980).

Coal	Extract Yield	Vehicle Solvent	Conversion Unextracted	Conversion + Extract[a]
Wyodak	9	Phenol	69	48
		Diphenyl ether	40	30
		Naphthalene	46	37
Bruceton	12	Phenol	84	60
		Diphenyl ether	54	43
		Naphthalene	51	45

a - conversion of extracted coal as % w/w daf original coal added to the yield of extract.

Larsen suggested that the extractables may be acting as a hydrogen donor or hydrogen transfer agent, though as in coal plasticity, other mechanisms probably occur additionally.

An interesting clue as to the mechanisms which may occur can be derived from the work of Narain and co-workers (1983). Experiments were performed to examine the incorporation of liquefaction solvents and model compounds into the coal structure under mild conditions

and its effect on liquefaction yields. Pretreatment of two American coals with two liquefaction solvents at 200°C for one hour resulted in increased liquefaction for both coals using both solvents. The results are given in Table 5.2.

Table 5.2 Effect of Pretreatment on Coal Liquefaction at 140 bar H_2 and 425°C (Narain and co-workers, 1983).

Coal	Solvent	Pretreament		Yield THF
		time	temp.	solubles %
Bruceton	Creosote[a]	none	--	61.5
Bruceton	Creosote	1 hour	200°C	66.7
Bruceton	SRC-II HD[b]	none	--	75.6
Bruceton	SRC-II HD	1 hour	200°C	78.2
W. KY 9/14[c]	SRC-II HD	none	--	85.7
W. KY 9/14	SRC-II HD	1 hour	200°C	88.1
W. KY 9/14	SRC-II HD	15 min	320°C	88.2
W. KY 9/14	Creosote	none	--	79.5
W. KY 9/14	Creosote	1 hour	200°C	81.8

a - Creosote oil

b - SRC-II heavy distillate

c - West Kentucky 9/14 coal

Though the increases are small (2-5%), there is a consistant trend. Experiments with quinoline and methyl naphthalene has shown that the pretreatment procedure results in a physical incorporation of the compounds into the coal structure, such that extraction with THF does not recover all the material taken up by the coal.

This suggests that the model compounds have been impregnated onto the coal in a manner which parallels the extractable material in coal. Furthermore impregnation with these model compounds improves the liquefaction yield to a similar extent to that observed due to impregnation with the liquefaction solvents. It sould be noted that neither quinoline nor methyl naphthalene has any hydrogen donating ability nor are they thought to be capable of hydrogen shuttling, implying that the principle mechanism by which the model compounds act is as solvating agents, involving radical stabilisation.

As can be seen, the extractable material present in coal has a significant influence on coal liquefaction. The mechanisms by which the low molecular weight extractable material act in liquefaction are probably numerous, involving perhaps hydrogen donation, hydrogen shuttling, free-radical stabilisation and physical solvating effects. All of these mechanisms probably occur to differing extents depending on the rank of coal, and the liquefaction conditions employed.

5.4 THE INFLUENCE OF LOW MOLECULAR WEIGHT EXTRACTABLE MATERIAL ON COAL PYROLYSIS

The major study, to date, of the influence of extractable material in coal pyrolysis was performed by Varhman and co-workers (Varman, 1970; Spence and Vahrman, 1970; Rahman and Vahrman, 1971; Palmer and

Vahrman, 1972a; 1972b; Vahrman and Watts, 1972a; 1972b). The study was limited to examining the pyrolysis of coal at low heating rates but significant conclusions can be drawn from its results.

Vahrman first studied the long term (250 hours) Soxhlet extraction with benzene/ethanol (70/30 mixture) of Thoresby, a British bituminous coal. The total yield was 5.03%. Although the bulk of the extract was released in the first 50 hours (3.26%), significant quantities continued to be produced over the whole time period (0.39% between 150-250 hrs), suggesting to Vahrman that even over such a time scale the extraction was incomplete.

In order to obtain a more complete extraction Vahrman resorted to more extreme conditions. Samples of the same coal were extracted under pressure using benzene at temperatures up to 290^{o}C over a long time scale (total time= 1750 hrs), followed by extraction with tetralin at 290^{o}C under pressure over a period of 230 hours. Neither of these extractions were thought to involve any chemical reaction between the solvent and the coal. The total yield of extract released was 10.73%, significantly higher than from the extraction at atmospheric pressure, though the time scale was shorter.

Vahrman then compared the yields of extract released with the yield of tar from slow pyrolysis experiments. The tar yield from a Gray-King Assay, with a heating

rate of 5°C/min and a peak temperature of 600°C, was 9.9%, while that from slow pyrolysis in a steam swept retort, again with a peak temperature of 600°C, was 10.9%. The tars and extracts were separated into solubility fractions and then analysed by gas chromatography and infra-red spectroscopy.

Vahrman pointed to broad similarities between the structures of the extract and those of the tars, though the two were not identical. Vahrman then concluded that the bulk of low temperature tar was formed from extractable material, the tar resulting from the evaporation of that material during pyrolysis. The observed differences between the structures of the tar and extract were assumed to be due to secondary reactions occurring during the evaporation of the tar, and due to the non-volatility of some heavier aromatic compounds.

Vahrman's hypothesis is acceptable within the bounds of the experiments performed. However it is known that use of higher heating rates in pyrolysis results in larger yields than can be formed in slow pyrolysis (Gibbins, in preparation). It is difficult to reconcile Vahrman's theory with this fact. The additional tar formed as a result of increases in heating rate cannot be formed from the evaporation of extractable, low molecular weight material.

CHAPTER 6 FLASH PYROLYSIS EXPERIMENTS

6.1 BACKGROUND

The effect of the use of high heating rates in pyrolysis was discussed in chapter 2. Pyrolysis at high heating rates is known to favour the formation of liquid products. It has been argued that this is due to fine sample dispersion inherent in pyrolysis reactors utilising high heating rates. However Gibbins (in preparation) has recently shown the effect of heating rate in coal pyrolysis over a wide range in a single pyrolysis reactor. Increases in tar yield as a result of the use of high heating rates were seen to be due to changes in intrinsic reaction pathways.

The fluidised bed reactor has been developed as a high heating rate pyrolysis system. The first major study of coal pyrolysis in a small scale (1-3 g/hour) fluidised bed flash pyrolysis apparatus was performed by Tyler (1979; 1980) at CSIRO, Australia. Tar yields of up to 30% were obtained at the temperature of maximum tar yield 580-600^{o}C. These results have been further discussed in chapter 2. Subsequent studies at the same research establishment (Edwards and co-workers, 1980a; 1980b) have shown similar results from a larger scale (20 kg/hour) reactor showing the similarity of the secondary cracking characteristics of the two reactors.

The working principle of the fluidised bed pyrolysis

reactor is that the coal is dropped into a heated, fluidised sand bed, where it is heated to the temperature of the bed very rapidly whilst undergoing pyrolysis. The volatiles and the char particles then leave the reactor to be quenched in a condenser. The heating rate of the coal particle when it enters a fluidised bed cannot be measured directly, however estimates suggest that the heating rate is greater than 1000^{o}C/s and perhaps greater than 10000^{o}C/s (Tyler, 1979). The residence times of the volatiles cannot be determined accurately, though estimates can be made.The residence time of coal/char particles cannot be determined in that some of the char is retained in the bed, whilst other particles are carried out of the reactor in the effluent gas stream.

However the fluidised bed is a reactor capable of the flash pyrolysis of samples of coal sufficiently large to generate enough tar for a detailed analysis. The fluidised bed can therefore best be used to make comparative studies in coal pyrolysis, comparing the flash pyrolysis of different coals, different catalyst impregnated onto the coal, or other pretreatments.

The fluidised bed flash pyrolysis reactor system employed in this study is a modified version of that designed by Weerasinghe (1981), and used subsequently by Lazarides (1983). The programme of experiments undertaken initially follows the work performed by these earlier workers, as reported by Kandiyoti and co-workers

(1984). The reactor, its peripherals and the experimental procedure are described in the following sections.

6.2 DESIGN OF FLUIDISED BED REACTOR

The reactor used in this study (see Fig. 6.1) is a modified version of that designed originally by Tyler (1979). The body of the reactor consists of a 52mm internal diameter (ID) quartz tube. The fluidising medium is 135g of acid washed sand with a particle size range of 100-40 mesh, which produces a unfluidised bed 40 mm deep. The bed is supported on a sintered quartz disc porosity No.3. Below this is another more porous quartz disc (porosity No.1) which acts to improve heat transfer to the fluidising gas stream. The temperature of the bed is measured by a 0.5 mm type K thermocouple (chromel/alumel obtained from Goodfellow Metals) which is placed 20mm below the surface of the unnfluidised sand bed. The thermocouple was spot-welded to ensure a good contact and its signal was indicated on a digital thermometer, type 275l-K from Digitron Insrumentation.

The coal feeder tube is a 4mm OD, 2mm ID quartz tube which extends 20mm into the unfluidised sand bed. During its passage down the drop tube prior to being fed into the sand bed, the coal is protected from pre-heating by the sheath surrounding the drop tube. Cold gas is passed down the sheath tube, to prevent the drop tube from becoming too hot. This is especially important in the

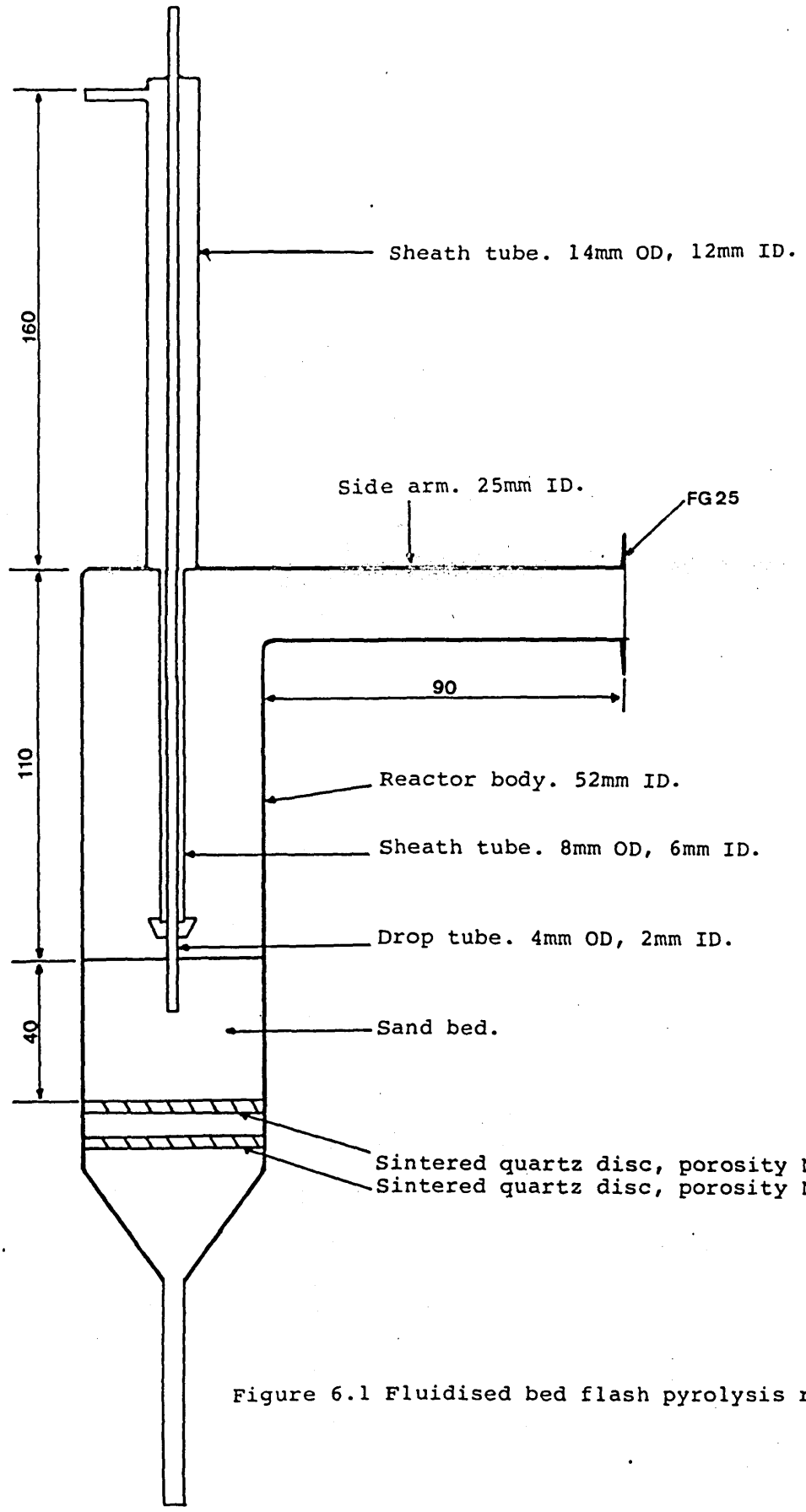


Figure 6.1 Fluidised bed flash pyrolysis reactor.

case of the pyrolysis of coals which becomes plastic when heated. If this type of coal is protected from heat in the drop tube, the latter is liable to block due to the pyrolysis and subsequent agglomeration of the coal within it.

The free-board of the reactor is approximately 110 mm long. When the volatiles and char particles leave the sand bed a partial quench is provided by the gas leaving the cooling sheath, which is directed upwards. The char and volatiles then pass down the side arm into the condenser section where they are cooled and collected.

6.3 FLUIDISED BED REACTOR-DESIGN OF PERIPHERALS

6.3.1 DESIGN OF FURNACE

The furnace in which the fluidised bed is heated during pyrolysis is shown in figure 6.2. The central core of the furnace, within which the reactor is positioned consists of 185 mm long, 60 mm ID, 66 mm OD quartz tube. Around this is wound a layer of Refrasil woven high temperature tape (supplied by The Chemical & Insulating Co.). The heating element for the furnace is wound around this tape. The heating element consists of 5.3 m of Nichrome flat ribbon, resistance 9.93 ohms/m, obtained from Goodfellows wound on a 6 mm pitch producing 28 turns. On top of the winding is wrapped another layer of Refrasil tape, and then a layer of 2mm thick Triton Kaowool paper (acquired from Morganite Ceramic Fibres

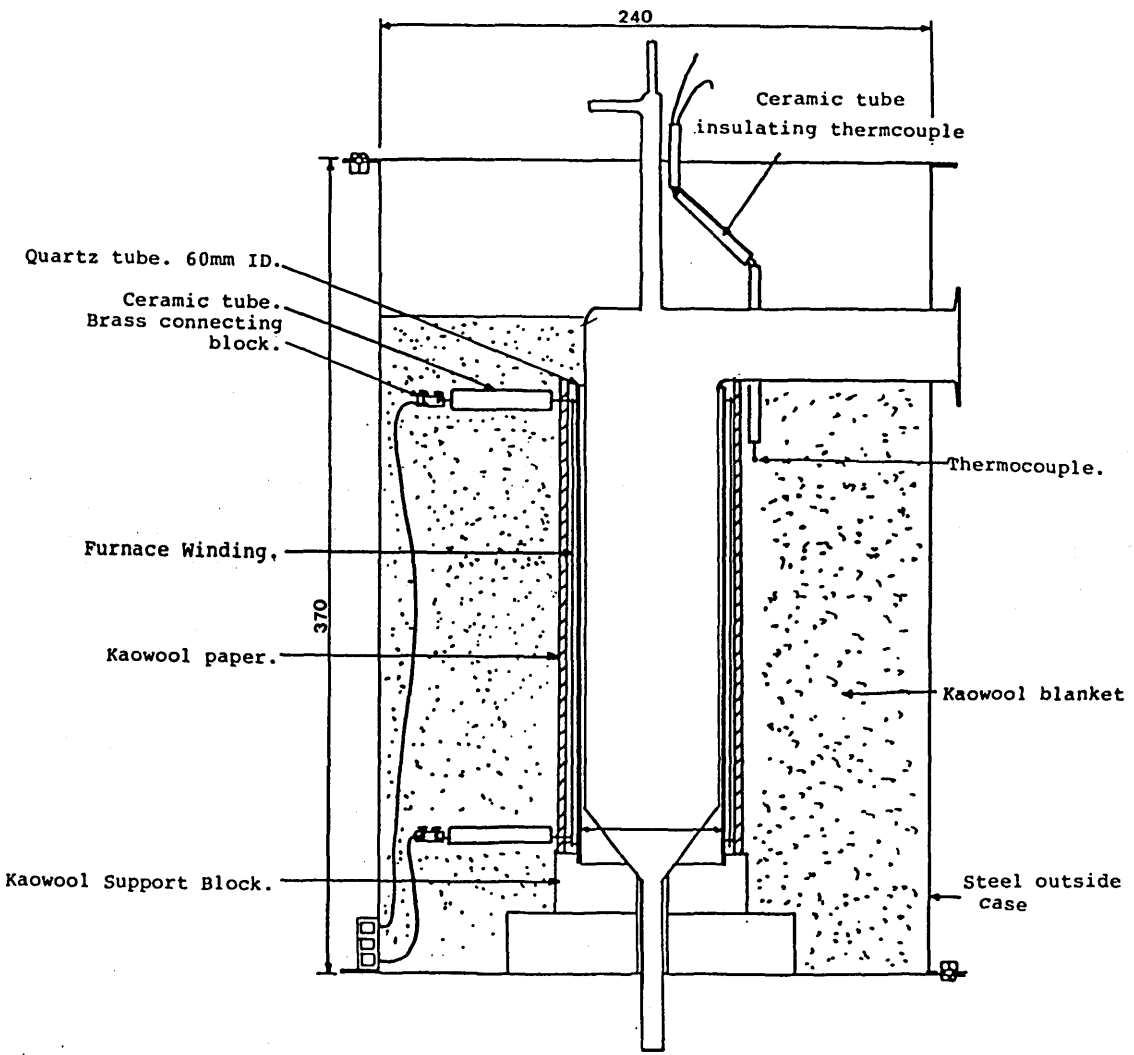


Figure 6.2 Furnace for fluidised bed reactor.

all dimensions in millimeters

Ltd), secured by nickel wire. The tails of the heating element are removed from the locality of the hot-zone within 5cm long ceramic insulators. After passing through these, the ends of the wire are attached to the power supply cables via brass connecting blocks.

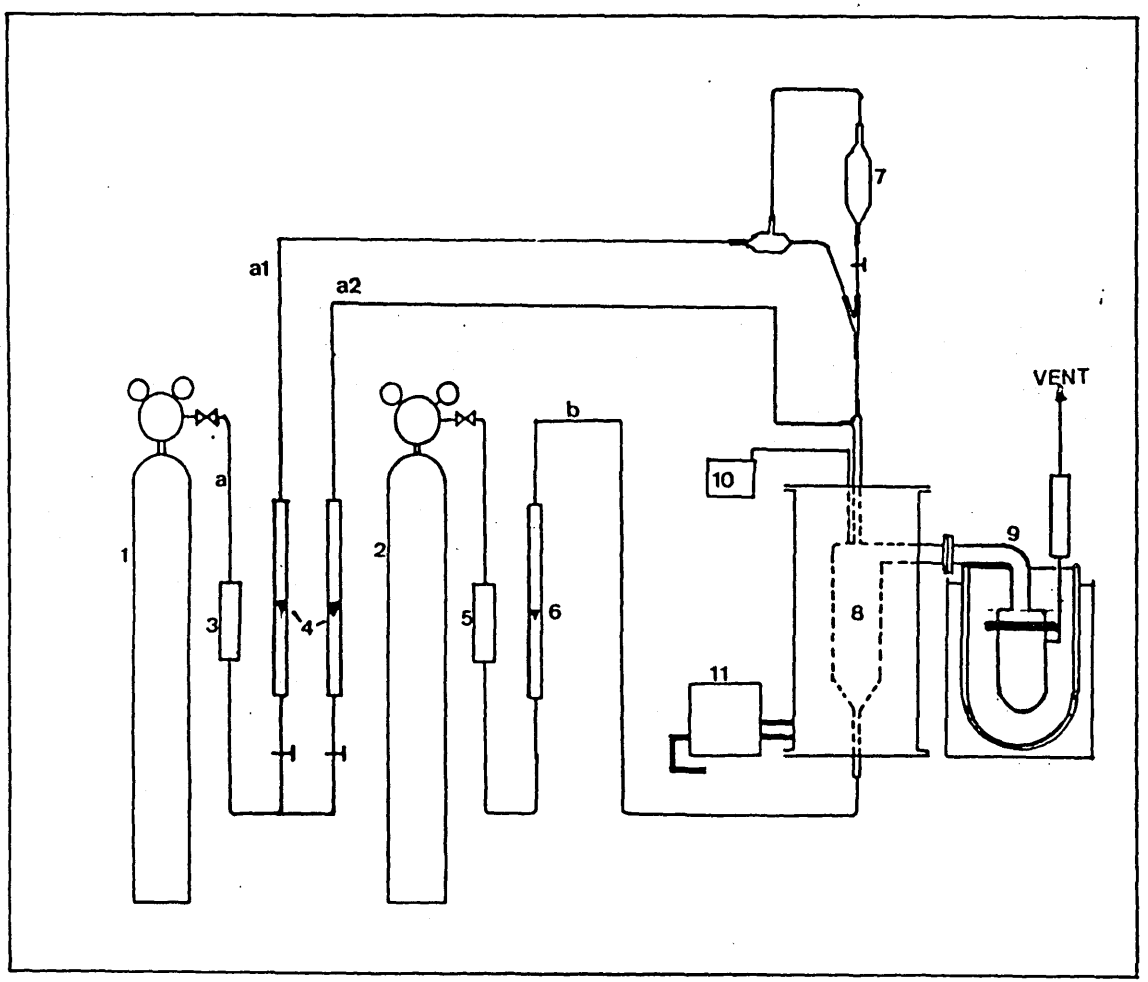
Further insulation is provided by Triton Kaowool blanket which fills the remainder of the space between the furnace core and the external steel case, which is fabricated from 1.5 mm thick steel. The gas inlet tube for the reactor protrudes through the bottom of the casing, while the reactor is supported internally on a Kaowool block. The coal feeder tube, and reactor themocouple protrude through a hole in the top of the casing, while the outlet side arm passes through a gap in the furnace wall.

The power is supplied to the furnace from a Skil solid state, three term switching controller (type S9C/S123) capable of supplying 12 Amps at 240V, and controlling furnace temperatures up to 1000^{o}C. The controller thermocouple, type K, was positioned close to the heating element. For safety the outer casing is electrically earthed.

6.3.2 DESIGN OF GAS SUPPLY AND COAL FEEDER SYSTEMS

The gas supply system and coal feeder system are shown in figures 6.3 and 6.4. The gas used in this reactor system was oxygen free nitrogen (OFN), supplied by BOC.

Figure 6.3 Gas supply system for fluidised bed reactor.



1. Nitrogen cylinder
2. Nitrogen cylinder
3. Silica gel
4. Rotameters
5. Silica gel
6. Rotameter
7. Coal feeder system
8. Reactor
9. Condenser
10. Digital thermometer
11. Skil power controller

The OFN was supplied from two separate cylinders (No.1 and 2 , one for the fluidising gas stream (stream b) and the other (stream a) for the coal feeder system and coolant sheath gas stream. Two cylinders were used to facilitate independent variation of upstream pressures, which made flowrate control easier.

Both streams of nitrogen were passed over silica gel (No. 3 and 5) to remove water. Stream b was passed through a rotameter (No. 6) and then into the bottom of the reactor (No.8). Stream a was split into two further streams, stream a2 for the cooling sheath, and stream a1 for the coal feeder system. The relative flows in streams a1 and a2 were controlled by clips on the plastic hose, while the flows were monitored on two rotameters (No.4). The flowrates set for streams a1, a2 and b were dependent on the experimental conditions employed, and will be discussed in the section describing the experimental procedure.

The coal feeder system (see Fig 6.4a) is a simpler arrangement than that used by Tyler (1979) in his fluidised bed. The coal is held in a hopper, through which gas is passed. The feeding rate of coal was controlled by a clip on the plastic hose immediately

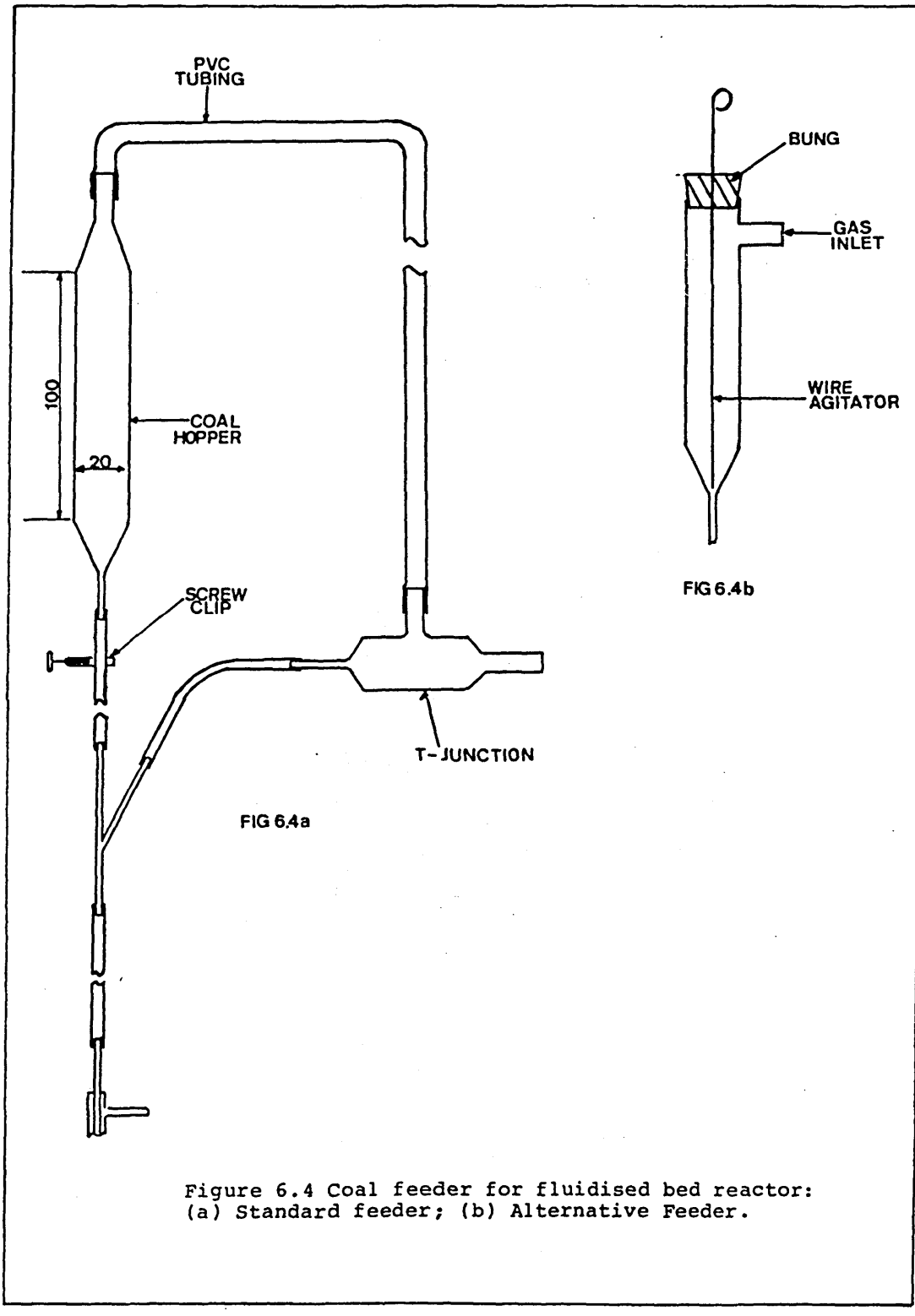


Figure 6.4 Coal feeder for fluidised bed reactor:
(a) Standard feeder; (b) Alternative Feeder.

below the hopper, and by external agitation of that hose by the operator. Below the controlling clip an additional gas stream is added to further disperse the coal particles.

An alternative feeder system is also available for feeding substrates which tend to "clump" together, for example coal samples with high surface concentrations of hygroscopic catalyst (See Figure 6.4b). This has an internal wire agitator, passing though a rubber bung, to enable the substrate to be "broken up", facilitating feeding.

6.3.3 DESIGN OF THE CONDENSER SYSTEM

The condensing system for the fluidised bed consists of two stages, the primary condenser which is cooled in liquid nitrogen, and the secondary condenser which is cooled by the cold gas stream from the first trap. The assembled system is shown in figure 6.5.

The primary condenser is connected to the reactor by a 25 mm ID, 50 mm OD flat flange. Sealing between the flange and the flange on the reactor outlet is provided by an expanded graphite gasket. This is formed when a ring, of the same radial dimensions as the flange, cut from 0.25 mm thick graphite ribbon (obtained from Le Carbon), is repeatedly soaked in liquid nitrogen and then warmed to room temperature. As a result of this process, the ribbon expands to 3-4mm thickness, which is

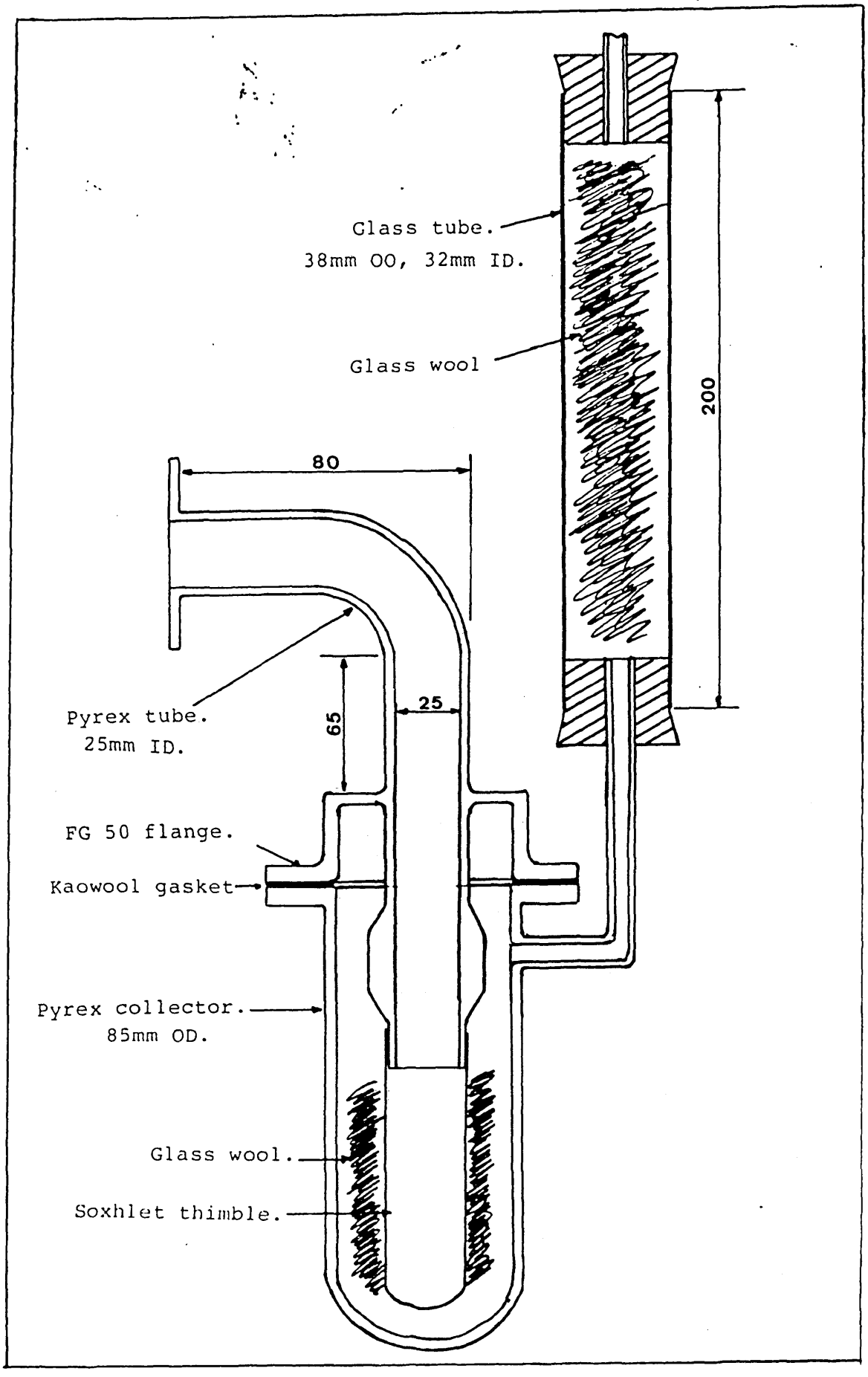


Figure 6.5 condensers for fluidised bed reactor

then compressed between the flanges to form a seal.

The primary condenser consists of two sections: a cooling section and a collecting section. As the hot char/tar aerosol passes along the horizontal and vertical sections of the inlet tube it is cooled. The vertical length must be entirely covered in liquid nitrogen in order to cool the gas sufficiently before it enters the cellulose Soxhlet thimble, which may undergo degradation if its temperature is allowed to rise above 220^{o}C.

The char particles which are carried over collect in the Soxhlet thimble (22 mm ID single thickness obtained from Whatman), together with a substantial quantity of tar. The remainder of the tar collects on the glass wool wrapped around the thimble, on the walls of the primary trap or in the secondary trap.

The secondary trap consists of a 30 mm ID glass tube lightly packed with 0.5 g glass wool. It acts principally to remove the tar mist from the gas stream leaving the primary trap, and is not cooled other than by the cold gas entering it.

6.4 EXPERIMENTAL PROCEDURE AND ITS LIMITATIONS

The experimental procedure is described in three sub-sections. These are coal sample handling, pyrolysis and product recovery. Coal sample handling includes a

description of catalyst impregnation methods, and the soxhlet extraction procedure.

6.4.1 COAL SAMPLE HANDLING

6.4.1.1 SAMPLE PREPARATION AND STORAGE

Coal is highly heterogeneous and is liable to undergo oxidation under ambient conditions in air. Grinding and storage of coal samples requires care. The preparation of samples for this project was performed in the manner described below.

Four British coals were used in this study together with a Turkish lignite. The British coals were supplied by the National Coal Board Coal Research Establishment, Stoke Orchard, Cheltenham. The Canakkale Can Turkish lignite was supplied from the sample collection of the Department of Chemical Engineering of Istanbul Technical University. The average properties of the coals are shown in Table 6.1. Proximate analyses were performed according to the procedure specified by the British Standard. The NCB classification is based on the properties of the coal with respect to the proximate analysis and the Gray-King Coking test. Taff Merthyr is a Welsh semi-anthracite, Cortonwood Silkstone a Yorkshire Coking coal (Gray-King coke type G_9), while Daw Mill and Linby are low rank, high volatile, non-swelling bituminous coals.

Coal samples were ground and seived to the required particle size range which was between 75 and 150 microns (-100 +200 mesh). Samples were then stored under a constant flow of nitrogen gas to protect against oxidation.

Table 6.1 Properties of coals used in this study.

COAL	PROXIMATE ANALYSIS			ULTIMATE ANALYSIS				
	Moist. a.r[a]	Ash d.b[b]	V.M[c] d.a.f[d]	C	H	N	O	S
				-----d.a.f.------				d.b
Taff Merthyr type[e] 201	0.8	4.0	13.3	92.4	4.2	1.5	1.6	0.7
Cortonwood Silkstone type 501	1.0	2.2	35.8	87.2	5.6	1.7	3.9	0.7
Daw Mill type 902	5.4	11.8	40.6	82.6	5.2	1.5	9.7	1.6
Linby type 902	2.1	5.3	40.2	81.5	5.2	1.8	10.6	1.5
Canakkale Can type -	9.7	24.0	50.4	66.2	5.4	1.8	--26.6[f]--	

a - a.r - as received
b - d.b dry basis
c - V.M - Volatile matter
d - d.a.f - dry, ash free basis
e - type - NCB classification
f - by difference

The particle size range used was chosen to avoid heat

and mass tranfer limitations during pyrolysis. As discussed in chapter 2, Howard has shown that at the heating rates used in this study, use of this particle size range should prevent intraparticle heat and mass transfer being an limiting factor.

In order to quote experimental results on a dry, ash free basis, the moisture level of stored samples was periodically measured.

6.4.1.2 CATALYST IMPREGNATIONS

The catalyst impregnation procedure used in this study was developed to improve the contact between catalysts and the coal, and simultaneously avoid oxidation of the coal samples. Intimate contact between the coal and some catalyst has been shown to have a substantial effect on conversions in coal liquefaction (Weller, 1950a), although for other catalysts, in both liquefaction and carbonisation, the effect of the catalyst has been shown to be independent of the initial method of mixing (Wood and Wiser, 1976; Kandiyoti and co-workers, 1984).

Catalysts were impregnated onto the coal from solution in either methanol or water depending on solubility. Methanol was prefentially used due to its lower boiling point. The solvents used for the various catalyst are specified in Table 6.2. The catalyst loading level was determined on a dry, ash free basis of the coal plus catalyst mixture, the catalyst weight used being

calculated on a water-of-crystallisation free basis.

Procedure

A weighed quantity of coal was mixed with the required amount of catalyst and the solvent was added. The amount of solvent used was sufficient to make stirring of the mixture possible without undue difficulty. The coal/catalyst slurry was then stirred magnetically for three hours.

Table 6.2 Conditions used for catalyst impregnation.

CATALYST	FORMULA	SOLVENT	LOADING[a]
Zinc Chloride[b]	$ZnCl_2$	Methanol	2.75-20%
Zinc Bromide[c]	$ZnBr_2$	Methanol	10%
Zinc Iodide[c]	ZnI_2	Methanol	10%
Tin Chloride[d]	$SnCl_2$	Methanol	10%
Cobalt Chloride[c]	$CoCl_2.6H_2O$	Water	12.5%
Cadmium Chloride[b]	$CdCl_2.2.5H_2O$	Water	9.7%
Iron Chloride[d]	$FeCl_3.6H_2O$	Water	10%
Iron Sulphate[b]	$FeSO_4.7H_2O$	Water	10%
Sodium Chloride[c]	NaCl/	Water	5% NaCl +
+ Zinc Chloride	$ZnCl_2$		5% $ZnCl_2$
Sodium Chloride +	NaCl/	Water	3.5% NaCl +
Potassium Chloride[b]	KCl/		3.5% KCl +
+ Zinc Chloride	$ZnCl_2$		3.5% $ZnCl_2$
Aluminium Chloride[b]	$AlCl_3$	Added as dry powder	10%

b - Obtained from BDH Chemicals, Analar Grade >99.5%

c - Obtained from BDH Chemicals, GPR Grade >98%

d - Obtained from Aldrich Chemicals, >98%

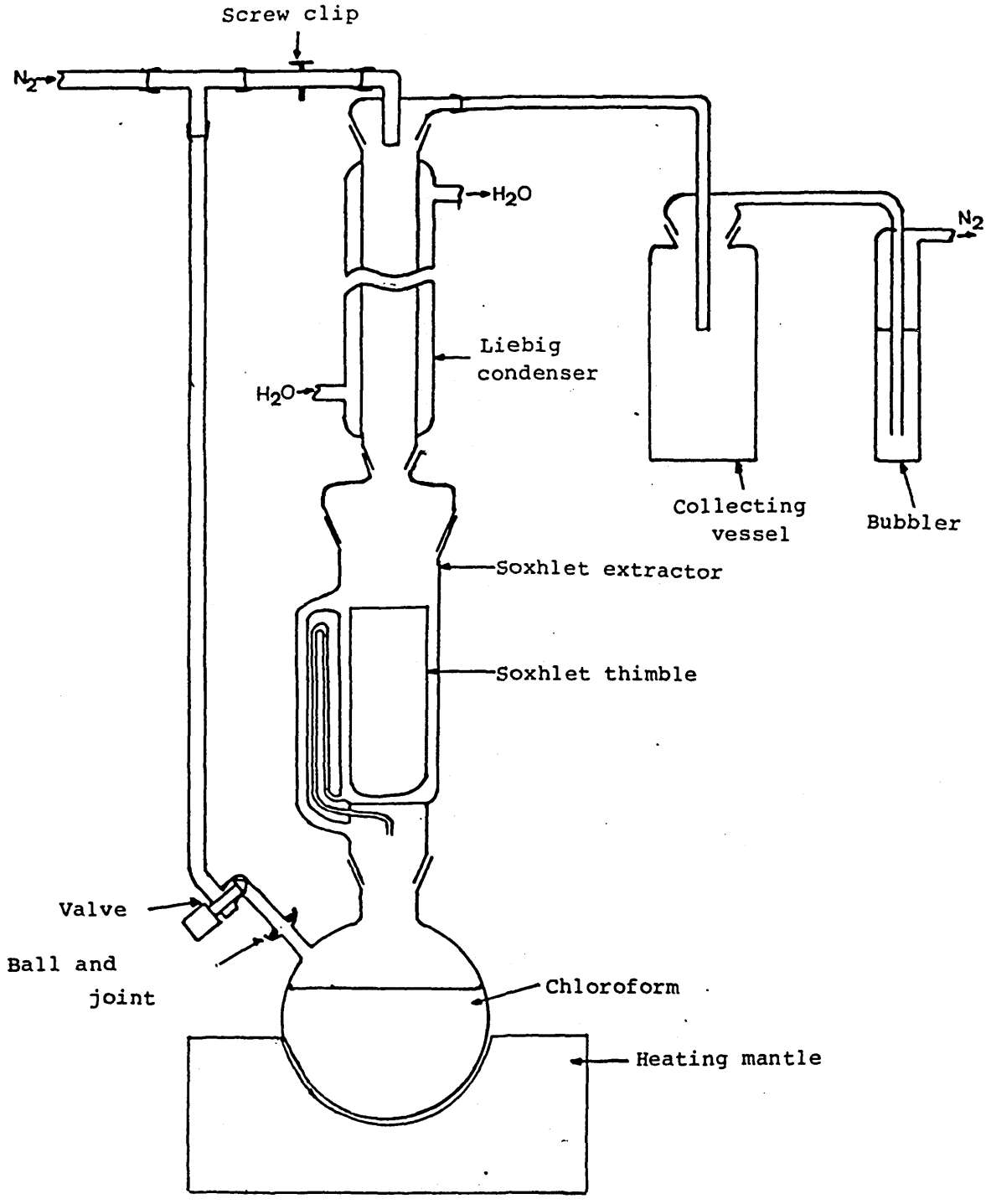
After this time the solvent was evaporated. This was achieved using mild heating and a jet of nitrogen gas to prevent oxidation, while continuing the stirring. When the bulk of the solvent had been removed (after approximately 30 mins), and the slurry could no longer be stirred (magnetically or manually), the coal was placed in a nitrogen swept oven at 70°C for one hour. The impregnated coal was then seived and when necessary reground. The sample was further dried for 8 hours at 105°C under nitrogen and then stored.

6.4.1.3 COAL EXTRACTION

Coal extractions were carried out in a standard Soxhlet apparatus modified to prevent oxidation of samples. The apparatus is shown in Figure 6.1. When the Soxhlet extractor empties, gas is drawn down the condenser into the thimble. In the absence of the nitrogen blanket, air could be sucked into the thimble causing oxidation. The modifications enable the system to be purged with an inert atmosphere of nitrogen prior to the extraction, and to be able to maintain a flow of nitrogen gas across the top of the condenser during the extraction.

Extractions were performed in Whatmans single thickness cellulose Soxhlet thimbles (33 mm ID, 100 mm long). The required amount of coal, usually 20 g, was weighed into the thimble. A plug of glass wool was then pushed into the top of the thimble to prevent the coal splashing

Figure 6.6 Modified Soxhlet apparatus.



out. Following the extraction, the extract solution was filtered and the solvent evaporated in the manner described in chapter 7. The thimble was dried in a vacuum oven for 24 nours at 70°C. The extraction residue was then seived and further dried at 105°C for 8 hours to remove all traces of solvent. The residue was then stored under nitrogen until required for further use.

6.4.2 THE PYROLYSIS PROCEDURE

The first stage of the pyrolysis procedure was the assembly of the apparatus. The glass wool and the Soxhlet thimble were weighed before the condenser was assembled as shown in Figure 6.4b. The required amount of sand was weighed and then added to the reactor which was then also weighed. The reactor was then placed in the furnace and the pipework was attached. A weighed quantity of coal was placed in the hopper which was then attached to the reactor. The condenser was then attached to the reactor using the expanded graphite gasket as described previously.

The temperature of the furnace could then be raised. The set point temperature of the Skil controller was increased in small steps (25°C) at 5 minute intervals in a manner which prevented the controller from delivering full power. If the full power was delivered to the furnace for an extended period, then the lifetime of the wiring was severely diminished.

During the heat up period, the flow of gas through the system was kept at a low level, 25% of operating value. The first gas stream opened was that down the coal drop tube. This was to prevent the tube blocking with sand, which occured when other flows were opened first. When the temperature reached 200^{o}C, the liquid nitrogen coolant was placed in position around the primary condenser.

When the temperature of the furnace reached 30^{o}C below the required pyrolysis temperature the gas flows were slowly increased to their required values. These values will be dealt with later in this section. The set point of the Skil controller was then adjusted over a very small range in order to achieve the required temperature. When a satisfactory steady state had been reached, that is a steady temperature at the required gas flows, coal feeding could be commenced.

The coal feeding rate was nominally set at 5 g/hour, however a non agglomerating coal could be fed at a rate of up to 10 g/hour, while a coking coal could only be fed at 2-3 g/hour. Similarly the maximum capacity of coal depended on the rank, for non agglomerating coals, up to six grams of coal vould quite easily fed, while for coals developing plasticity, this was limited sometimes to less than one gram.

The fluidising gas flowrate used in tthe reactor was set at four times the minimum fluidisation flowrate. This

flowrate was measured as a function of reactor temperature by Lazarides (1983). His results are shown in figure 6.7. The other flowrates were arbitrarily set, the drop tube flow set at 1.5 standard litres/min, and the coolant gas flowrate set at 3 standard litres/min. These values were not varied for experiments at different reactor temperatures.

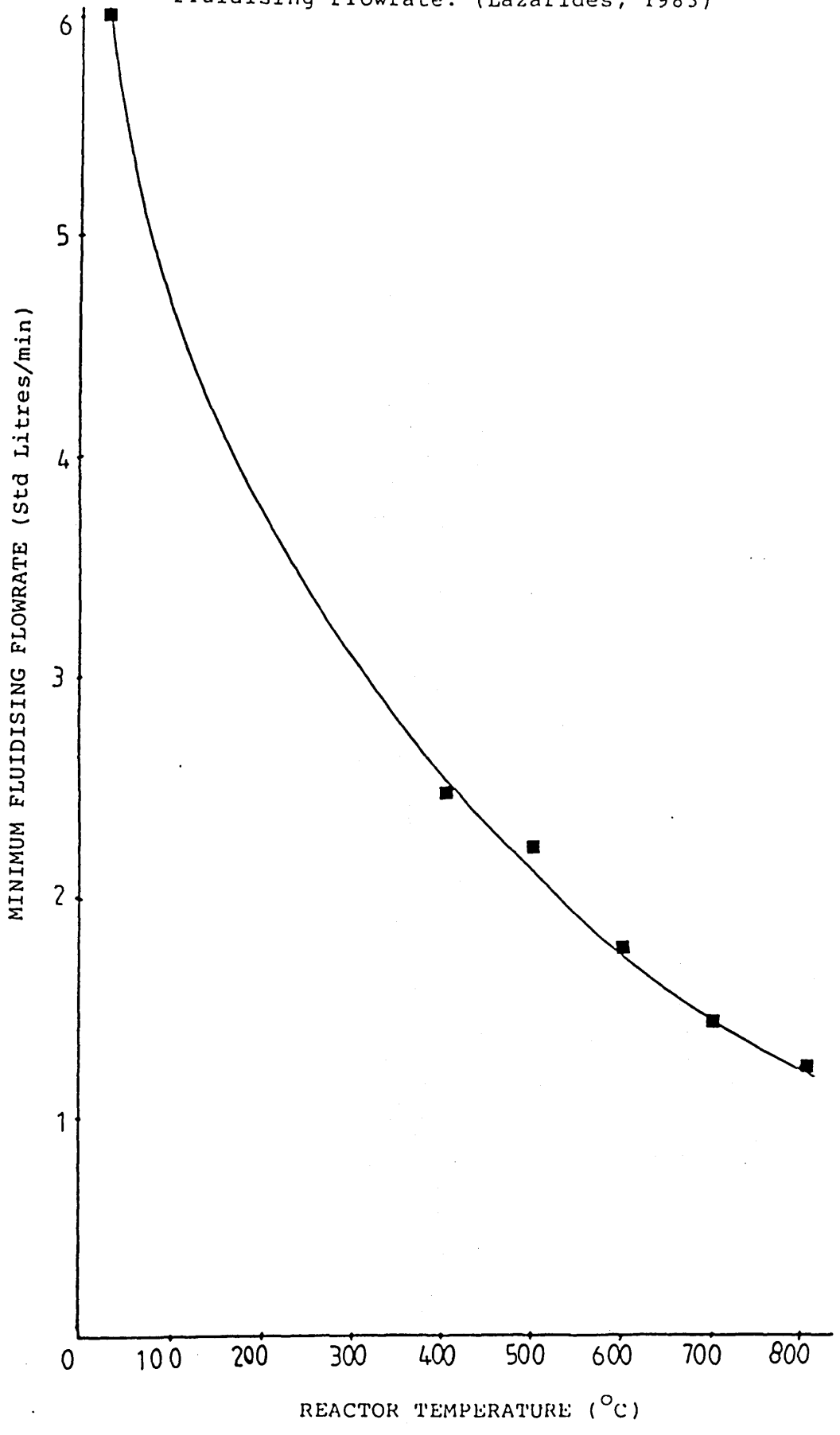
When the coal which had been placed in the hopper had been fed, the furnace was switched off, and the gas flows turned down to 30% of the operating values, while the furnace cooled down.

6.4.3 PRODUCT RECOVERY

In this experiment only the char and tar are recovered. No gas recovery was attempted. The major task involved in the product recovery was the separation of the tar from the char. Some of the char is carried over into the primary condenser, where it mixes with tar. Tar was arbitrarily defined as material soluble in dichloromethane or methanol, and which was non-volatile when the solvents are removed.

Before the product recovery was commenced, the reactor was allowed to cool down to less than 200^{o}C. The reactor was then removed from the furnace and the primary condenser removed from the liquid nitrogen. The secondary trap was disconnected from the primary condenser, and the gas flows turned off. Any solid

Figure 6.7 Effect of reactor temperature on the minimum fluidising flowrate. (Lazarides, 1983)



material (sand and char) which had collected in the side arm and in the horizontal section of the primary condenser was poured into the Soxhlet thimble.

The flange connection was then disconnected and the reactor was allowed to cool further. The primary trap was then disassembled. The glasswool was unwound from the thimble and placed in Soxhlet extractor. The remaining char adhering to the walls of the cooling section of the primary trap was then washed into the thimble using methanol. The filtered methanol solution of tar leaving the thimble was collected.

When all methanol had filtered through the thimble, the thimble was removed and stored prior to further extraction. The primary trap was then washed repeatedly with dichloromethane and methanol. The secondary trap was also disassembled and the glasswool packing placed in the Soxhlet extractor. The trap was then also washed with dichloromethane and methanol. The tar solutions in dichloromethane and methanol were collected separately in 250 ml round bottomed flasks. When the washing was complete, the solution level in the flasks was brought up to 200 ml in order that they could be used in the extraction.

The extraction procedure was then commenced. The glasswool was extracted with dichloromethane, followed by the Soxhlet thimble. The two were then extracted with methanol. Extraction were continued until the solutions

leaving the extractor was colourless. The length of time this involved was dependent on the amount and type of coal fed. Typically the glasswool extractions lasted 15 to 20 minutes each, while the thimble extraction in dichloromethane lasted as long as 90 minutes. The thimble extraction in methanol lasted 30-60 minutes.

When the extractions were complete the solutions were filtered using a weighed filter paper (Whatmans No.1). The solvents were then distilled off in a pre-weighed 100 ml round flask. Dichloromethane was evaporated first maintaining the level in the flask between 40 and 70 ml. When only 30-40 ml of solution remained in the flask, the methanol was added as for dichloro methane. When the amount of methanol present fell below 40 ml, the amount of heat reaching the flask was reduced. When 20 ml of solution remained, the flask was removed from the heater and the bulk of the remaining solvent evaporated using a jet of nitrogen, while gently warming the flask using a hair-dryer. Any remaining solvent was removed in a vacuum oven at 70^{o}C for 60 minutes. The flask was then allowed to cool before being weighed to determine the tar yield.

The char yield was determined by weighing the cooled reactor, and weighing the dry Soxhlet thimble, glasswool, and filter paper. The char could then be determined. The yield of gas was determined by difference and included the water produced during the pyrolysis.

6.4.4 LIMITATIONS OF THE FLUIDISED BED FLASH PYROLYSIS EXPERIMENT

The fluidised bed is somewhat limited as a pyrolysis reactor. The number of parameters which can be independently varied is small. Only the temperature of the flash pyrolysis and the substrate pyrolysed can be genuinely varied independently. The heating rate is fixed though it cannot be precisely measured. The residence time of the coal/char particles is a function of the type of coal and the gas flows which are determined in order to maintain constant fluidisation conditions, and to ensure that the coal could be fed without blockage problems. These gas flows also determine the residence time of the volatiles in the hot free-board. The pressure cannot be varied in a quartz reactor, while variation of the particle size of the substrate affects the heating rate, coal/char residence time and feeding characteristics.

To date gas collection and analysis has not been attempted.

6.5 MODIFICATIONS MADE TO THE FLUIDISED BED REACTOR

There were a series of modifications made to the fluidised bed pyrolysis apparatus and experimental procedure as used by Weerasinghe (1981) and Lazarides (1983). These modification were made in order to ensure

that the tar collected represented all the tar produced from the coal pyrolysis, and to simplify the experimental procedure.

The modifications introduced are as follows:
(i) The addition of the glass wool packed secondary trap. This produced increases in tar yields from Linby coal of 3% compared to the results of Weerasinghe (1981).
(ii) Increases in the coolant sheath gas flowrate. Additional quenching in the free-board resulted in tar yield increasing by 5-6% again compared to Weerasinghe).
(iii) Addition of a second gas supply cylinder to facilitate improvement (ii), and make gas flow control easier and independent.
(iv) Use of an expanded graphite gasket to seal the flange between the reactor and the condenser. Previous methods were less effective.
(v) Use of ball and cup connection to seal the thermocouple in place. Previous use of araldite was time consuming and destructive to the reactor.
(vi) Revised condenser design, particularly the length of the vertical cooling section. This was necessary with the use of higher gas flowrates to prevent Soxhlet thimble degradation.

These modifications resulted in substantial increases in the measured tar yield which will described in more detail in section 6.1.1.

6.6 FLUIDISED BED EXPERIMENTAL PROGRAMME

Experiments were undertaken to determine the effect of a number of parameters on the flash pyrolysis of coal and lignite in the fluidised bed reactor. The tars produced in experiments were analysed using the techniques described in Appendix I.

The initial experiments were performed on Linby coal. Base-case data for Linby was aquired over a temperature range from 400°C to 800°C. The effect of impregnation with zinc chloride was investigated in two series of experiments. Firstly, the effect of the catalyst was studied firstly using a constant loading over the same temperature range investigated for untreated Linby. Secondly the effect of variation of $ZnCl_2$ loading at a constant temperature was studied. The effect of impregnation with a number of other Lewis acid type catalysts on the flash pyrolysis of Linby coal was examined a 580°C.

The flash pyrolysis of Canakkale Can, a Turkish lignite, was then studied. Experiments were performed over a similar temperature range to those performed on Linby. The effect of impregnated zinc chloride on Can pyrolysis was also examined, studying the effect over a small temperature range, and with increased catalyst.

The effect of zinc chloride on the pyrolysis of a series of three other British hard coals (Daw Mill, Cortonwood

Silkstone and Taff Merthyr) was then examined. Untreated and 5% zinc chloride impregnated coals were flash pyrolysed at 580^{o}C.

The final study performed on the fluidised bed was the flash pyrolysis of pre-extracted coal. Samples of coal which had been extracted with chloroform for 25 hours were flash pyrolysed. Additionally, the solid residue from the extraction of Linby coal was impregnated with zinc chloride and flash pyrolysed.

The results of these experiments are described and discussed in the following chapter.

CHAPTER 7 FLASH PYROLYSIS EXPERIMENTS - RESULTS AND DISCUSSION

Flash pyrolysis experiments were performed in the quartz fluidised bed described in Chapter 6. The experimental programme followed is also given there. The results obtained are described and discussed in the following sections. Experimental results not given in detail in this chapter are presented in Appendix II, in Tables II.1 to II.5.

7.1 FLASH PYROLYSIS OF LINBY COAL

7.1.1 UNTREATED COAL

7.1.1.1 PRELIMINARY EXPERIMENTS

Preliminary experiments on untreated Linby coal were performed to determine the effect of the improvements in experimental procedure described in section 6.5. The experiments were performed at 580^{o}C, which has been shown to be the temperature of maximum tar yields for bituminous coals (Tyler, 1980; Kandiyoti and co-workers, 1984). The results of these experiments and those obtained by Weerasinghe (1982) prior to experimental the modifications are given in Table 7.1.

The majority of the observed increase in the tar yield results from the modifications to the experimental procedure; however, experiments with the sample of coal used by Weerasinghe, showed that the improved coal sample preparation procedure resulted in an increase of the tar yield of 2%, at

the expense of a small decreases in char and gas yields.

Table 7.1 Preliminary results of the flash pyrolysis of Linby coal at 580°C. Yields on % w/w daf basis.

	unmodified procedure[a]	modified procedure
Tar	21.0	31.0
Char	58.6	57.0
Gas (by diff)	21.4	12.0

a - Data obtained by Weerasinge (1982)

The addition of a secondary tar trap resulted in an additional tar yield of 3%, at the expense of the gas, while increases in the coolant sheath gas flowrate resulted in 5% increases in tar, again with a corresponding decrease in gas formation. The sheath gas flow rate was increased to counteract the enhanced tendency of the fresh sample of Linby to pyrolyse and agglomerate within the drop tube, which caused the latter to block. The reason for the effect on tar yield of the increased sheath gas flowrate is due to a combination of the additional quench provided by this stream to volatiles upon their exit from the fluidised sand bed, and its effect in reducing the residence time of the volatiles in the hot freeboard.

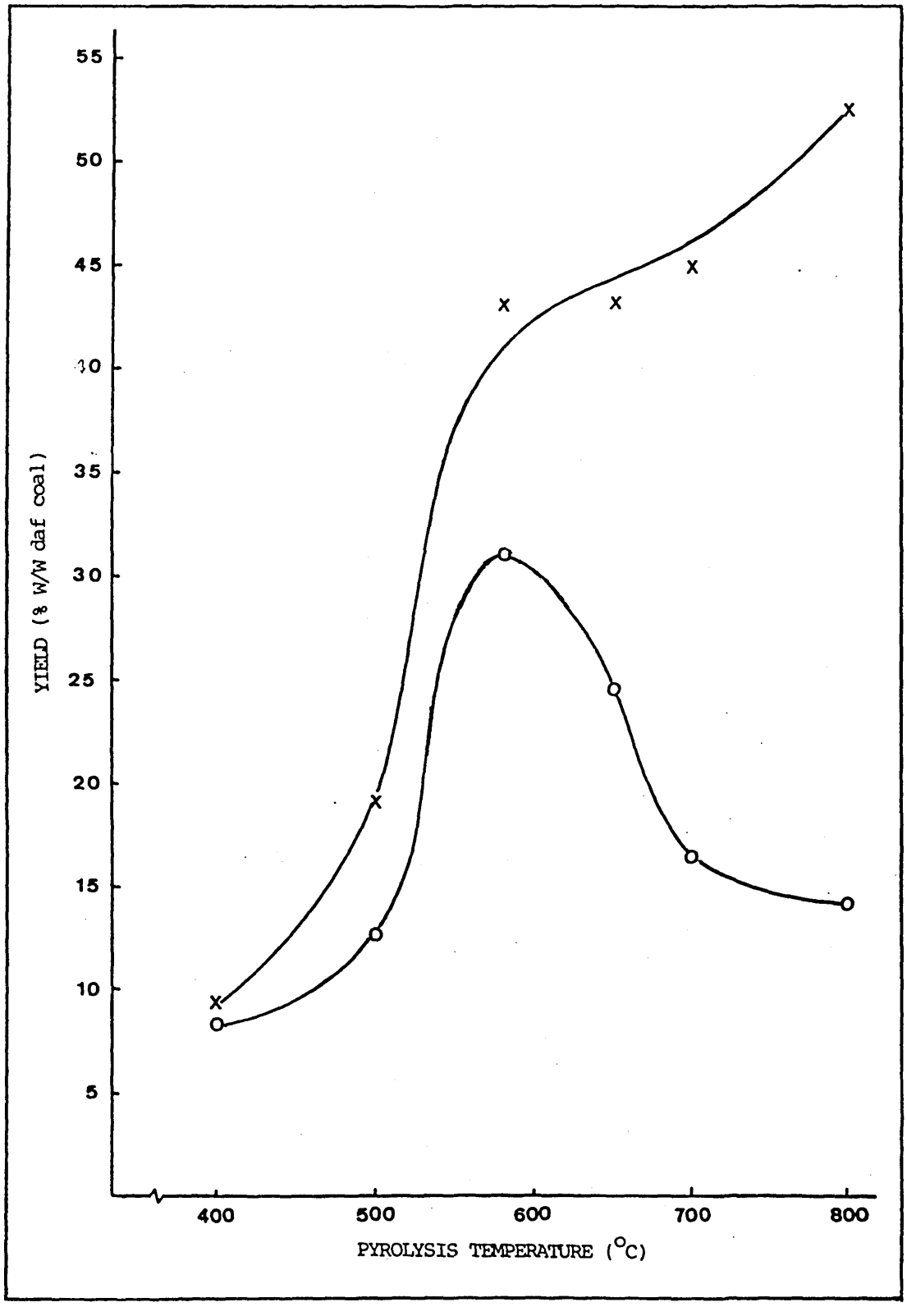
7.1.1.2 THE EFFECT OF TEMPERATURE

Following these preliminary results, the effect of temperature on the flash pyrolysis of Linby coal was examined. Flash pyrolysis experiments were performed on

Linby coal at temperatures between 400 and 800°C. The amount of coal fed depended on the temperature being studied. Below 580°C, 3-4 grams of coal could be fed easily. In experiments at pyrolysis temperatures at and above 580°C, the amount of coal which could be fed was limited by the tendency of Linby coal to agglomerate in the fluidised sand bed. This agglomeration resulted in the formation of large lumps of sand and char in the bed (diameter 3-5mm) and a large bulk of char/sand agglomerate adhering to the tip of the feeder tube. This agglomeration resulted in a phenomenon which can best be described as a loss of fluidisation, which manifested itself externally as a rapid rise or fall in temperature, accompanied by an increase in the pressure drop. The loss of fluidisation resulted in the premature termination of an experiment. For Linby this condition was noted after feeding 1.2-1.5 grams of coal at 580°C, and at higher temperatures, after feeding smaller amounts. The amount of Linby which could be fed was limited by this behaviour at and above 580°C. This phenomenon was also observed by Tyler (1980).

The effect of temperature on the yield of tar and total volatiles is shown in Figure 7.1. More complete results for these experiments are presented in Table II.1. The tar yield reaches a maximum at 580°C, which is in the same region as in the results of other workers (Tyler, 1980; Kandiyoti and co-workers, 1984). The decrease in tar yield above this temperature corresponds to a substantial increase in gas formation, suggesting that

Figure 7.1 Tar (O) and total volatiles (x) yield as a function of pyrolysis temperature for the flash pyrolysis of Linby coal.



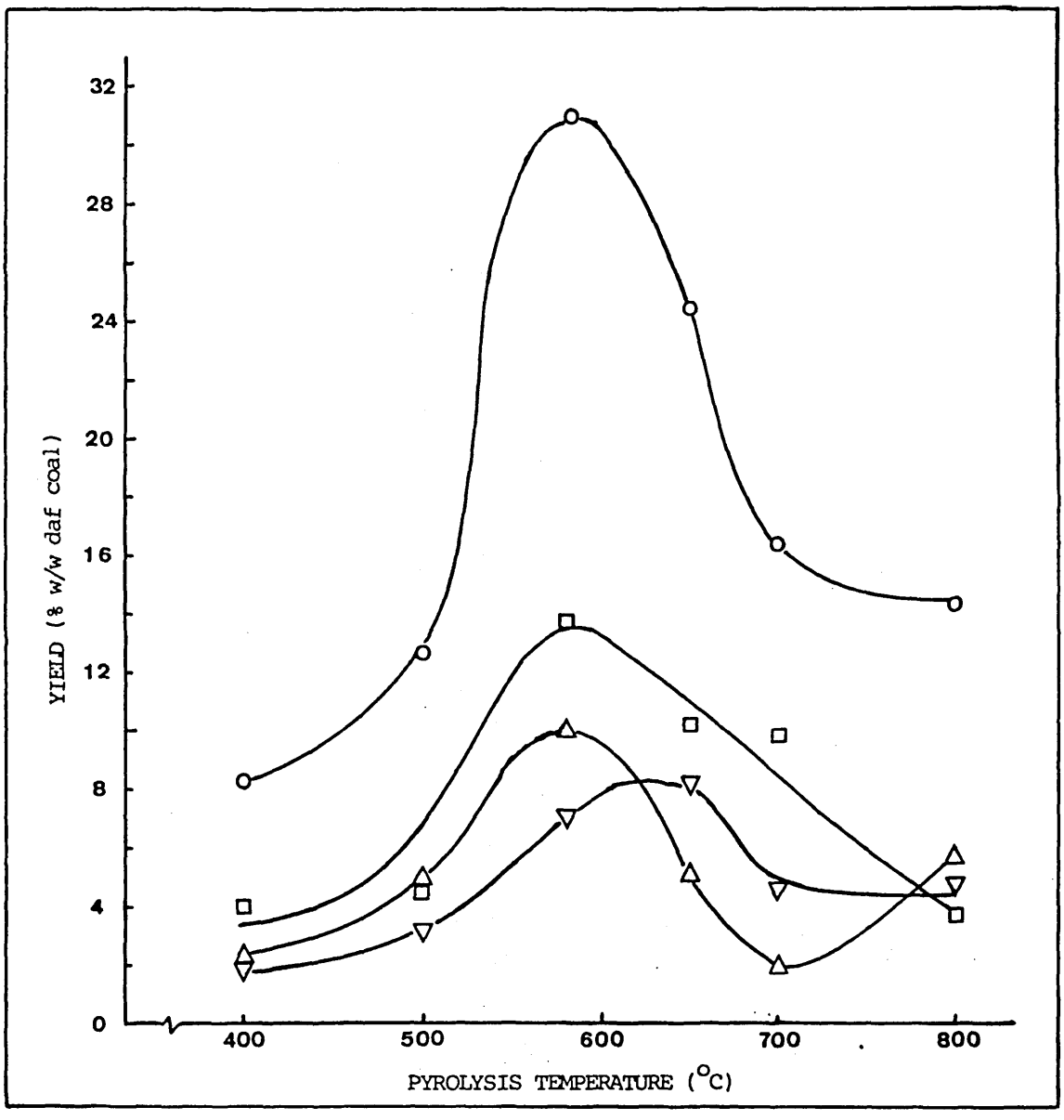
much of the tar undergoes secondary cracking above 580°C in both the bed and freeboard of the reactor, resulting in increases in gas yields and decreases in tar yields. The yield of total volatiles rises rapidly as the temperature increases to 600°C, but increases more slowly above this temperature.

The effect of temperature on the yields of tar fractions, that is the oil, asphaltene and preasphaltene is shown in Figure 7.2. The tar was fractionated according to the procedure described in Appendix I. Yields of individual fractions also exhibit maxima as a function of temperature, those for the asphaltene and oil coinciding with that for the total tar at 580°C; the maximum for the pre-asphaltene is shifted to 630°C. The oil fraction shows the steepest decline as the temperature is raised above 580°C, but shows an increase at 800°C. This suggests that the oils are the least thermally stable species, and the preasphaltene the most stable. The increase in the yield of oil at 800°C may be due to secondary cracking of other fractions producing smaller or less polar molecules.

Analysis of the Tar Fractions

The oil and asphaltene fractions were analysed by ^{1}H-NMR spectroscopy, vapour pressure osmometry, elemental analysis and phenolic -OH titration according to the methods described in Appendix I. The preasphaltene fractions were analysed only by elemental microanalysis

Figure 7.2 Yield of tar and tar fractions as a function of pyrolysis temperature for the flash pyrolysis of Linby coal: Tar (O); Oil (Δ); Asphaltene (□); Preashaltene(▽)



as they were insufficiently soluble for other methods of analysis. Selected structural parameters are shown in Table 7.2. Increases in pyrolysis temperature have a substantial effect on the structure of the tar fractions.

The oil fraction contains a substantial amount of aliphatic material, the carbon aromaticity being 43% at 580^{o}C. There is very little polar material present as is suggested by the low phenolic hydroxyl contents. As the pyrolysis temperature is increased, the aromaticity of the oil and its mean molecular weight increase. Above 600^{o}C the hydrogen to carbon (H/C) ratio) falls. This is paralleled by the rapid rise in carbon aromaticity in this range. The phenolic hydroxyl content shows little change as a function of temperature, remaining in the 1-1.5% range.

The asphaltene fractions are more aromatic, less rich in hydrogen and more polar than the oils, and typically of higher molecular weight. As the pyrolysis temperature is increased, the aromaticity of the asphaltene increases. These increases are small below 600^{o}C, above which the aromaticity increases rapidly. The molecular weight of the asphaltene increases up to 500 at 650^{o}C. As the temperature is increased to 700^{o}C, the molecular weight falls to a value of 360, while the aromaticity of the asphaltene increases rapidly to 83% maintaining the fraction in the asphaltene solubility envelope, as discussed by Snape and Bartle (1984).

Table 7.2 Analysis of tar fractions from the flash pyrolysis of untreated and 5% $ZnCl_2$-impregnated Linby.

Oil fraction

Temp.	Untreated					5% $ZnCl_2$-impregnated				
(°C)	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
397	11	1.53	37	220	1.2	10	1.55	35	220	1.0
500	13	1.43	41	270	1.5	13	1.44	41	240	1.2
580	17	1.46	43	340	1.5	13	1.48	40	290	1.3
650	13	1.28	49	320	n.d[f]	19	1.20	56	280	n.d[f]
700	31	1.10	66	440	n.d[f]	28	1.12	63	300	1.4

Asphaltene fraction

Temp.	Untreated					5% $ZnCl_2$-impregnated				
(°C)	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
397	26	1.03	66	400	3.7	29	1.10	64	410	5.0
500	35	1.06	68	460	5.1	27	1.01	66	470	8.2
580	31	0.95	70	490	4.5	31	0.98	69	420	8.2
650	54	0.90	81	500	n.d[f]	n.d[f]	n.d[f]	n.d[f]	450	n.d[f]
700	59	0.91	83	360	4.5	49	1.01	76	400	6.4

a - H_{ar} - Hydrogen aromaticity, fraction of hydrogen atoms in aromatic groups

b - H/C - Hydrogen to carbon atomic ratio

c - F_a - Carbon aromaticity, fraction of carbon atoms in aromatic groups

d - MW - Number averaged mean molecular weight

e - OH - Phenolic hydroxyl content (% w/w)

f - nd - not determined

Changes in structure of the tar below 600°C are largely due to the changes in the primary pyrolysis reactions as a function of temperature. However the large changes in the structure of both the asphaltene and oil fraction above 600°C are due to secondary reactions which affect the structure of the tar as well as influencing the distribution of products. The rapid rise in both the carbon and hydrogen aromaticity and fall in the H/C ratio is due to dealkylation reactions and the dehydrogenation of hydroaromatics. Additionally dehydroxylation and ring closure reactions may occur.

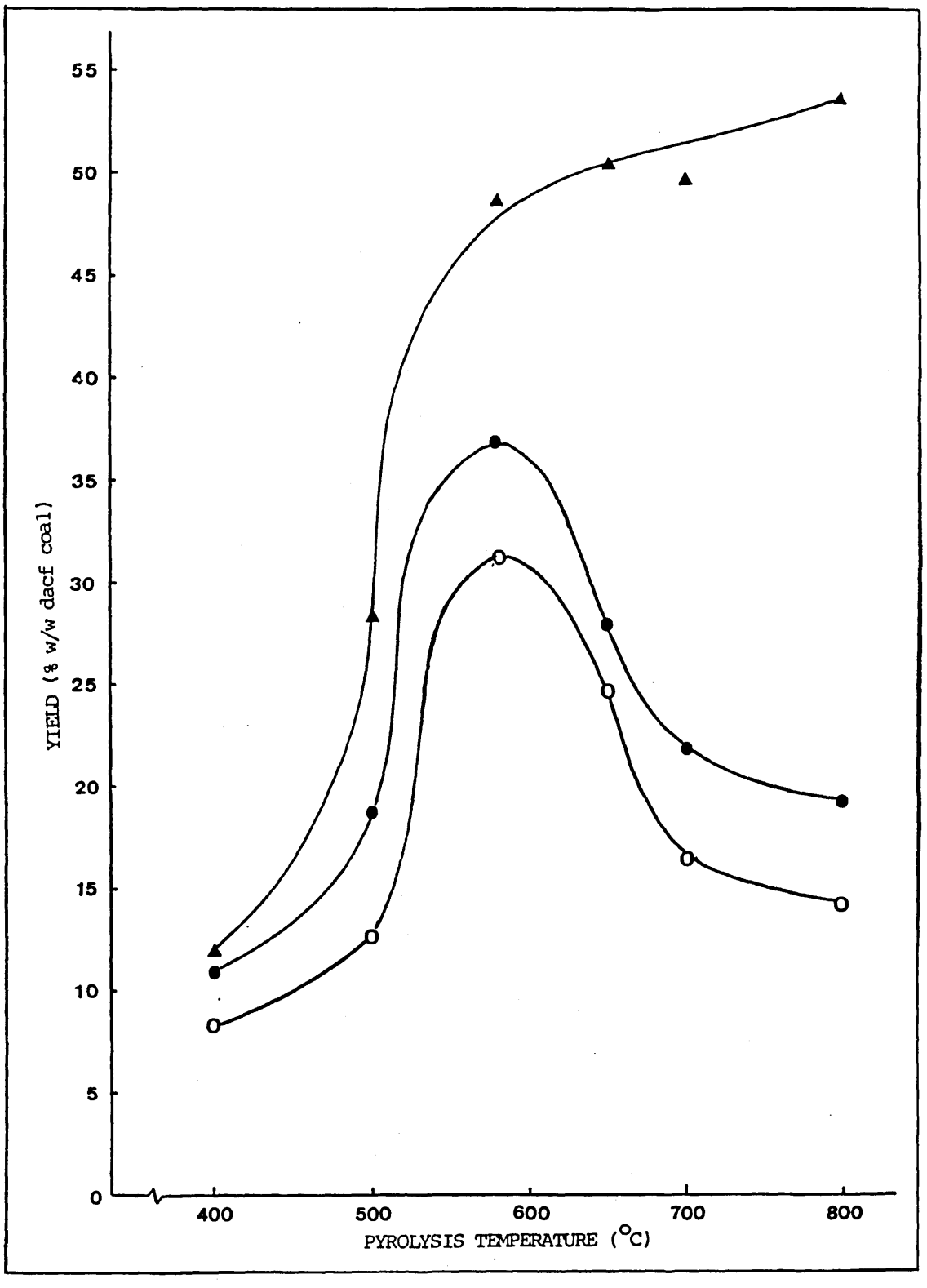
Overall, the effect of temperature on the yield and structure of the tar from Linby coal is similar to that observed by Tyler (1980) and Collin and co-workers (1980) for Australian bituminous coals.

7.1.2 FLASH PYROLYSIS OF ZINC CHLORIDE IMPREGNATED LINBY COAL

7.2.1.1 THE EFFECT OF $ZNCL_2$ AS A FUNCTION OF TEMPERATURE

The yields of tar and total volatiles from 5% $ZnCl_2$ impregnated Linby as a function of pyrolysis temperature are shown in Figure 7.3. More complete results are given in Table II.2. The tar yield from untreated Linby coal is also shown for comparison. All yields are calculated on a dry ash and catalyst free basis. The catalyst is assumed to remain with the char. This hypothesis will be

Figure 7.3 Tar (●) and total volatiles (▲) yield as a function of pyrolysis temperature for the flash pyrolysis of 5% $ZnCl_2$-impregnated Linby coal. Tar yield from untreated Linby (○).



discussed in section 7.2.1.3.

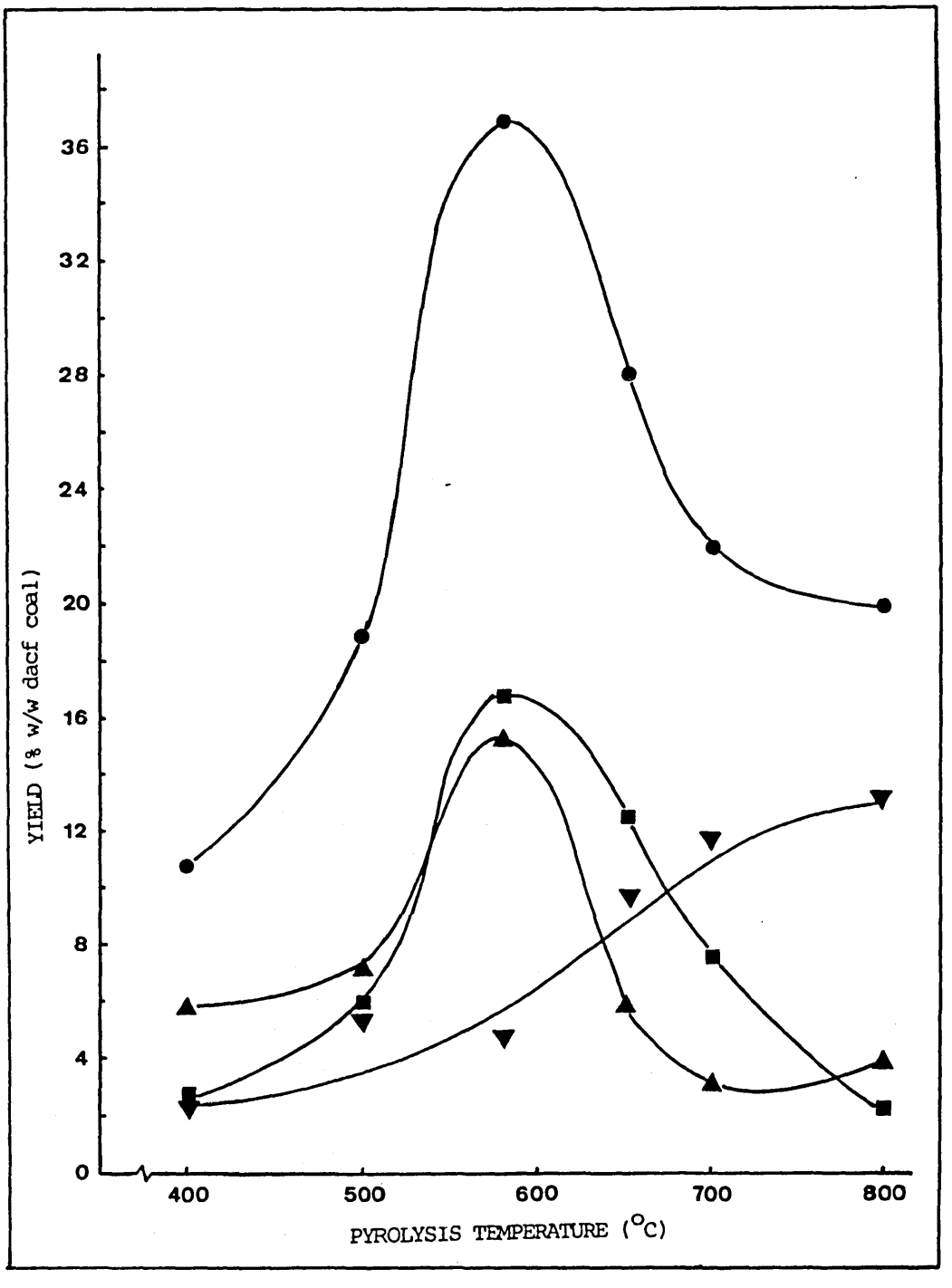
The tar yield from the 5% $ZnCl_2$ impregnated coal reaches a maximum at 580°C, which is the same temperature as the tar maximum from untreated Linby coal. The tar yield at this temperature is 36.8%. The previous result for the flash pyrolysis 5% of $ZnCl_2$ impregnated Linby at 580°C, was a tar yield of approximately 27% (Kandiyoti and co-workers, 1984). The magnitude of the increase in tar yield as a result of the experimental modifications is similar for the 5% $ZnCl_2$ impregnated and the untreated Linby.

The curves for the tar and total volatiles yields are qualitatively very similar to those for the untreated coal. In both cases quite a sharp asymmetric peak is observed for the tar yield, while the yield of total volatiles increases rapidly up to 580°C, with a shallower increase above that temperature. Over the whole temperature range studied, impregnation with 5% zinc chloride causes a substantial increase in tar yield. At the temperature of maximum tar yield, the increase is from 31% to 36.8%. This is a reversal of the trend observed at low heating rate, where in a Gray-King assay (heating rate = 5°C/min) the effect of impregnation with $ZnCl_2$ was to reduce the tar yield from Linby from 14.6% to 12.7% (Kandiyoti and co-workers, 1984). The zinc chloride also modifies the physical behaviour of the coal in the fluidised bed, the catalyst impregnated coal showing no tendency to agglomerate.

The yields of tar fractions from the catalyst impregnated coal are shown as a function of pyrolysis temperature Figure 7.4 and also in Table II.2. The oil yield again shows a maximum at 580^{o}C, with the maximum for the asphaltene shifted to a slightly higher temperature. The downward slope of the asphaltene curve at temperatures above 580^{o}C is shallower than that for the oil fraction, as was the case for the untreated coal. The preasphaltene yield shows no maximum, the yield increasing monotonically up to 800^{o}C. At 580^{o}C, the yield of oil from the 5% $ZnCl_2$ impregnated Linby is 15.2%, compared to 7.1% from the uncatalysed sample, while the yield of asphaltene increases from 13.8% to 16.8% as a result of the presence of the catalyst. The yield of preasphaltene decreases from 7.1% to 4.8%. This shows that the presence of zinc chloride favours the formation of lighter fraction of the tar under this set of conditions.

At 800^{o}C the oil yield from the uncatalysed sample is higher than the yield from the 5% $ZnCl_2$ impregnated coal. Presumably this is manifestation of the structure of the primary tar from the catalysed coal being less liable to the secondary reactions which lead to an increase in the oil yield at 800^{o}C. This may be due to the lower molecular weight of the asphaltene from the catalysed coal.

Figure 7.4 Yield of tar and tar fractions as a function of pyrolysis temperature for the flash pyrolysis of 5% $ZnCl_2$-impregnated Linby coal: Tar (●); Oil (▲); Asphaltene (■); Preashaltene▼



Analysis of the Tar Fractions

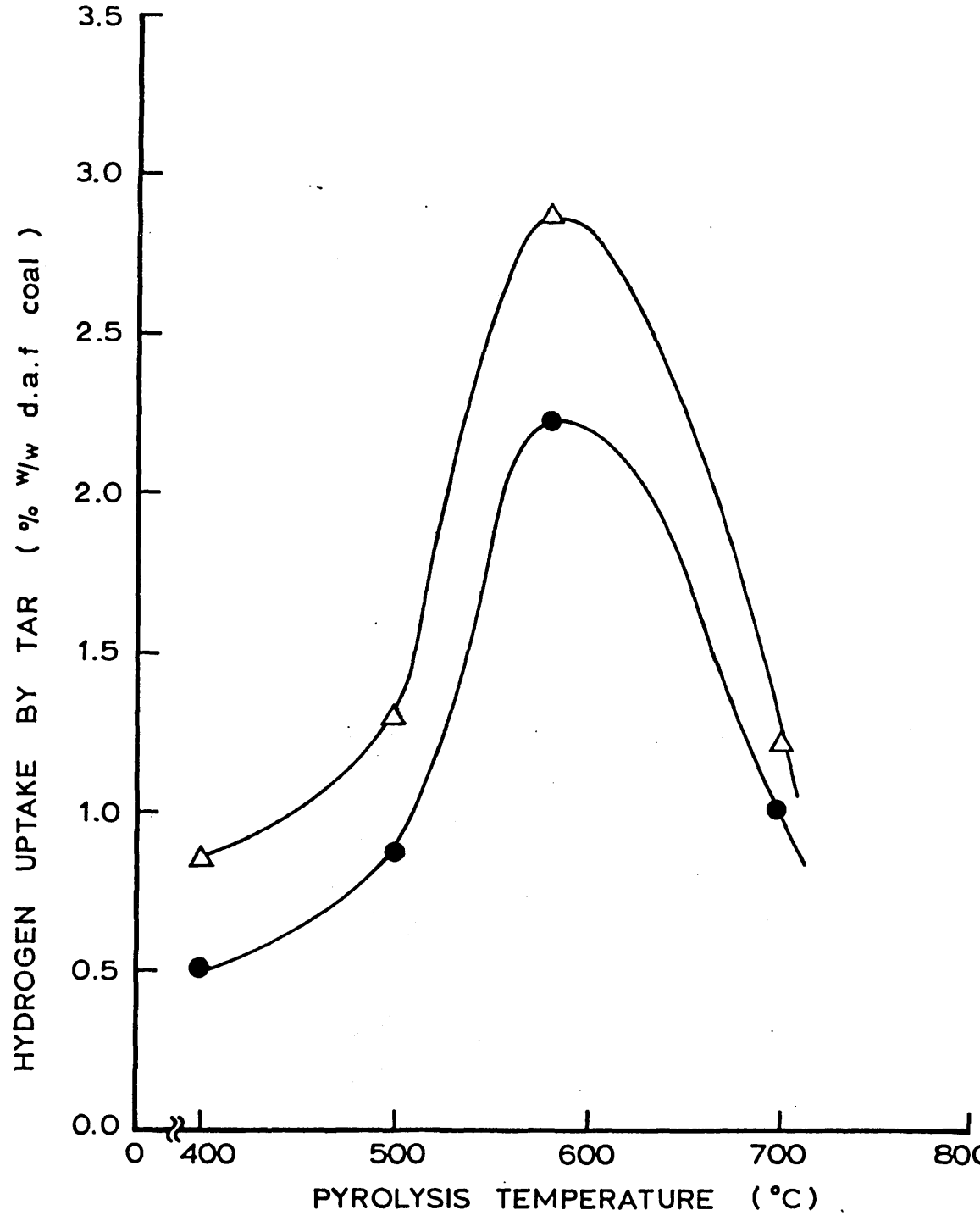
The results from the analysis of the tar fractions are shown in Table 7.2. As a function of temperature, the tar fractions for the catalyst impregnated sample show similar trends to those of the untreated coal. For the oil fraction, the aromaticity of the 5% $ZnCl_2$ impregnated Linby was consistently lower than that for the corresponding untreated sample. Similarly the molecular weights of the oil fractions from the catalysed sample are lower than those from the raw coal.

Similar results are seen for the asphaltene fractions. The molecular weights and aromaticities of the asphaltene from the catalysed sample being lower than those from the untreated coal.

The phenolic -OH content of the catalysed asphaltene is consistently higher than that of the asphaltene from the untreated sample. This may show some mechanistic trend, or may be due to the catalyst reducing the molecular weight of more polar material to within the asphaltene solubility classification.

Overall the tar from the zinc chloride impregnated Linby is richer in hydrogen than the tar from the untreated coal. Figure 7.5 shows the total hydrogen uptake by the tar as a percentage of the original coal for the catalysed and untreated Linby. In flash pyrolysis, zinc chloride appears to be acting as a hydrogenation

Figure 7.5 Hydrogen taken up by the tar as a % of the coal as a function of pyrolysis temperature for the flash pyrolysis of untreated (Δ) and 5% $ZnCl_2$-impregnated (●) Linby coal.



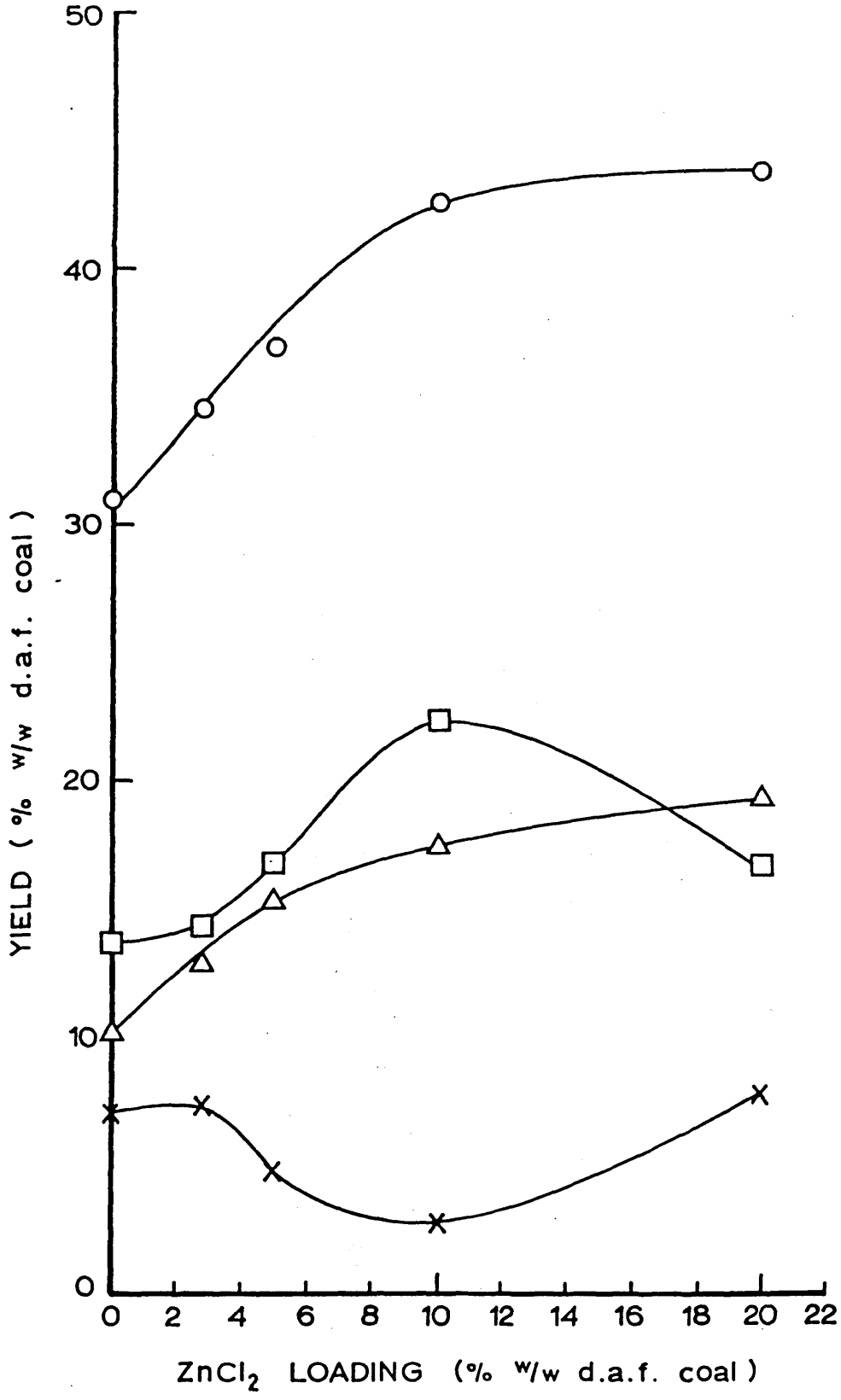
catalyst, utilising hydrogen native to the coal.

7.1.2.2 THE EFFECT OF $ZNCL_2$ AS A FUNCTION OF CATALYST LOADING

The yield of total volatiles, tar and tar fractions as a function of zinc chloride loading on Linby coal is shown in Figure 7.6. Pyrolysis experiments were performed at 580^{o}C, the temperature of maximum tar yield. As the catalyst loading is increased up to 20% the tar yield appears to reach a plateau, with a yield of 43.6% at 20%. The char yield continues to fall as the catalyst loading increases, with a corresponding rise in the gas yield. This latter finding may be due to a false assumption that all the catalyst remains with the char as $ZnCl_2$. Degradation of the catalyst, producing for example HCl and zinc metal, would diminished the char yield and cause an erroneous increase in the gas yield. At 20% catalyst loading this increase in the gas yield could be up to 10% of the daf coal.

The yield of oil also increases with catalyst loading approaching a plateau at 20% loading. The yield of asphaltene passes through a maximum between 10% and 15% $ZnCl_2$. The yield of preasphaltene shows no particular trend as a the catalyst loading increases.
Attempts to pyrolyse Linby impregnated with higher loadings of zinc chloride were thwarted by the hygroscopic nature of the catalyst, and its tendency to make the impregnated coal "clump" together in the

Figure 7.6 Yields of tar and tar fractions as a function of catalyst loading for the flash pyrolysis of $ZnCl_2$-impregnated Linby coal at 580°C: Tar (O); Oil (Δ); Asphaltene (□); Preasphaltene (X).



hopper, making it impossible to feed at such loading levels.

The analysis of the tar fractions from the flash pyrolysis of 20% $ZnCl_2$ impregnated Linby is also shown in Table 7.2. The effect of increased catalyst loading on the structure of the tar fractions is similar to those observed in the temperature series. That is, as the catalyst is increased the aromaticity and mean molecular weight of both the oil and asphaltene fraction are reduced. Similarly, the phenolic -OH content of the asphaltene is increased.

Both the oil and asphaltene fractions become richer in hydrogen as the catalyst loading increases, again demonstrating the hydrogenating ability of the zinc chloride, both in enhancing the yields of these fractions and in modifying their structures.

10.1.2.3 DISCUSSION - THE EFFECT OF ZINC CHLORIDE ON THE FLASH PYROLYSIS OF LINBY COAL

The effect of impregnation of Linby coal with zinc chloride is to cause an increase in the tar yield from flash pyrolysis. The presence of the catalyst also increases the yields of the oil and asphaltene fractions, but the effect on the preasphaltene is unclear. Additionally the structure of the oil and asphaltene fraction is modified by the zinc chloride. Overall they are richer in hydrogen as a result of the

presence of the catalyst. The total hydrogen taken up from the coal in the tar is increased as a result of the presence of the zinc chloride, showing that the catalyst is acting as though it is a hydrogenation catalyst, utilising hydrogen native to the coal.

In pyrolysis at a low heating rate, the trend is reversed. Zinc chloride has been shown to act as a carbonisation catalyst, increasing the char yield at the expense of the tar (Georgiadis and Gaillard, 1956; Bodily and co-workers, 1975; Kandiyoti and co-workers, 1984).

The ability of Lewis acids to act as coal hydrogenation catalysts, under high pressure hydrogen, was discussed in Chapter 4, as was their ability to act as carbonisation catalysts. The mechanisms which have been proposed to explain the action of $ZnCl_2$ and other Lewis acids in both processes involve Friedel-Crafts chemistry and the formation of carbonium ions.

In $ZnCl_2$ catalysed hydrogenation, the dominant reaction is thought to involve carbonium ion formation, followed by bond scission and hydride ion abstraction (Bell and co-workers, 1981). In catalysed carbonisation, where there is a low availability of hydrogen, it is thought that carbonium ions are liable to undergo Scholl condensation reactions resulting in the formation of larger molecules (Kandiyoti and co-workers, 1984). In slow pyrolysis the presence of zinc chloride has also

been shown to promote the dehydrogenation of hydroaromatics and dealkylation reactions (Bodily and co-workers, 1974; Neuberg and co-workers, in print).

More recent work has shown that the presence of zinc chloride and other Lewis acids affects ESR spin intensities, exhibiting changes in free radical concentrations, under both carbonisation and hydrogenation conditions(Yokono and co-workers, 1985a; 1985b). These changes can be explained in terms of Friedel-Crafts type mechanism: it is possible to envisage the formation of radical ions, which would produce changes in ESR spin concentrations, and undergo Lewis acid catalysed processes.

Irrespective of the precise mechanism by which zinc chloride acts, the net effect of the catalyst in coal conversion represents the competition between carbonisation and hydrogenation. The relative rates of these processes depend on the local availability of hydrogen.

It is clear that in flash pyrolysis, in an inert atmosphere, at atmospheric pressure, there is a high availability of hydrogen, such that the zinc chloride appears to act predominantly as a hydrogenating catalyst. This results in an increase in the tar yield, and the tar becoming richer in hydrogen. The additional hydrogen taken up by the tar may be available due to the high heating rate used in the pyrolysis, or may be

formed due to the activity of the catalyst in promoting condensation or dehydrogenation reactions, the hydrogen release coinciding with tar production due to the high heating rate used. In the former hypothesis, the $ZnCl_2$ must play a hydrogenating role, increasing hydrogen uptake in the tar. In the latter theory, the catalyst may merely play a role in increasing hydrogen availability, or may also play a hydrogenating role, utilising this hydrogen.

Bell and co-workers (1981) in a study of the effect of Lewis acids on model compounds under hydrogenation conditions, have suggested that a major source of hydride ions was Lewis acid catalysed Scholl condensation reactions. In flash pyrolysis, zinc chloride catalysed condensation reactions may play a similar role.

7.1.3 THE EFFECT OF OTHER LEWIS ACID CATALYSTS

7.1.3.1 THE EFFECT OF OTHER LEWIS ACIDS ON THE YIELD AND STRUCTURE OF THE PYROLYSIS PRODUCTS

The effect of a number of Lewis acid type catalysts impregnated onto Linby coal was examined in flash pyrolysis experiments at 580°C. The catalysts considered were impregnated according to the procedures described in Chapter 6. Most of the catalysts (or very similar compounds) have in the past been used as coal hydrogenation catalysts (Weller and co-workers, 1950;

Kawa and co-workers, 1970; Wood and Wiser, 1976), and some have been used to catalyse carbonisation, enhancing char yields (Georgiadis and Gaillard, 1956; Bodily and co-workers, 1975). The results of these studies are discussed in detail in Chapter 4.

The results of the fluidised bed pyrolysis experiments are shown in Table 7.3.

Table 7.3 Effect of an array of catalyst on the flash pyrolysis of Linby coal. Yields on % w/w dacf basis.

Catalyst	Char	Gas[a]	Tar	Oil	Asph.	Preas.
10% $AlCl_3$	52.1	9.1	38.8	15.6	9.0	14.2
10% $ZnBr_2$	51.2	13.0	38.5	14.5	12.5	11.5
10% ZnI_2	53.1	11.1	35.8	10.3	12.5	13.0
Untreated	57.0	12.0	31.0	10.1	13.8	7.1
9.7% $CdCl_2$	62.5	8.9	28.6	11.0	10.0	7.6
12.5% $CoCl_2$	64.5	8.3	27.2	11.2	6.7	9.3
10% $SnCl_2$	66.8	6.4	26.8	10.3	9.6	6.9
10% $FeCl_3$	71.6	6.2	22.2	8.4	4.3	9.5
10% $FeSO_4$	n.d[b]	n.d[b]	22.1	7.6	7.9	6.6
$ZnCl_2/KCl$[c]	58.4	11.6	30.0	10.7	9.2	10.1
$ZnCl_2/KCl/NaCl$[d]	64.0	8.0	28.0	13.7	7.5	6.8

a - Gas - determined by difference

b - n.d - not determined

c - 5% $ZnCl_2$ and 5% KCl

d - 3.5% each of $ZnCl_2$, KCl and NaCl

Zinc bromide and iodide both cause the tar yield to rise. Aluminium chloride, known as a strong Lewis acid also causes an increase in the yield of tar, despite the fact that the catalyst was merely admixed to the coal prior to pyrolysis.

Amongst the catalysts which cause the tar yields to decline, perhaps the most surprising is tin (II) chloride, which has been shown by many workers to be a very active coal hydrogenation catalyst (see Chapter 4). In several studies the relative activity of zinc chloride and tin chloride has been compared, with an implicit assumption that they act by similar mechanisms (Weller and co-workers, 1950; Zielke and co-workers, 1966; Kawa and co-workers, 1970; Wood and Wiser, 1976). In this case however, they appear to act differently upon a change in heating rate.

Ferric chloride, although it is known as a strong Lewis acid, is known to have a retrograde effect on coal liquefaction (Weller and co-workers, 1950a). Ferrous sulphate however has been shown increase conversion in coal hydrogenation (Weller and co-workers, 1950a). In this case, ferrous sulphate acts in the same manner as ferric chloride. Additions of sodium and potassium chloride have been shown to enhance the catalytic activity of both zinc and tin chloride under hydrogenation conditions (Nomura and co-workers, 1982; 1983; 1984; 1985), however under flash pyrolysis conditions, the alkali salts appear to diminish the

effect of zinc chloride in enhancing the tar yield.

Analysis of the Tar Fractions

Analyses of selected tar fractions were performed. Structural parameters are presented in Table 7.4. The analyses of the oil fractions are all similar, though a few systematic differences are apparent. The oil fractions from the samples whose tar yield was enhanced in comparison to the untreated sample, had lower carbon and hydrogen aromaticities and mean molecular masses than the oil from the untreated Linby coal. The hydrogen to carbon (H/C) atomic ratios were similar for both sets of samples. The analyses of the remaining oil fractions were similar to those from the untreated coal, excepting the oil from the iron (III) chloride impregnated sample. This sample has substantially higher aromaticities and mean molecular mass than the untreated sample. The H/C atomic ratio was also substantially lower for the $FeCl_3$ impregnated sample.

Additionally the asphaltene from the tin (II) chloride and cobalt chloride impregnated samples were analysed. Comparison of these with the asphaltene from the untreated samples shows that the both asphaltene fractions have higher hydrogen and carbon aromaticities than the asphaltene fraction from the untreated coal. The H/C atomic ratios were similar however, while the mean molecular weights were lower for the catalysed samples. The phenolic hydroxyl contents of asphaltene

Table 7.4 Analysis of Tar from the flash pyrolysis of Linby coal impregnated with an array of Catalysts.

Oil fraction

Catalyst	Loading	H_{ar} [a]	H/C [b]	F_a [c]	MW [d]	OH [e]
$ZnCl_2$	20%	12	1.47	40	250	0.7
$AlCl_3$	10%	14	1.50	40	310	0.7
$ZnBr_2$	10%	14	1.45	42	290	1.6
ZnI_2	10%	15	1.44	43	300	1.6
Untreated	--	17	1.46	43	340	1.5
$CdCl_2$	9.7%	15	1.43	43	380	1.4
$CoCl_2$	12.5%	13	1.47	43	340	1.1
$SnCl_2$	10%	15	1.44	43	340	1.6
$FeCl_3$	10%	14	1.34	47	410	1.5
Asphaltene fraction						
$ZnCl_2$	20%	30	1.13	63	310	10.3
Untreated	--	31	0.95	70	490	4.5
$SnCl_2$	10%	34	0.98	71	400	7.4

a - H_{ar} - Hydrogen aromaticity, fraction of hydrogen atoms in aromatic groups

b - H/C - Hydrogen to carbon atomic ratio.

c - F_a - Carbon aromaticity, fraction of carbon atoms in aromatic groups

d - MW - Number averaged mean molecular weight

e - OH - Phenolic hydroxyl content

from the $SnCl_2$ and $CoCl_2$ impregnated samples were substantially higher than the untreated sample in a similar manner to $ZnCl_2$ impregnated samples.

7.1.3.2 DISCUSSION - THE EFFECT OF A RANGE OF LEWIS ACIDS ON THE FLASH PYROLYSIS OF LINBY COAL

Summarising the results, there is no apparent correlation between the hydrogenation activity of the catalysts, and their effect under flash pyrolysis conditions. The exception to this is ferric chloride, which is known not to catalyse coal hydrogenation, and in flash pyrolysis substantially diminishes the tar yield. However ferric chloride is known to be a strong Lewis acid, showing that there is also no correlation between Lewis acid strength and the action of the catalysts in either hydrogenation or flash pyrolysis.

As in the case of the action of zinc chloride, the net effect of the Lewis acids on the flash pyrolysis of Linby represents the competition between the action of the catalyst in enhancing carbonisation and in promoting hydrogenation. In cases where the tar yield is enhanced, the hydrogenation effect predominates, while where the tar yield is diminished the carbonisation ability of the catalyst is the dominant effect.

A clue to the nature of processes occurring in coal flash pyrolysis is shown in Figure 7.7 which presents a graph of the molecular weight of the oil fraction versus

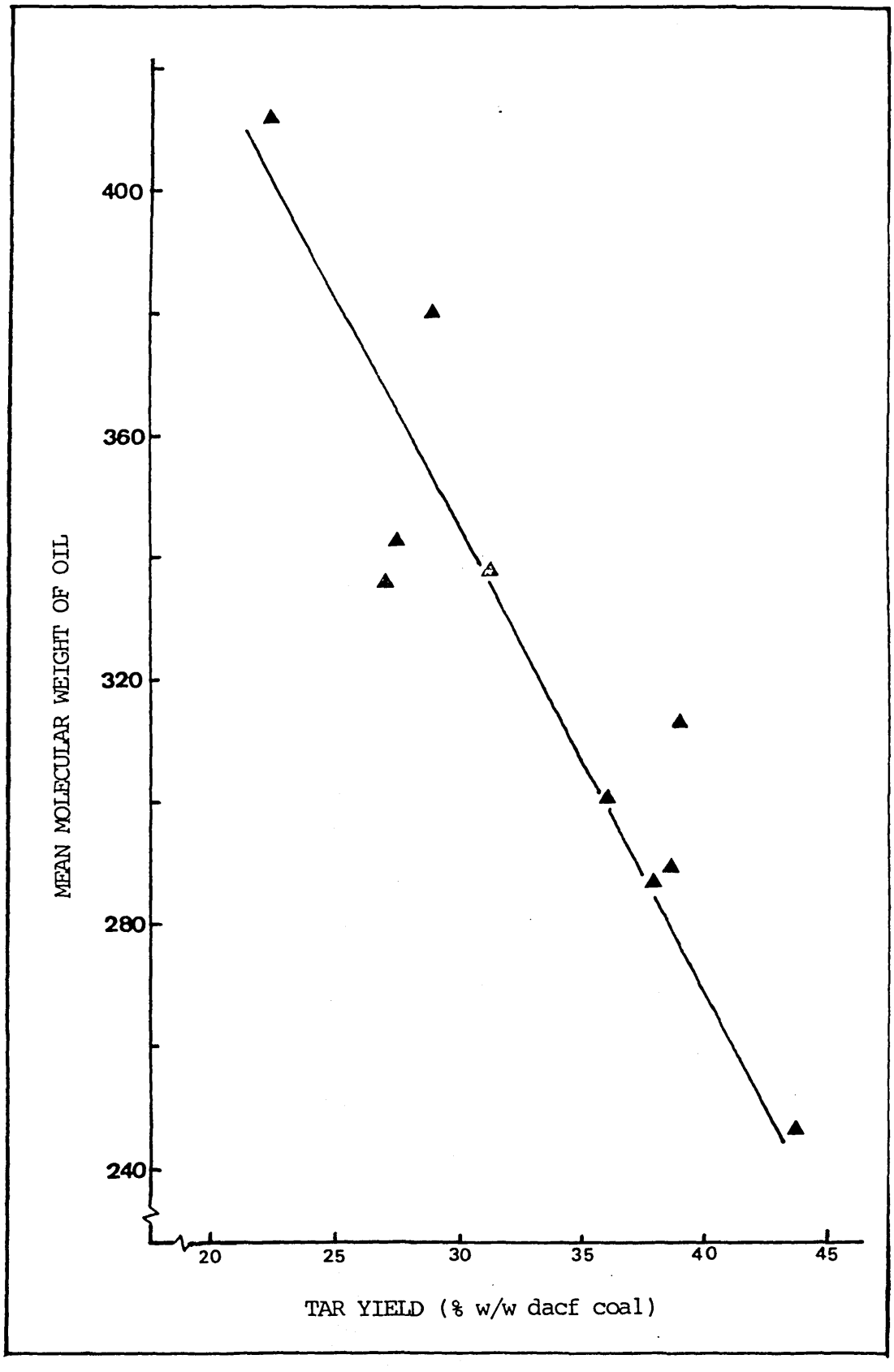


Figure 7.7 Mean molecular weight of the oil fraction as a function of tar yield for the flash pyrolysis of Linby coal impregnated with a range of Lewis acids at 580°C.

the tar yield for the flash pyrolysis experiments performed at 580°C. It can be seen that there is a considerable correlation between the two parameters. The higher tar yield obtained, the lower the molecular weight of the oil. This suggests that there may be some form of auto-hydrogenation mechanism occurring in catalytic flash pyrolysis, whereby the tar produced acts to modify and hydrogenate the oil fraction. It should be noted that the results from the untreated Linby coal also fit the correlation

The effect of tin (II) chloride in reducing the tar yield is the most surprising reported in this section. The relative activity of tin and zinc chloride in coal hydrogenation has received considerable attention, with an assumption that the mechanisms for the two catalysts were essentially the same (see Chapter 4). The differing effects of the two catalysts in coal flash pyrolysis indicates that this may not be the case. Some recent work on the mechanism of the catalyst promoted hydrogen exchange reaction anthracene/catalyst/D_2O, suggests that zinc chloride promotes exchange with the central ring, whereas antimony chloride, a strong Lewis acid, is considerably less specific (Yokono and co-workers, 1985c). It would appear possible that the action of tin chloride in this reaction is directed towards the side ring (Sanada, personal communication).

7.1.3.3 THE DISTRIBUTION OF CATALYSTS IN COAL AND CHAR

7.1.3.3.1 THE EFFECT OF IMPREGNATION

The effect of impregnation on the activity of catalysts in coal hydrogenation and pyrolysis was discussed in Chapter 4. Early work showed that impregnation had a substantial effect on the activity of several catalysts (Weller and co-workers, 1950b). However more recent work has shown that the activity of zinc chloride, in both hydrogenation and slow pyrolysis, was insensitive to the method of coal/catalyst mixing (Wood and Wiser, 1976; Kandiyoti and co-workers, 1984).

The effect of the impregnation procedure on catalyst distribution was examined for samples of Linby coal impregnated with zinc chloride and tin (II) chloride. The distribution of catalyst across coal particles was studied using scanning electron microscopy, and electron microprobe analysis. The techniques used are described in more detail in Appendix I. The impregnation procedure is described in Chapter 6. The electron photomicrograph and distribution maps for zinc, chlorine and sulphur of a typical particle of 5% zinc chloride impregnated Linby coal are in Figure 7.8.

It can be seen that the zinc and chlorine are concentrated around the periphery of the coal particle, in contrast to the sulphur, which is evenly distributed. The analogous distributions for the 10% tin chloride

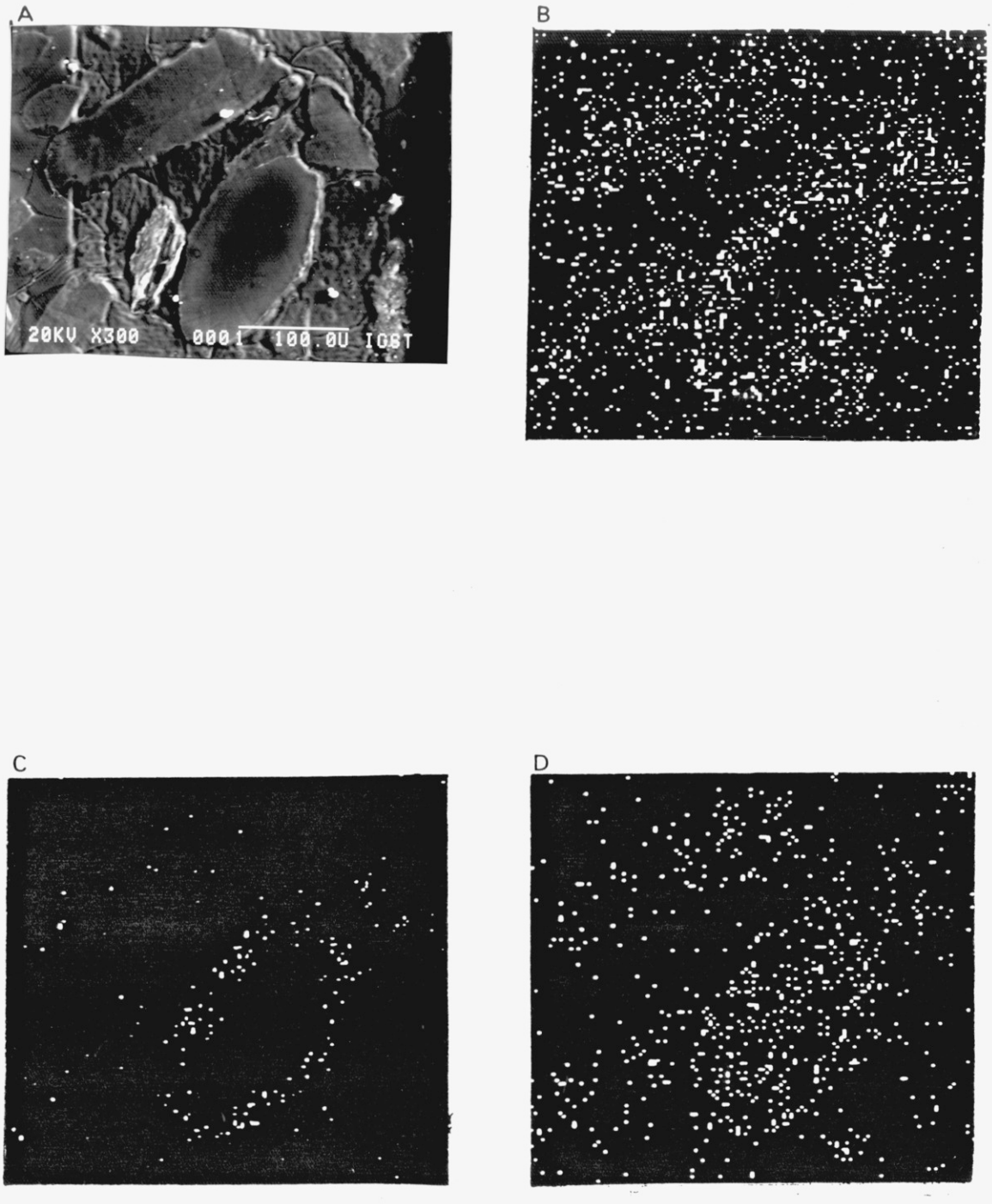


Figure 7.8 Distribution of zinc, chlorine and sulphur in unheated 5% $ZnCl_2$-impregnated Linby coal. (a) Electron micrograph. (b) Zinc distribution for area shown in 7.8(a). (c) Chlorine distribution for area shown in 7.8(a). (d) Sulphur distribution for area shown in 7.8(a).

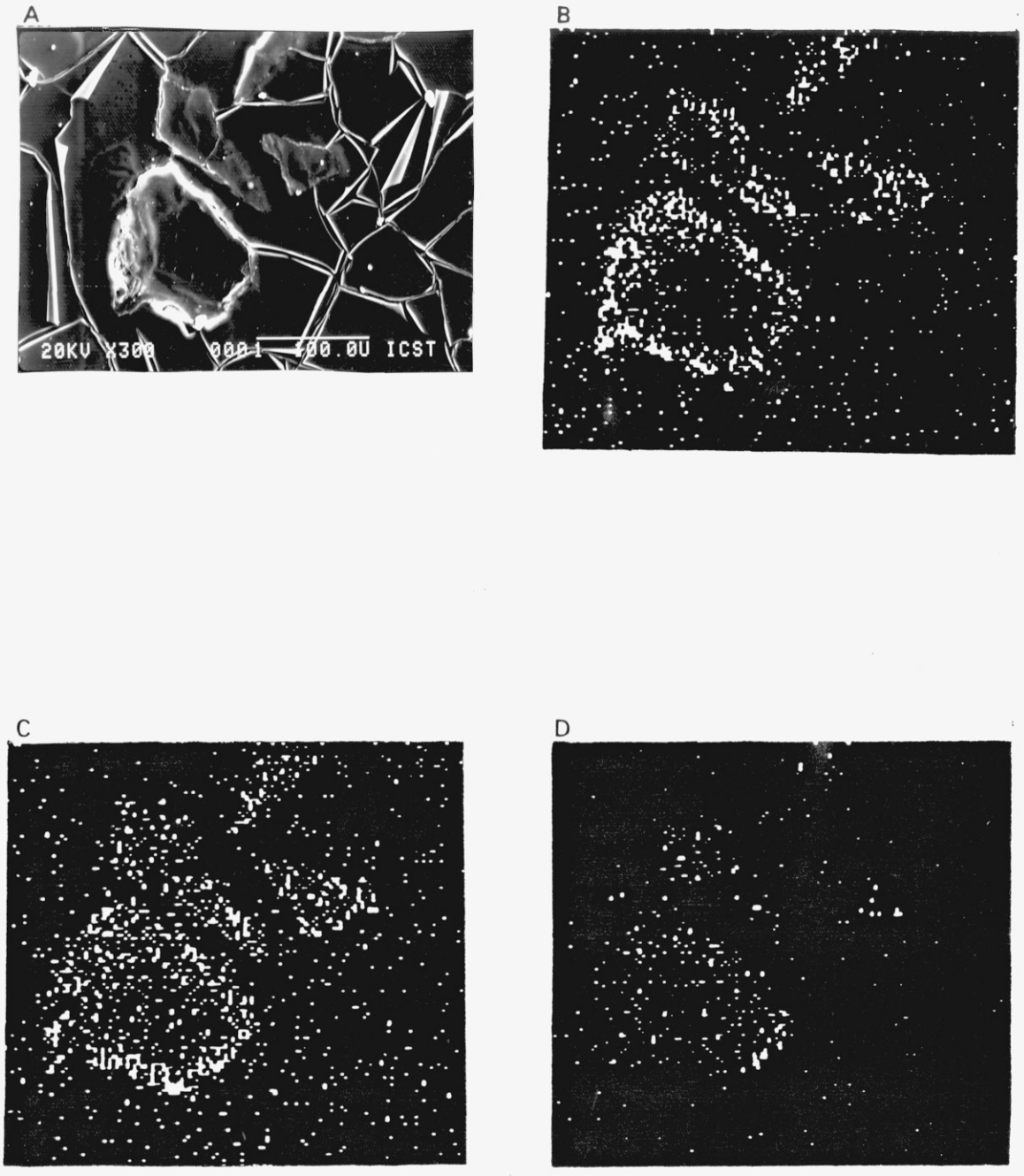


Figure 7.9 Distribution of tin, chlorine and sulphur in unheated 10% $SnCl_2$-impregnated Linby coal. (a) Electron micrograph. (b) Tin distribution for area shown in 7.9(a). (c) Chlorine distribution for area shown in 7.9(a). (d) Sulphur distribution for area shown in 7.9(a).

impregnated sample are presented in Figure 7.9, showing similar results. The findings suggest that during impregnation from methanol solution, neither catalyst penetrates the coal particle, but is deposited oround the periphery. This would explain why the activity of catalysts appeared insensitive to the method of mixing.

7.1.3.3.2 CATALYST MOBILITY

The distribution of tin chloride was similar to that found by Shibaoka and co-workers (1980) following the impregnation from ethanol solution. Shibaoka also showed that in coal hydrogenation at low temperatures, tin chloride appeared to be mobile within coal particles. Other studies have shown that both tin chloride and zinc chloride are chemically active in this temperature range (Cook and co-workers,1985; Neuberg and co-workers, in print). The results described in this subsection examine the mobility of tin chloride and zinc chloride in flash pyrolysis, and the mobility of zinc chloride at pre-pyrolysis temperatures.

The mobility of tin chloride and zinc chloride in flash pyrolysis was studied by examination of the chars formed in the experiments described in the previuos section. The distribution of tin chloride and zinc chloride in typical particles from the flash pyrolysis chars are shown in Figures 7.10 and 7.11. In both chars, the catalyst appears to be have migrated into the coal particles during pyrolysis. Although catalyst

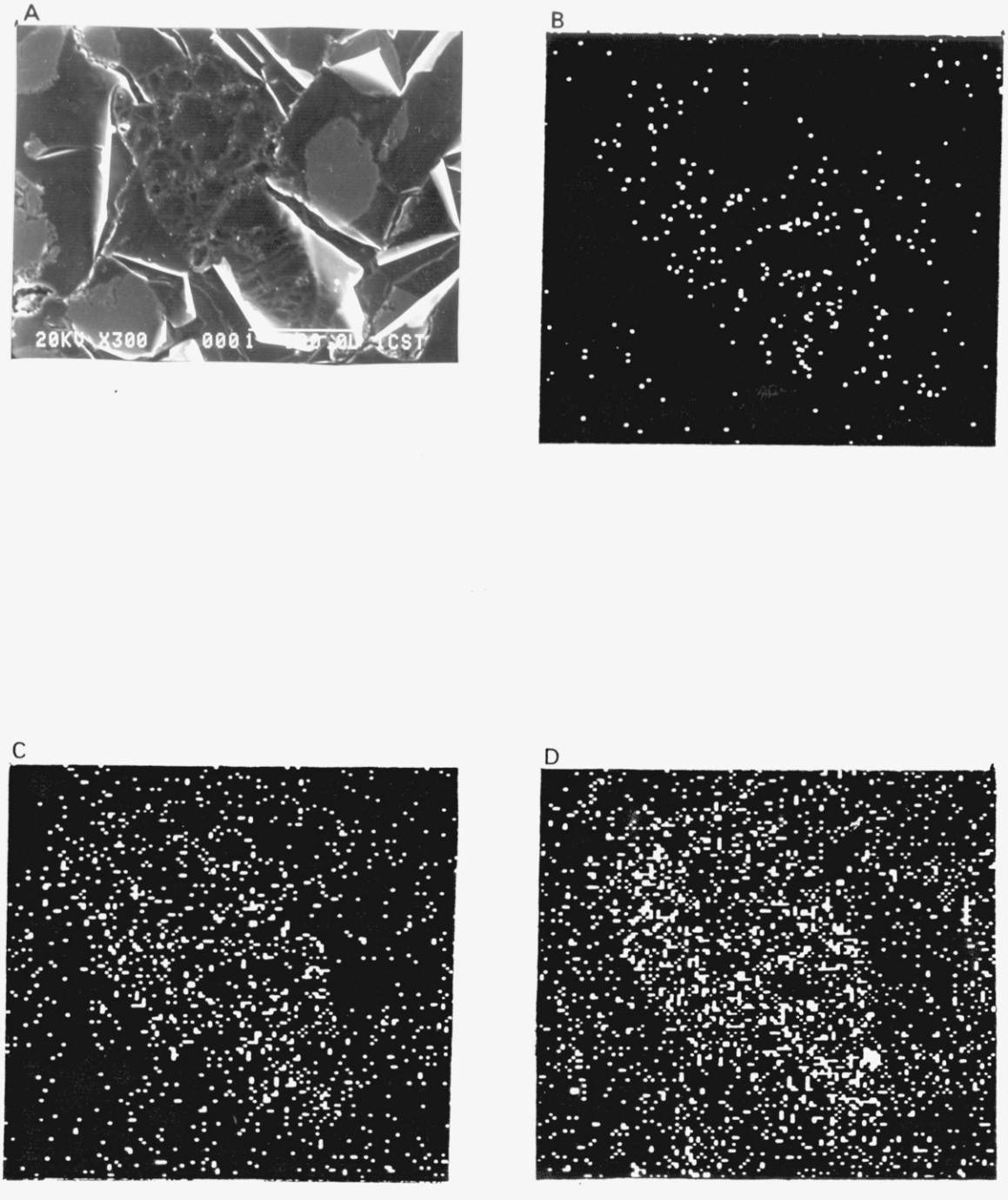


Figure 7.10 Distribution of zinc, chlorine and sulphur in char from the flash pyrolysis at 580°C of 5% $ZnCl_2$-impregnated Linby coal. (a) Electron micrograph. (b) Zinc distribution for area shown in 7.10(a). (c) Chlorine distribution for area shown in 7.10(a). (d) Sulphur distribution for area shown in 7.10(a).

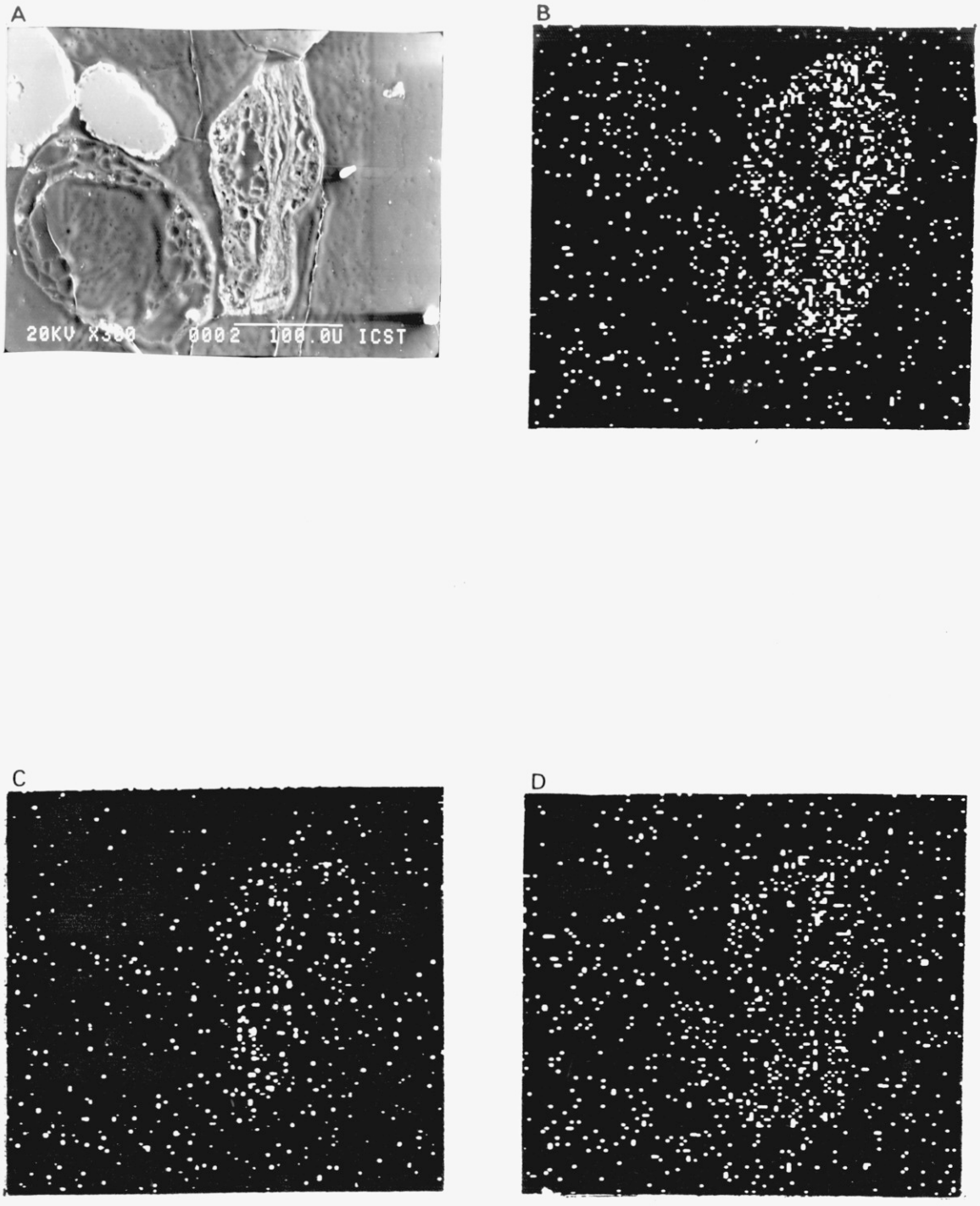


Figure 7.11 Distribution of tin, chlorine and sulphur in char from the flash pyrolysis of 10% $SnCl_2$-impregnated Linby coal. (a) Electron micrograph. (b) Tin distribution for area shown in 7.11(a). (c) Chlorine distribution for area shown in 7.11(a). (d) Sulphur distribution for area shown in 7.11(a).

distributions are affected by the porous nature of the chars, but both tin chloride and zinc chloride are evenly distributed across the particle.

In the char from the zinc chloride impregnated coal, the locations of the zinc and chlorine appear to correspond. However, in the char from the tin chloride impregnated Linby, the location of the tin does not appear to correspond to either the chlorine or the sulphur over the whole particle, suggesting that some tin may be present either as an oxide or as the metal. Both forms of tin have been reported to be present in chars from coal hydrogenation experiments. (Shibaoka and co-workers, 1980; Cook and co-workers, 1985).

In addition, the mobility of zinc chloride at pre-pyrolysis temperatures was studied. The distribution of catalyst was examined in samples of 5% $ZnCl_2$-impregnated coal samples heated to seven different temperatures in the range 150-375^{o}C. Samples were heated to prepyrolysis temperatures in a Gray-King (BS 1016, 1981) retort at 5^{o}C/min to the required temperature, under nitrogen, with a 15 minute holding period at the peak temperature.

All the samples showed a uniform distribution of zinc and chlorine across the catalyst particle, indicating the catalyst penetration was occuring at temperatures considerably below the melting point of zinc chloride (283^{o}C). This may be occuring through the formation of

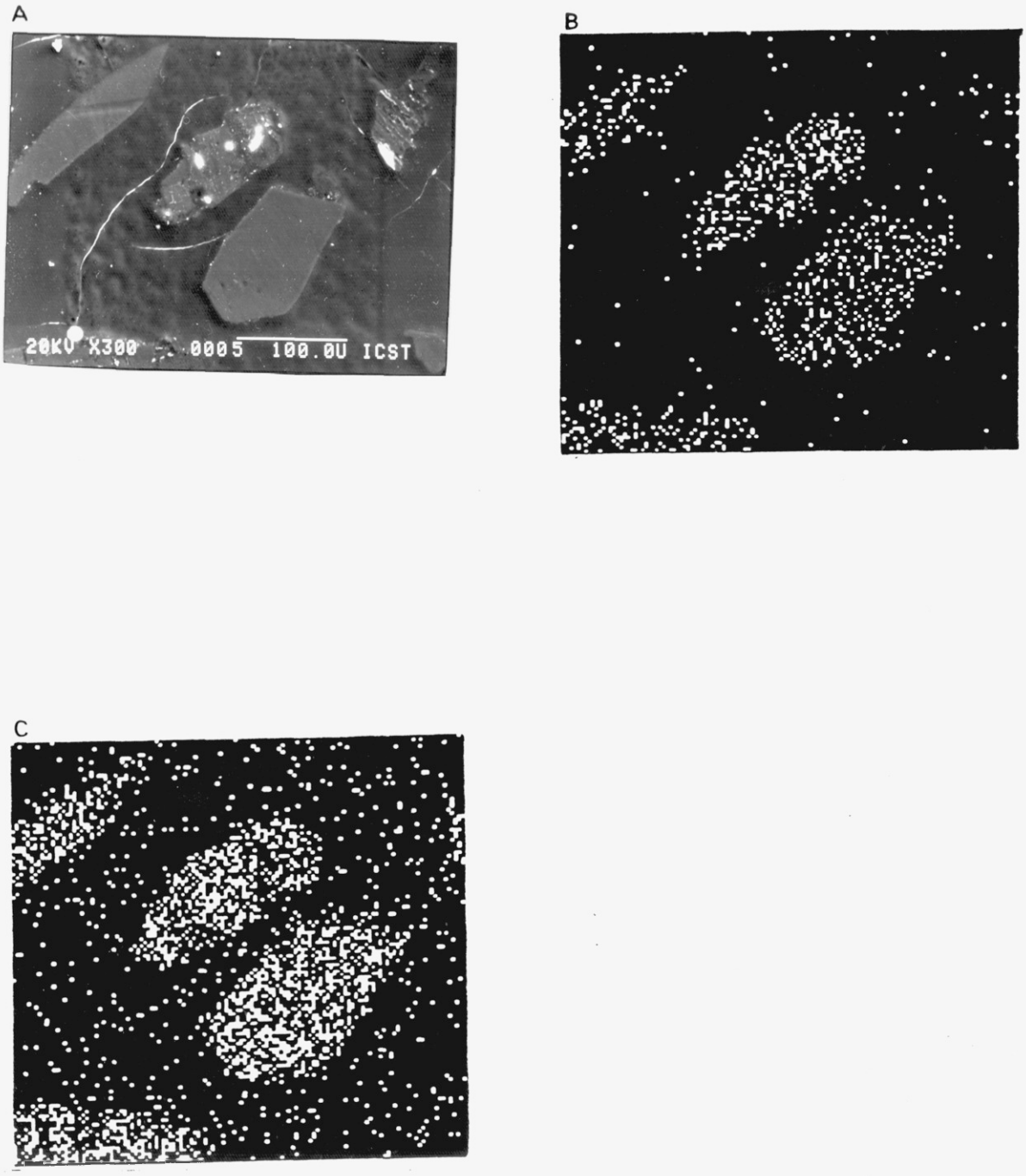


Figure 7.12 Distribution of zinc and chlorine in 5% $ZnCl_2$-impregnated Linby coal heated at 5°C/min to 375°C. (a) Electron micrograph. (b) Zinc distribution for area shown in 7.8(a). (c) Chlorine distribution for area shown in 7.8(a).

local eutectic mixtures. One example of these distribution, all of which look similar, is shown in Figure 7.12.

These results show that the distributions of tin chloride and zinc chloride, following impregnation, are similar, and that both catalysts are mobile at comparatively low temperatures. This confirms that the divergent effect of the catalysts on tar yields in flash pyrolysis must be due to different reaction mechanisms.

7.2 FLASH PYROLYSIS OF CANAKKALE CAN LIGNITE

This section considers the flash pyrolysis of Canakkale Can Turkish lignite. Previous studies on the pyrolysis of lignite at high heating rate, in a wire-mesh reactor, have shown that the tar yield from a lignite is much smaller than for a bituminous coal, and that tar production ceases at a lower temperature in the lignite (Suuberg and co-workers, 1978; Suuberg and Scelza, 1982; Suuberg and co-workers, 1985). However Tyler (1979) studied the flash pyrolysis of an Australian brown coal, of comparable carbon content, in a fluidised bed reactor, and showed that the tar yield was only 5-6% less than for a bituminous coal. Additionally, the maximum for tar production occurs at 580-600^{o}C, the same temperature as bituminous coals.

This section presents data showing the effect of flash

pyrolysis temperature on the yield and structure of tar and tar fractions from Can lignite. Additionally, the effect of impregnation with zinc chloride is shown.

7.2.1 EFFECT OF TEMPERATURE

Figure 7.13 shows the effect of temperature on the yield of tar and total volatiles from the flash pyrolysis of Can lignite in the fluidised bed reactor. More detailed results are presented in Table II.4. As can be seen, the maximum tar yield occurs at 530^{o}C, a lower temperature than for Linby coal. The maximum tar yield is 11.6% which is considerably less than the 31% observed for Linby. The shift in the peak to a lower temperature for the low rank substrate is probably due to the more oxygenated nature of both the lignite and the volatile products.

The reason for the small magnitude of the tar yield is less clear. Snape (1986) has shown that a similar trend is observed in coal liquefaction under certain conditions. Snape hypothesised that the reason for this behaviour may be that, although the bonds in lignites are more labile, the pyrolysing structure of the lower rank substrate is more liable to undergo retrograde "charring" reactions under certain conditions, diminishing liquefaction yields. The role of these processes in pyrolysis was discussed in Chapter 2.

The yield of tar fractions as a function of pyrolysis

Figure 7.13 Tar (O) and total volatiles (x) yield as a function of pyrolysis temperature for the flash pyrolysis of Canakkale Can lignite.

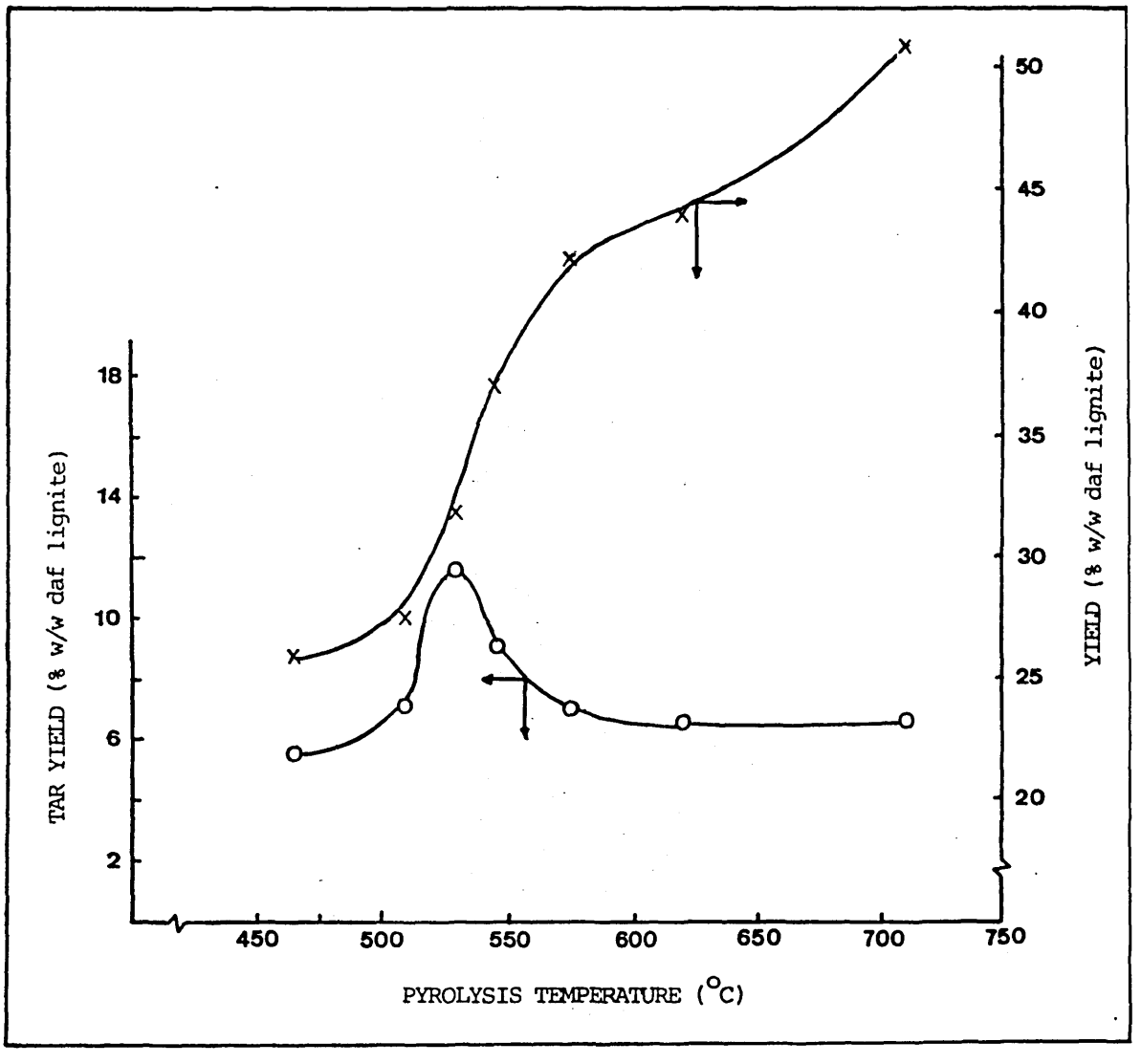
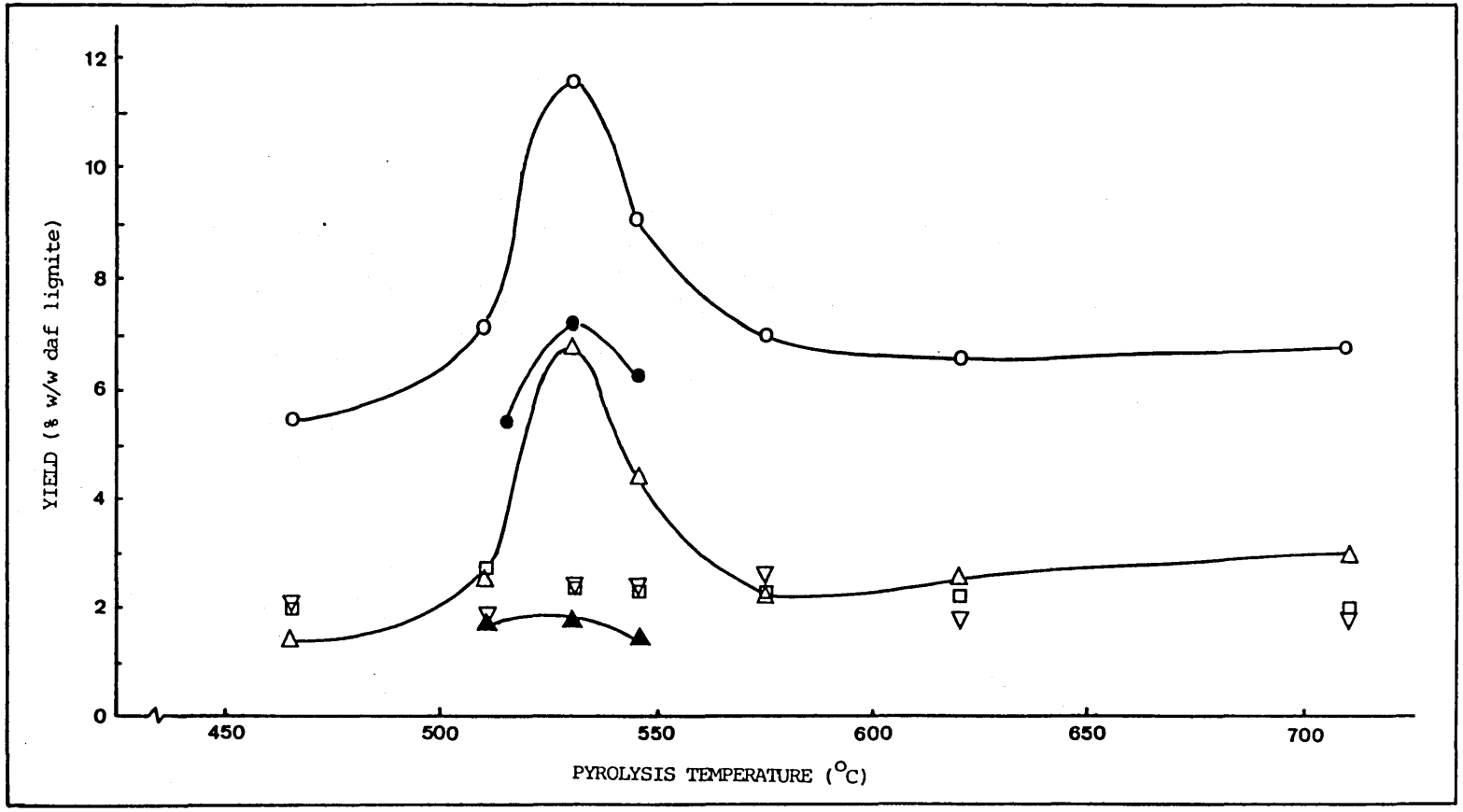


Figure 7.14 Yield of tar and tar fractions as a function of pyrolysis temperature for the flash pyrolysis of untreated and 5% $ZnCl_2$-impregnated Canakkale Can lignite. Untreated lignite: taf (O), oil (Δ), asphaltene (□), preasphaltene (▽); 5% $ZnCl_2$-impregnated lignite: tar (●), oil (▲).



temperature is shown in Figure 7.14. The oil yield goes through a maximum at the same temperature as the total tar, while the other fractions remain approximately constant over the temperature range. As in the case of Linby, the oil yield drops rapidly above the temperature of the peak tar yield, but shows a slight rise at higher temperature. The reason for this is presumably secondary reactions of larger tar molecules from the asphaltene and preasphaltene fractions yielding smaller, n-pentane soluble molecules.

Analysis of the Tar fractions

Structural parameters for the oil and asphaltene fractions are presented in Table 7.5. For the oil fractions, as the temperature is increased, the aromaticity rise, while the H/C atomic ratio remains substantially constant. The mean molecular weight falls up to 575°C above which it remains approximately constant. For the asphaltene fraction, the hydrogen and carbon aromaticities remain approximately constant up to 530°C, and then rise substantially as the temperature is further increased. The mean molecular weight falls as the temperature rises to 545°C, and then stays constant up to 709°C, when it rises again.

From this data we can conclude that secondary reactions play a substantial role in modifying the structure of lignite tars, especially above 530°C. It is clear that dealkylation and dehydrogenation reactions occur

Table 7.5a Analysis of tar fractions from the flash pyrolysis of Canakkale Can.

Temp.	Oil					Asphaltene				
(°C)	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
465	7	1.50	37	380	1.5	18	1.11	58	540	nd[f]
510	12	1.45	41	340	2.2	25	1.06	63	490	nd[f]
530	11	1.55	39	340	0.7	22	1.13	60	480	nd[f]
545	14	1.51	41	330	1.3	28	1.11	64	340	nd[f]
575	11	1.40	42	300	1.3	33	1.01	68	370	nd[f]
621	16	1.38	47	280	2.8	39	0.97	73	360	nd[f]
709	16	1.44	47	300	n.d[f]	43	0.98	74	410	nd[f]

Table 7.5b Analysis of tar fractions from the flash pyrolysis of 5% $ZnCl_2$-impregnated Canakkale Can.

Temp.	Oil					Asphaltene				
(°C)	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
515	11	1.46	40	330	n.d[f]	n.d[f]	1.04	n.d[f]	n.d[f]	n.d[f]
530	10	1.51	39	340	n.d[f]	n.d[f]	1.03	n.d[f]	n.d[f]	n.d[f]
545	12	1.20	52	340	n.d[f]	33	1.07	67	n.d[f]	n.d[f]

a - H_{ar} - Hydrogen aromaticity, fraction of hydrogen atoms in aromatic groups

b - H/C - Hydrogen to carbon atomic ratio

c - F_a - Carbon aromaticity, fraction of carbon atoms in aromatic groups

d - MW - Number averaged mean molecular weight

e - OH - Phenolic hydroxyl content

f - nd - not determined

resulting in increases in aromaticities. This especially noticeable in the asphaltene fraction. Dehydroxylation of asphaltene may occur above 575°C, resulting in the observed increase in the yield of the oil fraction. The mean molecular weight of the asphaltene fraction is only slightly higher than that of the oil fraction, and the sharp increase in the aromaticity of the oils at 620° may be a symptom of this occurring.

Comparing the structures with those from Linby, the influence of the more oxygenated nature of the lignite on the tar fractions is not clear from these analyses. The more aliphatic nature of the Can is reflected in both the oil and asphaltene fractions which are substantially more aliphatic than the tar fractions from Linby.

7.2.2 EFFECT OF ZINC CHLORIDE

The effect of zinc chloride on the flash pyrolysis of Can is contrary to its effect on Linby and other bituminous coal which are discussed later. The tar and oil yield from 5% impregnated Can over a small temperature range is shown in Figure 7.14. More complete results for the 5% impregnated sample, for a 20% impregnated sample and for the untreated lignite for comparison are presented in Table 7.6.

The effect of impregnation with zinc chloride is to cause a decline in the tar yield. Although the char

yield does not rise for the 5% impregnated sample, a substantial rise is noted for the 20% loading. The peak of tar production occurs at 530°C in the same manner as the untreated lignite. The yields of the tar fractions are similar to those of the untreated sample excepting the yield of the oil fraction, which is greatly decreased for all experiments on catalyst impregnated samples. In the flash pyrolysis of Canakkale Can, zinc chloride does not act as a hydrogenation catalyst, as it does in the flash pyrolysis of Linby, but certainly at the higher loading, acts as carbonisation catalyst, in a similar manner to its effect at low heating rate in the pyrolysis of Linby.

Table 7.6 Effect of impregnation with $ZnCl_2$ on the flash pyrolysis of Canakkale Can. Yields on a % w/w dacf[a] basis.

Catalyst loading[c]	Temp. (°C)	Char	Gas[b]	Tar	Oil	Asph.	Preas.
5%	515	67.3	27.3	5.4	1.8	1.9	1.7
5%	530	64.5	28.3	7.2	1.7	2.5	3.0
5%	545	62.1	31.6	6.3	1.5	1.8	3.0
20%	530	74.0	19.1	6.9	1.1	3.0	2.8
none	530	68.3	20.1	11.6	6.8	2.4	2.4

a - dacf - dry, ash and catalyst free basis.

b - gas by difference

c - catalyst loading calculated as a % of a mixture of the dry ash free lignite + the catalyst.

Analysis of the tar fractions from the catalysed samples

Structural parameters for the tar fractions from the zinc chloride impregnated samples are shown in Table 7.5. The structures of the oil fractions are basically similar to those from the untreated sample, suggesting that these structures are dominated by solubility and secondary reactions. The asphaltene fraction from the 5% impregnated sample pyrolysed at 545°C has higher hydrogen and carbon aromaticities and a lower H/C ratio than the equivalent untreated sample.

7.2.3 DISCUSSION - THE FLASH PYROLYSIS OF CANAKKALE CAN

There are three main differences between Linby coal and Can lignite in terms of their flash pyrolysis behaviour. Firstly the magnitude of the tar yield is much lower from the lignite than from the bituminous coal, secondly the maximum for the tar yield is shifted from 580°C for the bituminous coal to 530°C for the Can, and thirdly the effect of impregnation with zinc chloride is to reduce the tar yield for the lignite, whereas a substantial increase is noted for the Linby.

There are two differences between the Can and Linby samples extending beyond the fact that the lignite is of lower rank than Linby. Firstly, the ash content of Can is 24%, on a dry basis (see Table 6.1), is much higher than that of Linby (5.3%). Secondly, the Can was

supplied from a different source than the hard coals used in this study, and prior to the preparation of the sample for this study, may have undergone oxidation which would alter its properties. The effect of rank on the structure of coals was discussed in section 1.3. The principle differences expected between the structures of the lignite and Linby as a result of rank are:

(1) For lignites the carbon aromaticity is lower than for bituminous coals, and hence there is more aliphatic and hydroaromatic material present in the former (Davidson, 1982; Given, 1984)

(2) Associated with this, the average aromatic cluster size is expected to be smaller in lignites and the degree of condensation of the aromatic structures is lower (Davidson, 1982; Given, 1984)

(3) The oxygen content of the lignite is higher than the bituminous coal. This additional oxygen is probably present in carboxylic groups, though increased concentrations of ether and phenolic groups may also be present (Blom and co-workers, 1957)

(4) The degree of cross-linking of the macromolecular structure has been shown to be higher for low rank coals (Snape, 1986)

(5) The fraction of hydroaromatics present in coal has been shown to decrease with increasing rank above carbon

contents of 80% (Reggel and co-workers, 1964), though this trend cannot necessarily be extended for lower rank coals.

The following subsections discuss the deviations between the behaviour of Can and Linby in the fluidised bed, and the manner in which the above differences of structure between Can and Linby may have influenced these deviations.

Magnitude of the tar yield

Neither the difference between the ash content of Can and Linby nor the possible oxidation of the lignite are likely to be the reasons for the small magnitude of the tar yield from the flash pyrolysis of Canakkale Can. Although the possible oxidation of the lignite may have affected the tar yield, other workers have produced similar results for other, presumably unoxidised lignites (Suuberg and co-workers, 1978; Suuberg and Scelza, 1982). Similarly the high ash level (24%) of the Can may have catalytic effects, though the results of Suuberg and co-workers (1978) and Suuberg and Scelza (1982) were obtained with lignites with a considerably lower ash content (10-12%). It is therefore probable that the molecular structure of the lignite and the manner in which it differs from that of Linby is responsible for the different behaviour.

The less aromatic nature of the lignite structure and the more oxygenated nature of its structure suggests that the bonds in Can should be more labile than those in Linby. Furthermore, there is a higher proportion of hydrogen present in the lignite (H/C ratio = 0.98) compared to Linby (H/C ratio = 0.77). These two factors suggest that the tar and total volatile yield from Can should be higher than from Linby, though this is not the case.

Snape (1986) has reported that the degree of cross-linking in lignites is higher than in bituminous coals. Suuberg and co-workers (1985a; 1985b) have shown that in flash pyrolysis, the cessation of tar production coincides with an increase in the degree of cross-linking for a bituminous coal and also for a lignite. Suuberg has suggested that the two processes may be linked. The fact that lignites have a high level of cross-linking must act to inhibit tar formation. In additional, the higher proportion of oxygen present in the lignite may lead to the premature onset of cross-linking during pyrolysis, in a similar manner to the effect of oxygen groups introduced by the oxidation of bituminous coals (Ignasiak and co-workers, 1974; Grint and Perry, 1985). Such a retrograde reaction would also lead to decreases in the tar yield.

Another possible mechanism which may have lead to the observed lower tar yield involves utilisation of hydrogen by phenolic hydroxyl groups or other hydrogen

scavengers (eg sulphur) to form water or H_2S, preventing the hydrogen from acting to stabilise free radicals.

The Shift in the maximum tar yield peak

The maximum tar yield for Canakkale Can is is obtained at 530°C, which is a lower temperature than the maximum for Linby and other bituminous coal, which occurs at 580°C. A similar shift in the maximum is noted in the high pressure system (see Chapter 9), a result which has been confirmed elsewhere (Cypres and Moliner, 1986). This shift in the temperature of the maximum can be entirely attributed to the different thermal stabilities of the tar from the lignite and Linby. The tar from the lignite is more aliphatic than that from the Linby, and presumably contains more oxygen although this is difficult to confirm without direct determinations of oxygen levels.

Stiles (1986) performed experiments on the flash pyrolysis of more oxygenated substrates such as cellulose, wood and lignin. The temperature of the maximum tar yield was seen to be dependent on the proportion of oxygen in the substrate: the higher the oxygen content, the lower the temperature of the maximum tar yield, indicating the lower thermal stability of the tar from more oxygenated substrates. As Canakkale Can has a higher oxygen content than Linby, it should be expected that the tar from the lignite is less thermally than the tar from the Linby, and therefore that the

maximum tar yield from Can should occur at a lower temperature. The lower stability of tar from more oxygenated substrates is probably due to the higher oxygen contents of the tars. As carbon-oxygen bond are more labile than carbon-carbon bonds, the higher the oxygen content of a tar, the more liable it is to undergo secondary reactions.

The higher level of aliphatic material in the lignite tar may also affect its stability, though there is also a considerable amount of aliphatic material in the Linby tar, and there is no evidence of secondary reactions, eg. the formation of ethylene or propylene, below or at 580^{o}C in the flash pyrolysis of Linby (Snape, personal communication 1986).

Effect of zinc chloride

The effect of impregnation with $ZnCl_2$ on the flash pyrolysis of Can lignite is to reduce the tar yield which is a reversal of its effect on Linby. The reason for this reversal of trends is not clear. It is possible that the high ash level present in the Can interferes with the action of zinc chloride. The structural differences between the lignite and Can also may have an effect on the activity of the catalyst. However, Bell and co-workers (1981) have shown that ether linkages are as liable to the action of zinc chloride as methylene bridges under high pressure hydrogen, so any increase in the concentration of oxygen linkages is not likely to

affect catalytic activity. The supply of hydrogen to participate in the proposed hydride abstraction step (Bell and co-workers, 1981; Kandiyoti and co-workers, 1984) may be impeded in the lignite or the stability of carbonium ions may be affected by the smaller size of aromatic nucleii in the lignite.

It is not possible to determine the precise mechanistic differences between the action of zinc chloride in the lignite and Linby, without a more detailed knowledge of the action of zinc chloride in the flash pyrolysis of Linby coal.

7.3 FLASH PYROLYSIS OF A RANGE OF HARD COALS

The flash pyrolysis of three hard coals, in addition to Linby, was studied. The coals studied were: Daw Mill, a coal of similar rank to Linby; Cortonwood Silkstone, a coking coal; and Taff Merthyr a semi-anthracite. The ultimate and proximate analyses of these coals are given in Chapter 6, Table 6.1. A previous study of the flash pyrolysis of a range of bituminous coals by Tyler (1980) has shown that the tar yield correlated well with the the H/C atomic ratio of the coal and also with the reactive macerals content, these being exinite and vitrinite.

This sections shows changes in the yield and structure of the tar and tar fractions as a function of the coal

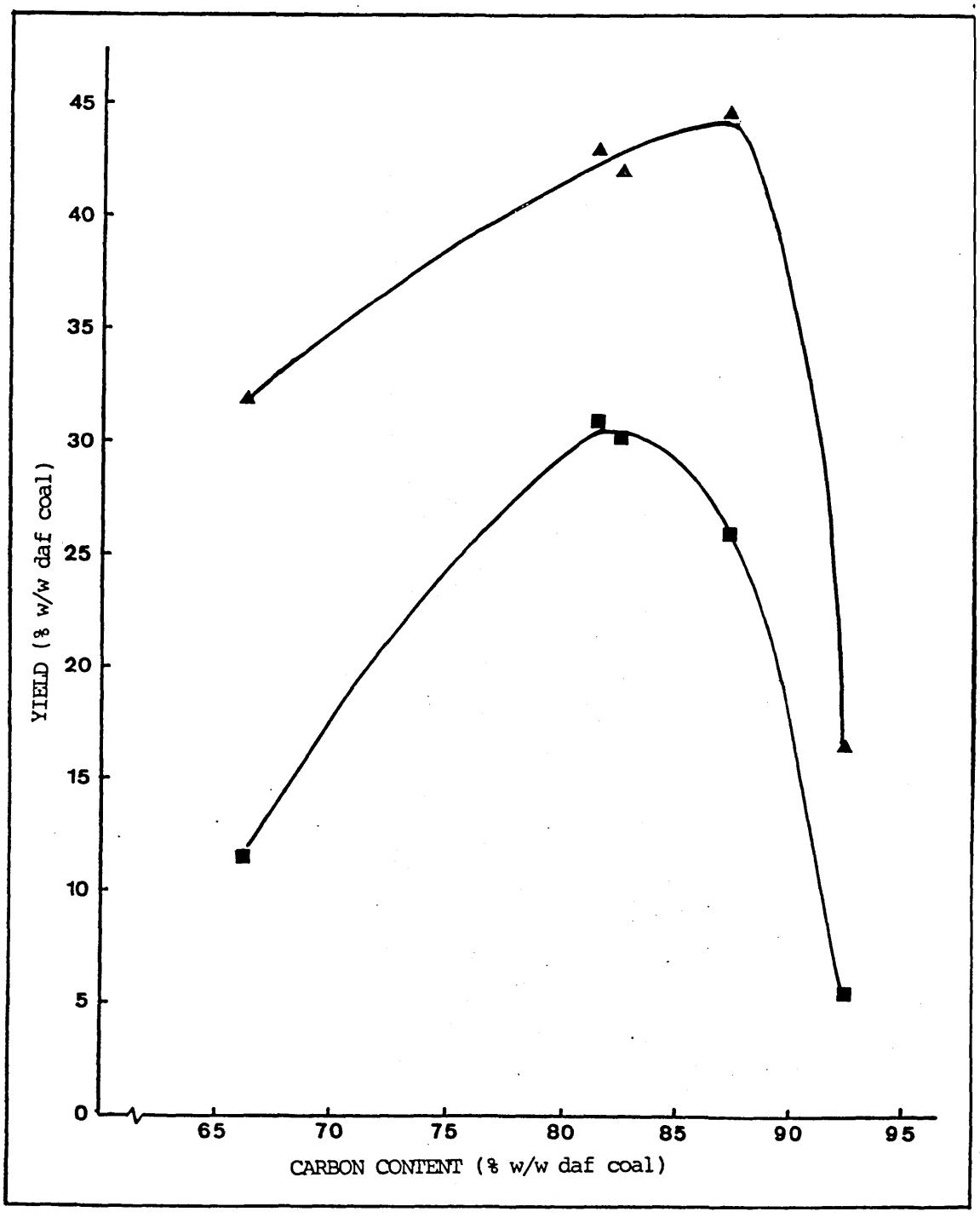
rank. The effect of impregnation with zinc chloride will also be shown.

7.3.1 FLASH PYROLYSIS OF THE UNTREATED COALS

Figure 7.15 presents the yields of tar and total volatiles as a function of coal carbon content from the flash pyrolysis of the range of coals at 580°C. Included on the figure are points for the flash pyrolysis of Can lignite obtained at 530°C. More complete results are presented in Table 7.7 and Table II.5. As can be seen the maximum yield of tar is obtained for the high volatile bituminous coals with carbon content of 80-82.5%.

The tar yield does not correlate well with the H/C atomic ratio of the parent coal. The H/C ratio is highest for Canakkale Can at 0.98, with the value for Taff Merthyr lowest at 0.55. The H/C ratios for the other coals are very similar, for Linby the value is 0.77, for Cortonwood H/C = 0.77 and for Daw Mill, H/C = 0.75. In comparing these results with those of Tyler (1980), it should be noted that the coals studied by Tyler were low rank bituminous coals with a smaller range of carbon contents than considered here. None of the coals studied by Tyler was a coking coal. Additionally a plot of tar yield versus carbon content for the coals used by Tyler shows no trend. This is due to the variability of maceral content, notable the proportion of inertinite, in the samples studied by

Figure 7.15 Tar (▲) and total volatiles (■) yield as a function of carbon content for the flash pyrolysis of a range of coals at 580°C (530°c for the lignite).



Tyler.

In Figure 7.15 the maximum total volatiles yield is shifted compared with the tar yield, to a carbon content of 87%, with the value of 44.6% for Cortonwood Silkstone, the coking coal. The reason for this high yield in the case of the coking coal may be its physical behaviour in the fluidised bed. As mentioned in section 7.1, Linby coal melts when it enters the fluidised sand bed, and to an extent agglomerates with the sand and sticks to parts of the reactor, notably the tip of the feeder tube. This agglomeration limits the amount of coal which can be fed, but also results in part of the char being retained in the bed and therefore having a much longer residence time than the char which carries out of the bed with the tar. Similar behaviour is observed for Daw Mill, in both cases the amount of coal which can be fed is 1-1.5 grams.

The agglomeration of Cortonwood Silkstone is more pronounced than that of Linby, since the coking coal becomes plastic to a greater extent. This limits the maximum amount of coal that can be fed to 0.5 grams. This suggests that the retention of the char in the case of the Cortonwood is substantially higher than in the case of either Linby or Daw Mill. If the mean residence time is much higher for the Cortonwood, then it would be more liable to undergo the slow gas producing reactions, which would result in a much higher yield of total volatiles for the Cortonwood. Taff Merthyr shows no

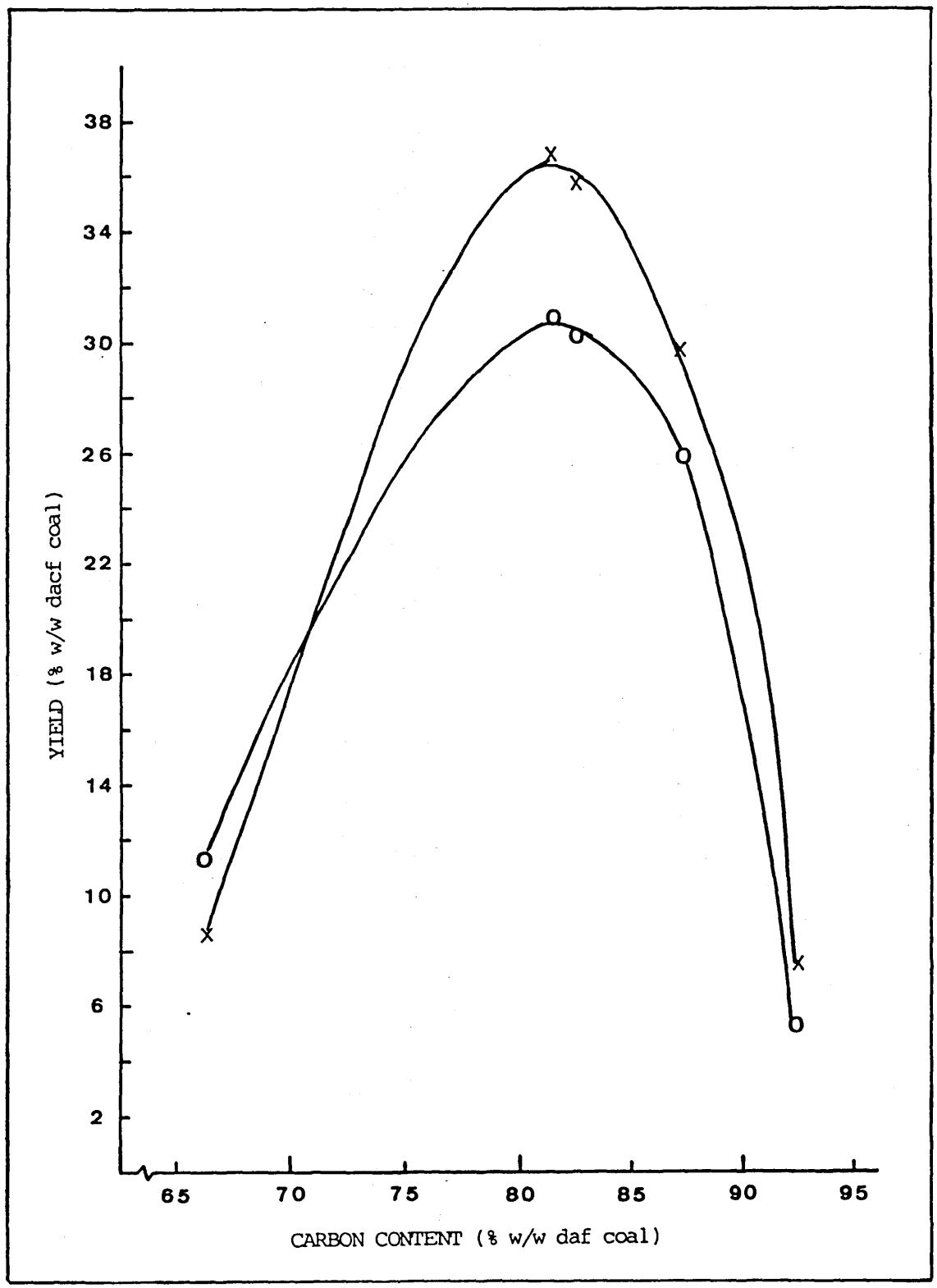
tendency to agglomerate in the fluidised bed.

The yield of the tar fractions is shown in Table 7.7. The results for Daw Mill are similar to those of Linby as would be expected. Structural parameters for the fractions are presented in Table 7.8. As might be expected the hydrogen aromaticity of the oil fractions rises as a function of rank, reflecting the increasing aromaticity of the substrate. The analysis of the oil Daw Mill is very similar to that from Linby, except that the fraction from Daw Mill has slightly higher hydrogen and carbon aromaticities. The oil fraction from Cortonwood has a higher molecular weight and carbon aromaticity than the oil fraction from any of the other coals. This may be due to the coking properties of Cortonwood which might retard the transport of the tar molecules following their formation, making them more liable to undergo secondary reactions. In the case of the asphaltene both the hydrogen and carbon aromaticities are seen to increase as a function of rank.

7.3.2 FLASH PYROLYSIS OF 5% $ZNCL_2$ IMPREGNATED COALS

Figure 7.16 shows the effect of impregnation with 5% zinc chloride on the range of hard coals studied. Also included is the data for Can lignite, which was described in the previous section. More complete results are shown in Table 7.7 and Table II.5. The effect of impregnation with zinc chloride was the same for all the

Figure 7.16 Tar yield as a function of carbon content for the flash pyrolysis of a range of untreated and 5% $ZnCl_2$-impregnated coals at 580°C (530°c for the lignite): Untreated coal (o); 5% $ZnCl_2$-impregnated coal (x).



hard coals studied in that it resulted in an increase in the tar yield. It also resulted in an increase in the total volatiles yield. Additionally, the tendency of Cortonwood and Daw Mill to agglomerate in the fluidised bed was removed by the presence of the zinc chloride, as was the case for Linby.

The effect of zinc chloride on the yields of the tar fractions is shown in Table 7.7. As should be expected the effect on the fractions for Daw Mill was similar to that observed for Linby, that is an increase in the yield of the oil fraction, a small increase in the asphaltene yield, and a drop in the yield of preasphaltene.

Table 7.7 Flash pyrolysis yields for a range of hard coals and 5% $ZnCl_2$ impregnated hard coals.

Coal	Char	Gas[a]	Tar	Oil	Asph.	Preas
Daw Mill	58.1	11.7	30.2	7.5	15.1	7.6
Daw Mill+$ZnCl_2$	53.8	10.5	35.7	12.2	16.3	7.2
Cortonwood	55.4	18.7	25.9	7.1	9.3	9.5
C´wood+$ZnCl_2$	29.8	16.4	29.8	6.0	14.8	9.0
Taff Merthyr	83.5	11.1	5.4	1.5	3.4	0.5
Taff + $ZnCl_2$	83.0	9.5	7.5	1.5	2.3	3.7

a - gas by difference

The effect of zinc chloride on Cortonwood Silkstone was to cause a small drop in the oil and preasphaltene yields, and a large rise in the yield of asphaltene. For Taff Merthyr however, the catalyst resulted in a rise in

Table 7.8 Analysis of tar fraction from the flash pyrolysis of a range of Coals at 580°C.

Oil Fraction

Coal	Untreated					5% $ZnCl_2$-impregnated				
	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
Daw Mill	17	1.37	48	330	nd	14	1.37	46	270	nd
Cortonwood	24	1.16	60	440	nd	22	1.19	58	410	nd
Taff Merthyr	24	1.30	57	380	nd	20	1.40	49	370	nd
Asphaltene Fraction										
Daw Mill	39	1.04	71	430	nd	35	0.99	70	395	nd
Cortonwood	41	0.86	76	530	nd	39	0.87	76	380	nd
Taff Merthyr	53	0.97	79	440	nd	39	1.02	71	350	nd

a - H_{ar} - Hydrogen aromaticity, fraction of hydrogen atoms in aromatic groups

b - H/C - Hydrogen to carbon atomic ratio.

c - F_a - Carbon aromaticity, fraction of carbon atoms in aromatic groups

d - MW - Number averaged mean molecular weight

e - OH - Phenolic hydroxyl content

the yield of preasphaltene, the oils remaining constant, and a small drop in the asphaltene.

The effect on the structures of these fractions is shown in Table 7.8. All the oil and asphaltene fractions from the catalyst impregnated samples have lower hydrogen and carbon aromaticities, and mean molecular mass than the corresponding sample from the untreated coal. The asphaltene fractions from both Cortonwood Silkstone, and from Taff Merthyr appear to have lower mean molecular masses than the oil fractions from the same tar sample. A similar effect was observed for untreated Linby coal at 700^{o}C. In that case a very high aromaticity was observed though the reason in this case is unclear.

To summarise, the effect of impregnation with zinc chloride on the flash pyrolysis of a range of three British hard coals is to increase the tar yield. Although the effect of the catalyst on the yields of individual tar fractions is not consistent, the tar fractions from the catalyst impregnated samples are less aromatic and have lower mean molecular weights than the tar fractions from the untreated coals.

In the flash pyrolysis of the hard coals, the zinc chloride appears to act predominantly as a coal hydrogenation catalyst, in a similar manner to its effect on the flash pyrolysis of Linby. The changes in coal structure, which occur with increasing rank, do not affect the action of the catalyst in promoting tar

formation.

7.4 FLASH PYROLYSIS OF CHLOROFORM EXTRACTED COALS

The ability of low molecular weight extractable material to influence the coking and liquefaction behaviour of coal was discussed in chapter 5. Additionally the work of Vahrman was reviewed, in which the participation of extractable material in the formation of tar in slow pyrolysis was examined (Vahrman, 1970; Spence and Vahrman, 1970; Vahrman and Rahman, 1971; Palmer an Vahrman, 1972a; 1972b; Vahrman and Watts, 1972a; 1972b).

One of the conclusions of Vahrman's work was that most of the tar formed in slow pyrolysis originated in the extractable low molecular weight material. This theory, although plausible for slow pyrolysis, cannot explain the large increase in the tar yield which results from the use of high heating rates in pyrolysis, a trend confirmed recently by Gibbins (OBrien, Gibbins and Kandiyoti, 1986). In order to investigate any role which extractables might play in pyrolysis at higher heating rates, flash pyrolysis experiments were performed on samples of pre-extracted coal.

This section presents data showing the effect of chloroform extraction on the fluidised bed flash pyrolysis of a range of hard coals and a lignite. The effect of impregnation with zinc chloride on the flash pyrolysis of extracted Linby coal is also demonstrated.

Analytical data for the structures of the tars from the extracted coal is also presented. Lastly, the nature of the chloroform extractables and the mechanisms by which they act is discussed.

7.4.1 FLASH PYROLYSIS OF EXTRACTED UNTREATED COAL

Coal samples were extracted with chloroform for 25 hours under nitrogen using the procedure described in chapter 6. The coals studied were Linby, Cortonwood Silkstone and Taff Merthyr, together with the Can lignite. Daw Mill was not studied further because of its similarity to Linby. The yield of extracts is shown in Table 7.9.

Table 7.9 25 hour chloroform extraction yields on a % w/w daf basis.

Coal	Extract yield	Pentane Soluble Fraction
Canakkale Can	1.17[a]	0.70[a]
Linby	1.97[a]	0.67[a]
Cortonwood Silkstone	0.25	nd[b]
Taff Merthyr	0.11	nd[b]

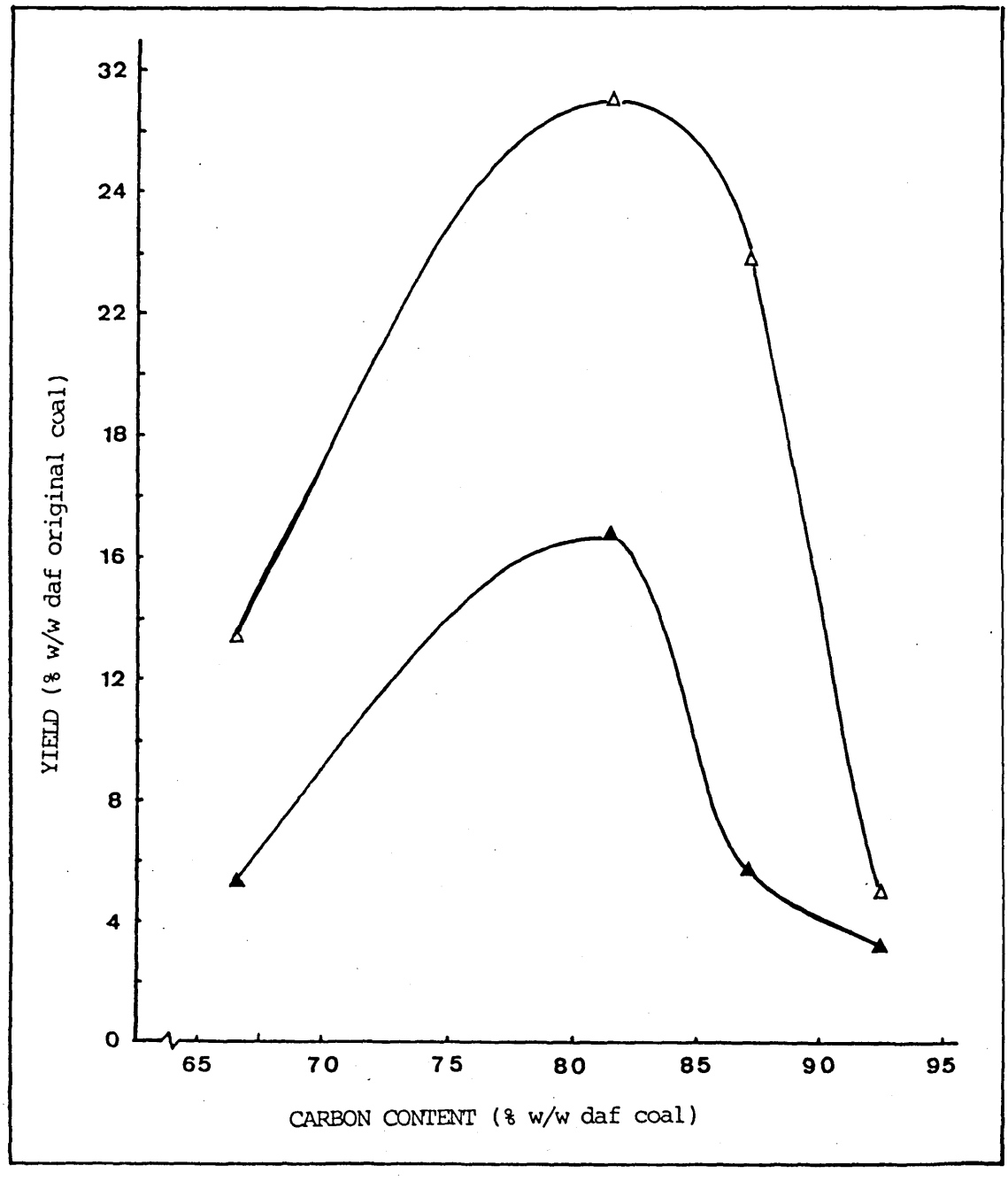
a - mean of two extractions

nd[b] - not determined

Figure 7.17 shows the tar yield from the flash pyrolysis of untreated and extracted coal as a function of carbon content. More complete results are shown in Table 7.10.

Pyrolysis experiments were performed at 580°C, except in the case of Canakkale Can when they were

Figure 7.17 Tar yield as a function of carbon content for the flash pyrolysis of a range of untreated and 25 hour chloroform extracted coals at 580°C (530°c for the lignite). Untreated coal (Δ); Extracted coal (▲).



performed at 530°C. Two experiments were performed for extracted Linby to confirm the data. The tar yield from the second experiment was within 0.5% of that from the first. Yields are presented on a dry, ash free basis as a percentage of the original coal.

It can be seen that for the three coals and the lignite, the difference between the tar yield from the untreated coal and that from the extracted sample is much greater than the amount of extract removed. Most dramatic is the effect on Cortonwood Silkstone, where the amount of extract removed was only 0.25%, but the tar yield decreased from 25.9% for the unextracted coal, to 5.3 for the extracted sample.

The effect of extraction on the tar fractions and the char yield is shown in Table 7.10. The biggest effect is on the oil and asphaltene fractions. There is no significant change in the char yield from Linby coal as a result of extraction, though there is a significant increase in yield in the case of Taff Merthyr.

Structural data for the tar fractions from the flash pyrolysis of extracted Linby and Can are shown in Table 7.11. The data do not show a consistent trend, in that the oil from the extracted Linby is more aromatic and of higher mean molecular weight than the oil from the untreated coal. However the asphaltene from Linby and the oil from Can are both less aromatic than the untreated sample, though the asphaltene from the Can

follows the same trend as the Linby oil. The difference in the effect for the different fractions probably reflects the different mechanisms occurring in the pyrolysis of Linby and Can.

Table 7.10 Flash pyrolysis yield from untreated and chloroform extracted samples. Yields on % w/w daf basis of the original coal sample.

Sample	Char	Gas[a]	Tar	Oil	Asph.	Preas.
Can Untr.[b]	68.3	20.1	11.6	6.8	2.4	2.4
Can Extr.[c]	nd[d]	nd[d]	5.4	1.6	1.7	2.1
Linby Untr.[b]	57.0	12.0	31.0	10.1	13.8	7.1
Linby Extr.[c,d]	58.8	22.3	16.9	3.5	6.0	7.4
C´wood Untr.[b]	55.4	18.7	25.9	7.1	9.3	9.5
C´wood Extr.[c]	nd	nd	5.3	1.2	1.5	2.6
Taff Untr.[b]	83.5	11.1	5.4	1.5	3.4	0.5
Taff Extr.[c]	92.3	4.5	3.1	1.5	1.1	0.7

a - gas by difference

b - Untr. - untreated sample

c - Extr. - 25 hour chloroform extracted sample

d - mean data from two experiments.

Clearly the extractable low molecular weight material is not merely acting as a volatile component during flash pyrolysis, but is acting to influence the pyrolysis reaction pathways. Proposed mechanisms by which the extractables may act will be discussed later in this section.

Table 7.11 Analysis of tars from the flash pyrolysis of 25 hour chloroform extracted Linby and Canakkale Can

Sample	Oil					Asphaltene				
	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]	H_{ar}[a]	H/C[b]	F_a[c]	MW[d]	OH[e]
Untr[f] Linby	17	1.46	43	340	1.6	31	0.95	70	490	4.5
Extr[g] Linby	17	1.31	50	400	nd	20	1.02	62	460	nd
Untr[f] Can	11	1.55	40	340	0.7	22	1.13	60	480	nd
Extr[g] Can	6	1.45	37	270	nd	23	1.05	63	400	nd
Linby + 5% $ZnCl_2$	13	1.48	40	290	1.3	31	0.98	69	420	8.2
Extr[g] Linby + 5% $ZnCl_2$	16	1.31	49	325	nd	21	1.03	63	440	nd

a - H_{ar} - Hydrogen aromaticity, fraction of hydrogen atoms in aromatic groups

b - H/C - Hydrogen to carbon atomic ratio.

c - F_a - Carbon aromaticity, fraction of carbon atoms in aromatic groups

d - MW - Number averaged mean molecular weight

e - OH - Phenolic hydroxyl content

f - Untr - Untreated coal

g - Extr - 25 hour chloroform extracted coal

7.4.2 FLASH PYROLYSIS OF EXTRACTED LINBY IMPREGNATED WITH ZINC CHLORIDE

A sample of Linby coal which had been extracted with chloroform for 25 hours was impregnated with 5% $ZnCl_2$ according to the procedure described in chapter 6. The impregnated, extracted sample was flash pyrolysed at 580°C in the fluidised bed reactor. Two experiments were performed and as for uncatalysed Linby the tar yields were within +/- 0.5%. The mean results for these experiment are presented in Table 7.12. along with data for uncatalysed, extracted Linby and for unextracted Linby for comparison

Table 7.12. Flash pyrolysis yields from extracted Linby coal, impregnated with 5% $ZnCl_2$. Yields on a % w/w dry ash and catalyst free basis of the original coal.

Sample	Catalyst	Char	Gas[a]	Tar	Oil	Asph.	Preas
Extr.[bd]	5% $ZnCl_2$	58.9	26.1	12.8	2.2	4.5	6.0
Extr.[bd]	--	58.8	22.3	16.9	3.5	6.0	7.5
Untr.[c]	5% $ZnCl_2$	51.3	11.9	36.8	15.2	16.8	4.8
Untr.[c]	--	57.0	12.0	31.0	10.1	13.8	7.1

[a] - gas by difference

b - Extr. - 25 hour chloroform extracted coal

c - Untr. - untreated coal

d - mean of two experiments

It can be seen that the tar yield is reduced as a result of the presence of the $ZnCl_2$ catalyst for the extracted

Linby, which is a reversal of the trend observed for the untreated coal. The oil and asphaltene fractions are reduced by the greatest proportion, though all fractions are diminished by the catalyst. Structural parameters for the oil and asphaltene fractions are presented in Table 7.11. The analyses of the two fractions from the catalyst impregnated, extracted Linby are substantially the same as those from the uncatalysed, extracted coal. For the extracted coal, the zinc chloride does not predominantly act as a hydrogenating catalyst, as is the case for unextracted coal, but has a similar effect to that in slow pyrolysis, where the zinc chloride acts as a carbonisation catalyst (Kandiyoti and co-workers, 1984). This implies that the catalyst uses the extractable material as an intermediate in promoting tar formation in flash pyrolysis. This nature of the role of the extractable material in catalytic flash pyrolysis will be discussed later in this section.

7.4.3 THE NATURE OF THE ACTION OF CHLOROFORM EXTRACTABLE MATERIAL

7.4.3.1 THE EFFECT OF HEATING RATE ON THE PYROLYSIS OF EXTRACTED COAL

The effect of chloroform extraction on the product distribution from flash pyrolysis of Linby coal in a fluidised bed reactor has since been confirmed in a wire-mesh reactor, where a substantial decline in the tar yield was also observed (OBrien and co-workers,

1986). The effect of chloroform extraction was examined over a wide heating rate range (0.1°C/s-1000°C/s). The results of this study are shown in Figure 7.18. It can be seen that at low heating rate, the tar yield from the extracted coal, when added to the extract yield, is equal to or exceeds the tar yield from the untreated coal. However the tar yield from the extracted coal is unaffected by increases in heating rate, and remains at a constant level, while the tar yield from the untreated coal rises substantially at heating rates above 50°C/s.

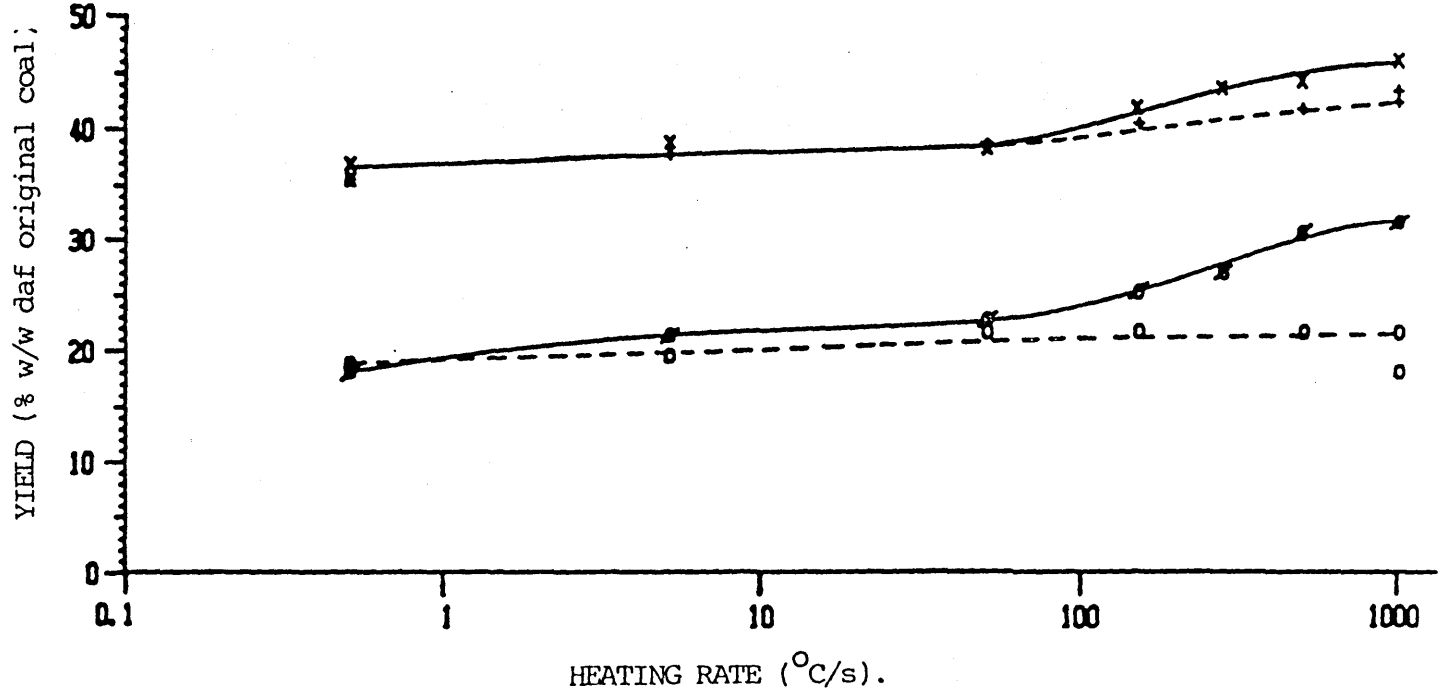
The implication of this finding, in conjunction with results presented previously in this section, is that the chloroform extractable material plays an important role in tar formation at high heating rates for coals of all rank, and appears to be responsible for the effect of increases of heating rate in enhancing tar yields.

The following subsections consider firstly the nature of chloroform extractable material, secondly suggests some possible mechanisms for the action of the chloroform extractables in coal flash pyrolysis, and lastly discuss the role of the chloroform extractables in catalytic flash pyrolysis.

7.4.3.2 THE STRUCTURE OF THE CHLOROFORM EXTRACTABLE MATERIAL

Previous studies examining the effect of material extracted by a variety of solvents on coking and

Figure 7.18 Tar and total volatiles yield as a function of heating rate for the pyrolysis of untreated and 25 hour chloroform extracted Linby coal in a wire mesh apparatus. Samples heated to 700°C with a 30 second hold at peak temperature. Untreated coal: tar (ø), total volatiles(x)Chloroform extracted coal: tar (o), total volatiles (+).



liquefaction properties have come to differing conclusions about the chemical nature of the extracts and the role they play. Several workers have hypothesised that the extractables may play a hydrogen donating role (Brown and Waters, 1966a; 1966b; Neaval, 1982) while others have questioned whether the extractable material possesses any hydrogen donating ability (Ouchi and co-workers, 1983; Chen and co-workers, 1985). Larsen and co-workers (1980) have suggested that the extractable material may play a hydrogen shuttling role in addition to one as a hydrogen donor, while Grint and co-workers (1985) hypothesises a combination of hydrogen shuttling and a physical solvating effect.

The above conclusions were reached for different coals from a variety of geographic origins, extracted to differing extents with a range of solvents. In order to assess the role of the low molecular weight material, and possibly extend the above theories to the role of extractable material in flash pyrolysis, detailed knowledge of the structure of the chloroform extracts is required.

The extracts of Linby coal and Can lignite were divided into pentane soluble and pentane insoluble fractions. The pentane solubles from each were further separated on a silica gel column (see Appendix I), into five fractions which were analysed by GC-mass spectrometry. The pentane insolubles, and samples of the whole

extracts were analysed by the same methods employed for the extracts from Taff Merthyr and Cortonwood Silkstone, ie. by ^{1}H-NMR spectroscopy and elemental analysis. In addition, samples of the extracts from Canakkale Can, Linby and Cortonwood Silkstone were analysed by size exclusion chromatography (SEC), to provide information about the molecular weight distribution. The results from these analyses are shown in Tables 7.13, 7.14 and 7.15.

Table 7.13 Results from ^{1}H-NMR and elemental analyses of of chloroform extracts.

Structural	Can		Linby		C´wood[a]	Taff
parameter	Asph[b]	T.E[c]	Asph[b]	T.E[c]		
H_{ar}[d]	vjg6	7.7	28.2	21.9	25.2	28.9
C	n.d[g]		81.2	82.5	84.3	86.5
H	n.d[g]		6.3	7.4	7.7	8.0
H/C[e]	n.d[g]		0.93	1.08	1.14	1.11
f_a[f]	n.d[g]		70.7	61.9	61.2	63.6

a - C´wood - Cortonwood Silkstone
b - Asph - n-pentane insoluble fraction
c - T.E - analysis of total extract
d - H_{ar} - hydrogen aromaticity
e - H/C - hydrogen to carbon atomic ratio
f - f_a - carbon aromaticity
g - n.d - not determined

Table 7.14 Results of size exclusion chromatography of coal extracts. Molecular weight distribution as a % of the whole extract.

Mol. Wt. Range	Can	Linby	Cortonwood
0-500	26.7	49.1	62.6
500-1000	18.6	23.2	16.1
1000-1500	10.9	10.7	8.3
1500-2000	8.5	6.5	5.2
>2000	35.3	10.5	7.1
Mol. Wt[a]	637	397	283

a - Number averaged mean molecular weight

From these analyses we see that the extract from the Can is quite different from the extracts from the hard coal. It is highly aliphatic and has a very high molecular weight range, suggesting that some colloidal material may be present. The presence of such material in coal extracts has been reported by Hombach (1982). The aromaticity of the extracts increases with carbon content, though the extract from Taff Merthyr contains a substantial amount of aliphatic material.

The GC-mass spectrometry analysis of the pentane soluble fraction of the Can and Linby extracts provides a substantial amount of information about the type of structures present in the fraction analysed.

Table 7.15 GC-MS results for the n-pentane soluble fraction from the chloroform extract from Linby and Canakkale Can

Sub-fraction[a]	Component	Linby Extract		Can Extract	
		% of subfraction	% of coal	% of subfraction	% of lignite
1	Alkanes	67	0.07	15%	0.03
	Terpenes, alkenes and cycloalkanes	33	0.03	85%	0.14
2	Light aliphatic polars	100	0.01	100%	0.05
3	Alkyl tetralins	20	0.006	80%[b]	0.06[b]
	Light polars	80	0.024	20%[b]	0.02[b]
4	Light hydroaromatics	45	0.03		
	Substituted naphthalenes and fluorenes	55	0.04		
5	Large substituted aromatics	65	0.36	20%	0.08
	Hydropyrenes	25	0.14	65%	0.27
	Complex polars	10	0.05	15%	0.06

a - Subfraction chromatographically separated according to the procedure described in Appendix I.

b - Subfractions 3 and 4 from Can were combined due to their small sizes.

It is probable that similar groups are present in the pentane insoluble fraction in more polar or larger units. Substantially more hydroaromatic material is present in the lignite fractions than in the Linby. However the Linby does contain more aromatic material including a small amount of pyrene and related compounds, which are known as good hydrogen shuttling species. The Linby extract also contains a small amount of hydropyrenes, which are known as hydrogen donors.

As an aside, the paraffinic fraction (subfraction 1) from the lignite contains a much proportion of cyclo-alkanes and similar compound such as terpenes, whereas subfraction 1 from Linby contains predominantly straight chain and branched alkanes. This is evidence of the different origins and different extents of coalification of Can and Linby.

7.4.3.3. THE MECHANISM OF THE ACTION OF CHLOROFORM EXTRACTABLE MATERIAL IN FLASH PYROLYSIS

The mechanisms invoked to explain the effect of extractable material on coking properties and liquefaction behaviour are hydrogen donation, hydrogen shuttling, and physical solvating effects resulting in increased free radical stability (Brown and Waters, 1966a; 1966b; Larsen and co-workers, 1980; Neaval, 1982; Ouchi and co-workers, 1983; Chen and co-workers, 1985; Grint and co-workers, 1985). It is probable that all of these mechanisms contribute to the overall effect of the

extractable material.

The extent of each process is likely to depend on the rank of the substrate. Hydrogen donation will occur when there is a high concentration of hydroaromatics such as tetralin or dihydropyrene and like structures. Hydrogen shuttling is likely to occur in the presence of high concentrations of polynuclear hydrocarbons (eg. Pyrenes) and phenols (Snape, 1986). When many hydrogen donor groups have donated their hydrogen, they revert to being hydrogen shuttler groups. Smaller aromatics, such as naphthalene, are likely to play a physical solvating role, as the aromatic cluster is insufficiently large to act as hydrogen shuttlers (Snape, 1986). The overall net effect of the solvating role is the same as the hydrogen shuttling role. In the former process, the radical is stabilised by a molecule from the extractable material, until a capping hydrogen atom is available. In the latter, a capping hydrogen atom is transferred to the free radical by the molecule from the extractable material.

In the flash pyrolysis of Can, there is a high concentration of hydroaromatic in the extractable material. Hydrogen donation appears to be the mechanism which is likely to predominate in this case, with the other mechanisms playing secondary roles. In the case Linby, the physical solvating effect is likely to play the dominant role as the concentration of hydroaromatics is low, and the size of aromatic clusters is small (2-3

rings). For the Cortonwood and Taff, the aromatic cluster size is larger suggesting that hydrogen shuttling is likely to play a greater role.

The effect of the chloroform extractables on pyrolysis behaviour is substantial compared to the amount of material actually removed. This suggests that they may merely play an initiating role, where volatile molecules formed in the pyrolysis become available to play a similar role to the extractable material. If this was the case, then an increase in the heating rate in the pyrolysis of the extracted coal would be expected to produce a smaller increase in the tar yield, as the tar formed would be present to play the same role as in the pyrolysis of the untreated coal. However, although slow pyrolysis of extracted Linby produces a substantial amount of tar, increases of heating rate have no effect on the tar yield. This suggests that the mechanism which results in the rise of the tar yield with increases in heating rate, occurs solely as a result of the presence of the extractable material.

7.4.3.4 THE MECHANISM OF THE ACTION OF THE EXTRACTABLE MATERIAL IN CATALYTIC FLASH PYROLYSIS

The effect of impregnation with zinc chloride on the flash pyrolysis behaviour of chloroform extracted Linby coal is to cause the tar yield to diminish, which is contrary to the effect on untreated Linby, where the tar yield is enhanced by the presence of $ZnCl_2$. This implies

that the zinc chloride uses the extractable low molecular weight material as an intermediate, whose role is critical to the apparent hydrogenating ability of the catalyst under flash pyrolysis conditions.

In the following hypothesis, the nature of this intermediary role is a combination of two observed effects. Firstly, the role of the extractables in the flash pyrolysis of untreated coal, and secondly, the role of the catalyst in the flash pyrolysis of unextracted coal.

The mechanism by which zinc chloride acts in coal hydrogenation was investigated by Bell and co-workers (Mobley and Bell, 1979; 1980; Taylor and Bell, 1980; Bell and co-workers, 1981) in studies of the hydrocracking of model compounds. Bell proposed Friedel-Crafts based reactions to explain the action of the catalyst. The mechanism shown in Figure 7.19 is an extension of those proposed by Bell and co-workers, adapted to explain tar formation in coal pyrolysis. The four principle steps in the mechanism are as follows:

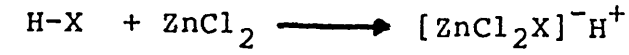
(1) Adduct formation

(2) Protonation

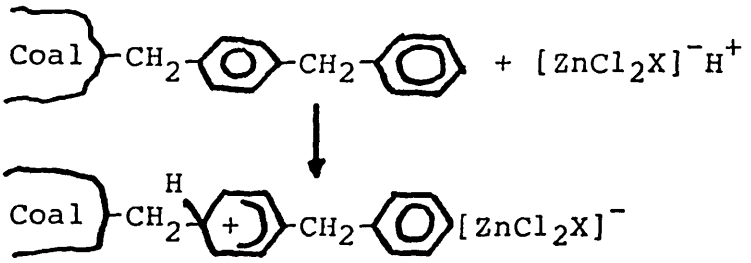
(3) Heterolytic bond scission

(4) Hydride abstraction

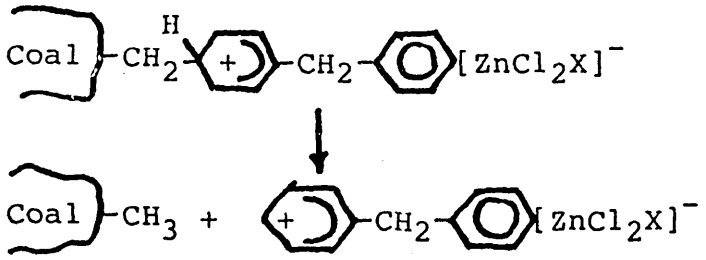
STEP 1 Adduct formation



STEP 2 Protonation



STEP 3 Heterolytic bond scission



STEP 4 Hydride abstraction

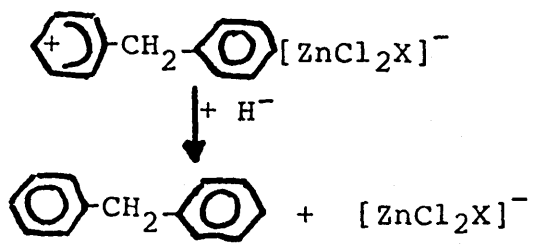


Figure 7.19 Proposed mechanism for the action of zinc chloride in promoting tar formation in flash pyrolysis. Diphenyl methane molecule represents tar.

Within this mechanism the low molecular weight extractable material may play any or all of a number of roles:

a) It forms the adduct with the zinc chloride (step (1)) and hence act as the source of the proton in step (2)

b) It could be the source of the hydride ion which is abstracted (step (4)) stabilising the carbonium ion formed by bond scission (step (3))

c) It could play a physical, solvating role acting to stabilise the carbonium ion.

The proposed carbonium ion mechanisms for the action of zinc chloride and other Lewis acids in catalysed hydrogenation and carbonisation has been questioned by studies of the effect of Lewis acids on ESR spin densities (Sakawa and co-workers, 1983; Yokono and co-workers, 1985a; 1985b), which suggest that the presence of the catalysts affects free-radical concentrations. It is possible to invoke radical ions as a means to explain this phenomenon, and utilise Friedel-Crafts chemistry to explain the action of the catalyst. Such radical ions may be formed in the zinc chloride catalysed hydrocracking of pyrolytically formed free radicals, or the pyrolytic cracking of carbonium ions formed by the attack of zinc chloride on the coal structure. Other mechanisms for the formation of such species involve the transfer of electrons.

In order to include the possibility of the formation of radical ions, the mechanisms shown above must be

modified. A proposal for such a mechanism is shown in Figure 7.19. The principal steps in this mechanism are as follows:

(1) Radical formation

(2) Adduct formation

(3) Protonation

(4) Heterolytic bond scission

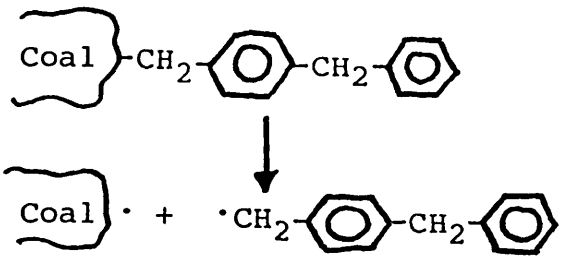
(5) Hydride abstraction

(6) Hydrogen atom transfer to free radicals.

This mechanism is the catalytic action of the catalyst superimposed on a conventional pyrolysis mechanism. As such the location of steps (1) and (6) in the mechanism are not fixed. The action of the extractable material in this mechanism may involve any of the stages discussed above, or may involve the hydrogen donation type mechanism discussed in section 7.4.3.2. The extractable material may fulfil both roles simultaneously, which may involve them acting as radical anions in the event of step (6) preceding step (5).

The importance of the interaction between the zinc chloride and the extractable material in the action of the catalyst suggests reasons why the action of the catalyst is different in the case of Canakkale Can. Although the extractable material from the Can contains substantial amounts of donatable hydrogen, the extracts are highly aliphatic, with presumably a small number of aromatic rings per cluster (1-2), and a low degree of condensation. This would make them less able to

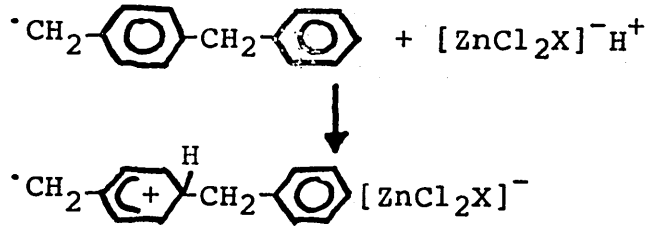
STEP 1 Radical formation



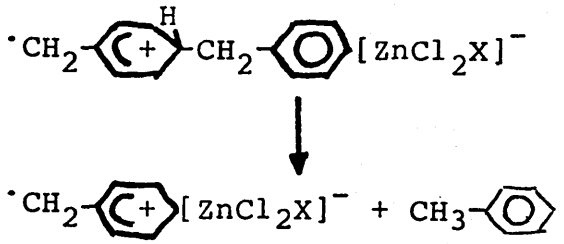
STEP 2 Adduct formation



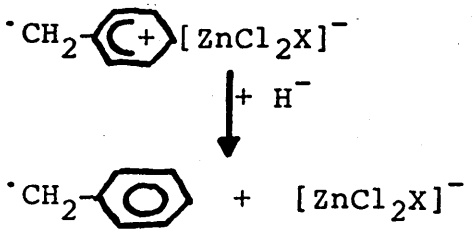
STEP 3 Protonation



STEP 4 Heterolytic bond scission



STEP 5 Hydride abstraction



STEP 6 Hydrogen transfer

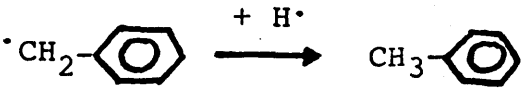


Figure 7.20 Proposed radical ion mechanism for the action of zinc chloride in promoting tar formation in flash pyrolysis. toluene molecules represents tar.

stabilise carbonium ions or radical cations or anions in their structure. In addition, the nature of the extracts gives indications about the structure of the lignite macromolecule. Presumably the low aromaticity of the lignite structure, and hence of pyrolytically formed fragments, would also make carbonium ions and radical cations much less stable than in the bituminous coals. This effect would reduce the ability of the zinc chloride to hydrogenate and hydrocrack the volatiles formed, and make the catalyst more likely to promote condensation reactions, as is observed.

CHAPTER 8 HIGH PRESSURE PYROLYSIS EXPERIMENTS

8.1 BACKGROUND

As discussed in Chapter 3, the effect of a high pressure gas atmosphere on pyrolysis is not well understood, particularly when that gas is hydrogen. The objective of this study on pyrolysis at high pressure was to perform experiments where the parameters affecting the product yields were well defined, and where possible variable over a wide range. The parameters of particular interest were the nature, reactivity and pressure of the ambient gas, heating rate, gas flowrates and vapour residence times, and peak temperature. Additionally it was necessary to be able to collect sufficient tar for detailed analysis.

It was impossible to incorporate all these criteria into a single reactor design. In order to be able to accurately determine heating rate, solid and vapour residence times, a fixed bed type reactor was required. In a fixed bed reactor, the maximum heating rate which can be achieved is limited due to the low thermal conductivity of coal. Therefore in the pyrolysis of large samples of coals (eg. 20g), the heating rate is limited to lower values ($<5^{o}C/s$). Conversely to achieve high heating rates ($1000^{o}C/s$), coals samples are necessarily small (10-20 mg). In order to design a fixed bed reactor in which heating rates greater than $100^{o}C/s$ could be achieved, the size of coal sample used would

be too small to produce sufficient tar for analysis.

The reactor which was designed and used for this project did not therefore fulfil all the criteria specified for it. The type of reactor which it was decided to construct was a "hot-rod" type reactor, of the sort originally used by Hiteshue and co-workers (1957) and more recently by the NCB (Finn and co-workers, 1980). In this reactor system, a sample of coal is held in place within a piece of tubing which acts as the pressure vessel and also as the resistance heater. These types of reactor have been used for the pyrolysis of coal at pressures up to 410 bar, and at temperature up to 900°C. The heating rates which have been used have been up to, and greater than 100°C/s, though the effective heating rate of the coal sample will be discussed later. The size of coal samples pyrolysed has been up to 10 g.

The design of the reactor and the experimental procedure adopted will be described below.

8.2 DESIGN OF THE HIGH PRESSURE PYROLYSIS SYSTEM

8.2.1 INITIAL DESIGN

The design of the hot-rod reactor had the following requirements in terms of performance:

Heating rate range --------- 5°C/min to 100°C/s

Maximum pressure ---------- 150 bar

Maximum temperature -------- 800°C

Coal capacity ---------- 1 gram

Minimum Gas Residence Time - 1.5 s

These requirements were incorporated into the initial design, though it was not possible to achieve some of them in the performance of the hot-rod. The reasons for this are discussed in section 8.5, and in the results section.

The overall initial design for the high pressure pyrolysis system is shown in Figure 8.1. Gas is supplied from a cylinder to a compressor, where the pressure is boosted to the required value. The gas pressure and flowrate are monitored before the gas passes through the reactor. Volatiles produced are collected in the condenser. The gas pressure is controlled by the let-down valve, while the flowrate is controlled by a mass flow controller upstream of the reactor. The reactor, condenser and gas circuit are described in more detail in the following sections.

8.2.2 MATERIALS OF CONSTRUCTION

Previous workers designing "hot-rod" reactors have used austenitic stainless steels for the heated section. Types 304 and 316 stainless steels have been widely used, due to their comparatively high strength at high temperature, their resistance to corrosion, and their non-vulnerability to embrittlement by high pressure hydrogen. However, Hiteshue and co-workers (1957)

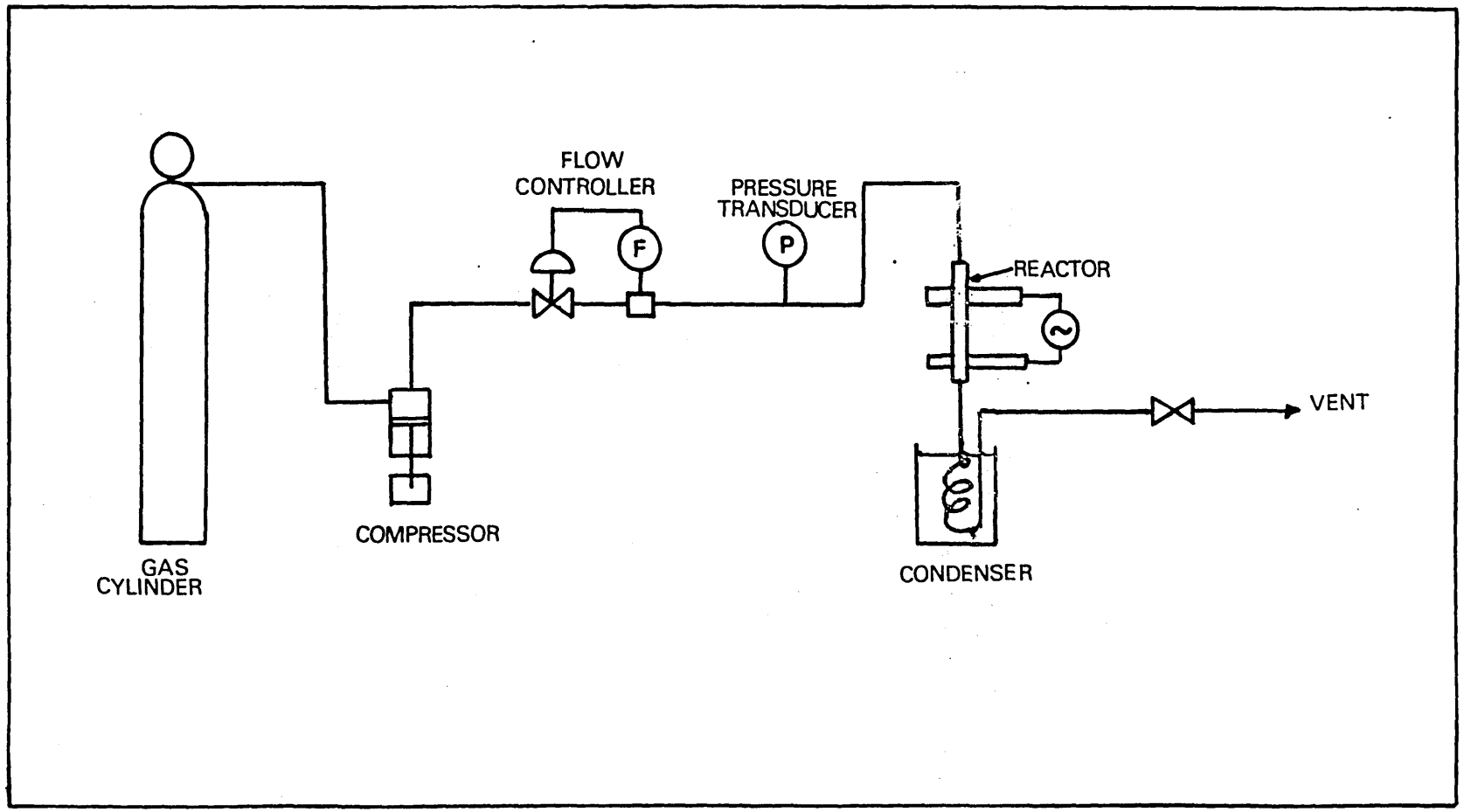


Figure 8.1 Preliminary design for high pressure pyrolysis apparatus.

demonstrated that such materials are liable to undergo creep at high temperatures (>500^{o}C) and therefore have a finite lifetime prior to rupture. To counter the possibility of rupture, workers have performed isolated high pressure pyrolysis experiments in safety cells, usually positioned in a separate room. This makes experimental operation and control more difficult. Additionally reactors were disposable with a finite lifetime.

It was decided in this design of a "hot-rod" to use a higher strength nickel alloy to act as the heated pressure vessel. Nimonic 80A (from Wiggin Alloys) was chosen because of its exceptionally high strength at high temperature. Figure 8.2 shows yield stress versus temperature for the Nimonic and for type 316 stainless steel. As can be seen, the tensile strength of Nimonic 80A at 800^{o}C is 400 MN/m^{2} , which is twice that of type 316 stainless steel at 25^{o}C. Similar improvements in the resistance to creep are also observed. Nimonic also shows a greater resistance to corrosion than stainless steels. Corrosion is particularly likely to result from the presence of Lewis acid catalysts, such as $ZnCl_2$. These may degrade during pyrolysis releasing hydrogen chloride which is also very corrosive.

Prior to machining the Nimonic was heat treated at 1080^{o}C for eight hours to render it in its "solution treated" state, which is the softest form of Nimonic 80A. After the vessel had been fabricated, the Nimonic

was "age hardened" at 750°C for 16 hours which produces the maximum strength of Nimonic.

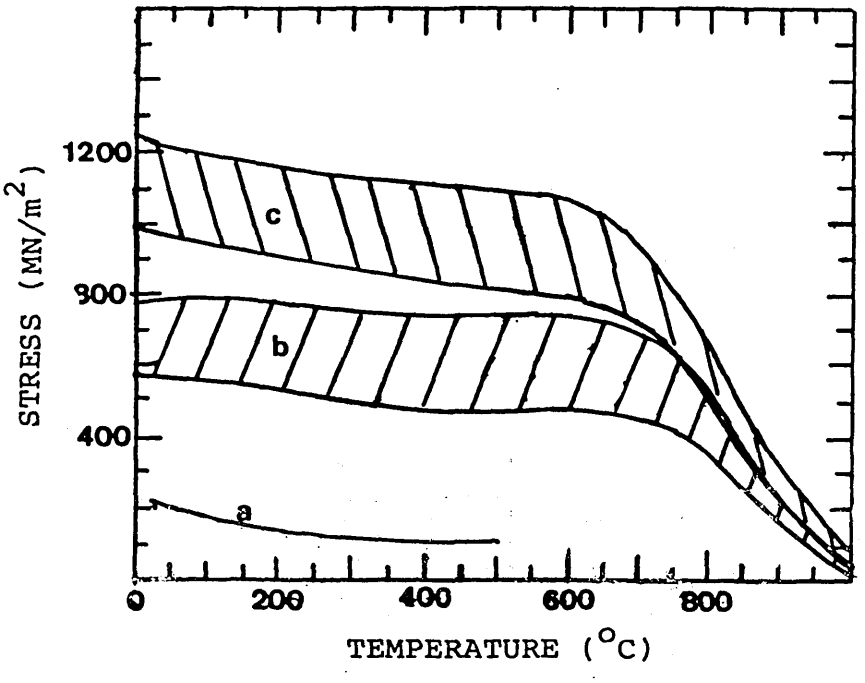


Figure 8.2 Diagram showing the relative strength of Nimonic 80A and type 316 stainless steel: a - 0.2% yield stress for type 316 stainless steel (BS 1503, 1969); b - 0.2% yield stress for Nimonic 80A; c - Ultimate tensile strength for Nimonic 80A (Wiggin Alloys, 1982).

8.2.3 DESIGN OF THE REACTOR

Figure 8.3 presents a diagram of the pyrolysis reactor. The reactor is 240 mm long tube of Nimonic 80A with an internal diameter of 6 mm. Except at either end, the outside diameter is 10 mm. Using the yield strength and ultimate tensile strength measured by Wiggin Alloys (see Fig. 8.2), together with the formulae given in The High Pressure Safety Code (1977), at 800°C, the yield pressure of the reactor is 1200 bar, while the bursting pressure is 2500 bar.

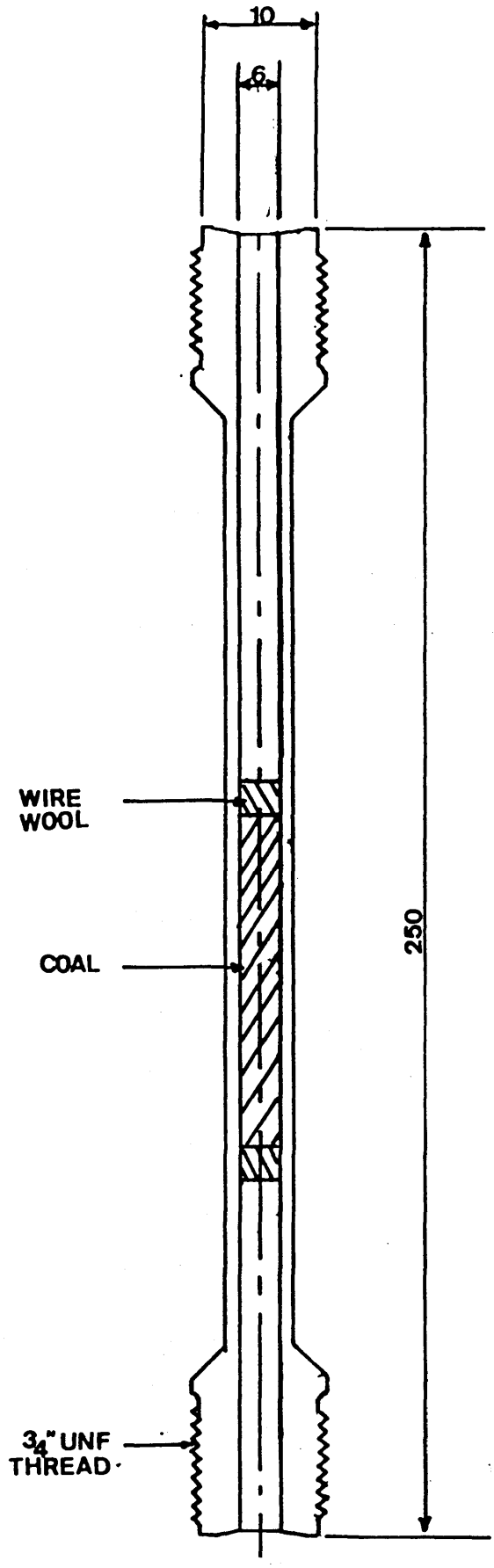


Figure 8.3 Diagram of hot-rod reactor.

all dimensions in mm

The maximum desired working pressure is 150 bar, giving a safety factor of 8 on the yield pressure. The expanded diameter sections at either end correspond with the diameters of the inlet and outlet tubes, which are extended at the end to hold the fixing nut in place.

The seals at either end (see Figure 8.4a) were designed to take account of temperature changes during their operation and the resulting thermal expansion. The seals are of a "Lens-Ring" type where the actual seal is provided at the junction between the inner edge of the ring and the surfaces above and below. Thermal expansion should be constant throughout as all the components are constructed from the same material, though the ring is free to expand outwards to take account of differential expansion without losing the seal.

Electrical connection for the power supply are milled from copper blocks. The blocks are split into two, with a 10 mm diameter semi-circular hole cut in each half. The two halves of the blocks are bolted together around the tube to ensure good electrical contact.

The coal is held in place within the "hot-rod" by small (5 mm) steel wire wool plugs. Although iron is known to catalyse hydrogenation reactions under the conditions present in the reactor, the effect has been neglected in this case due to the short residence time of volatiles in the wire wool.

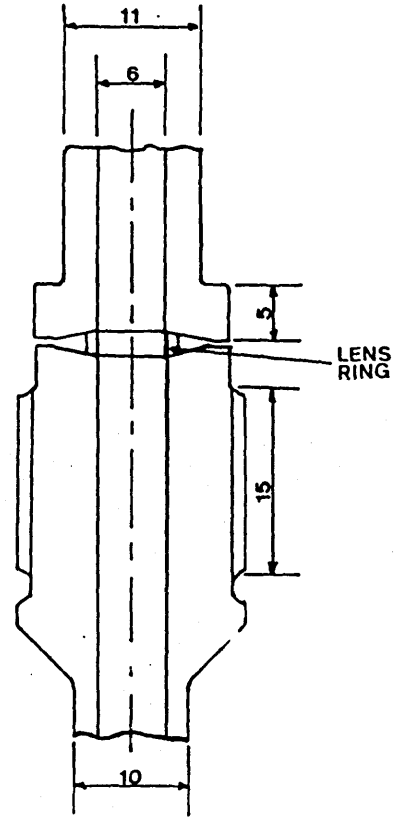


FIG 8.4A

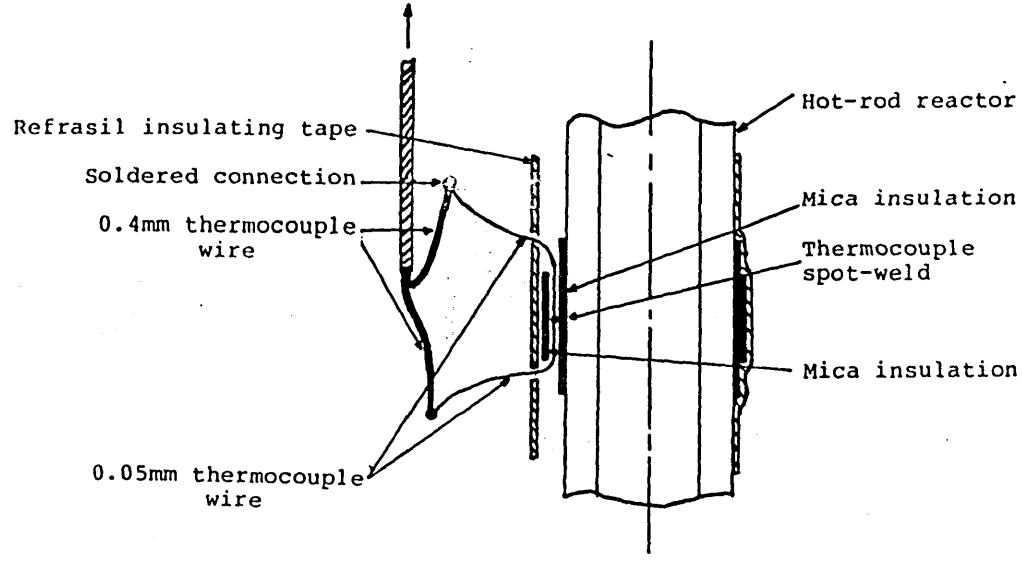


FIG 8.4B

Figure 8.4 Diagram showing (a) Lens ring seal for hot-rod reactor, (b) thermocouple fixing method.

all dimensions in mm

The plug above the coal mass acts to pre-heat the gas stream. Gas flows through the coal in a downwards direction, though this can be reversed if desired.

The temperature of the "hot-rod" during pyrolysis is measured externally using two type K thermocouples. The fixing method used for the thermocouples is shown in figure 8.4b. The thermocouples are formed from 2/1000" (0.05 mm) chromel and alumel wire, spot welded together. The thermocouple is electrically insulated from the "hot-rod" by a layer mica. The mica used is natural phlogopite or amber mica, and was chosen for its resistance to high temperature. It was obtained from East London Mica Ltd. and was split into thin flexible sheets prior to use. The thermocouples are held in position by being wrapped in a further strip of mica, which is in turn held in position by Refrasil high temperature tape. The 2/1000" thermocouple wire is soldered to more robust thermocouple cable, which carries the signal to a microcomputer. The power supply, and temperature ramping and control will be described in a later section.

8.2.4 INLET AND OUTLET CONNECTIONS

The "hot-rod" assembled with its inlet and outlet connections is shown in Figure 8.5a. Both the inlet and outlet connections, including part of the condenser are made from Nimonic 80A alloy. This is to prevent any thermal expansions effects if these sections heat up.

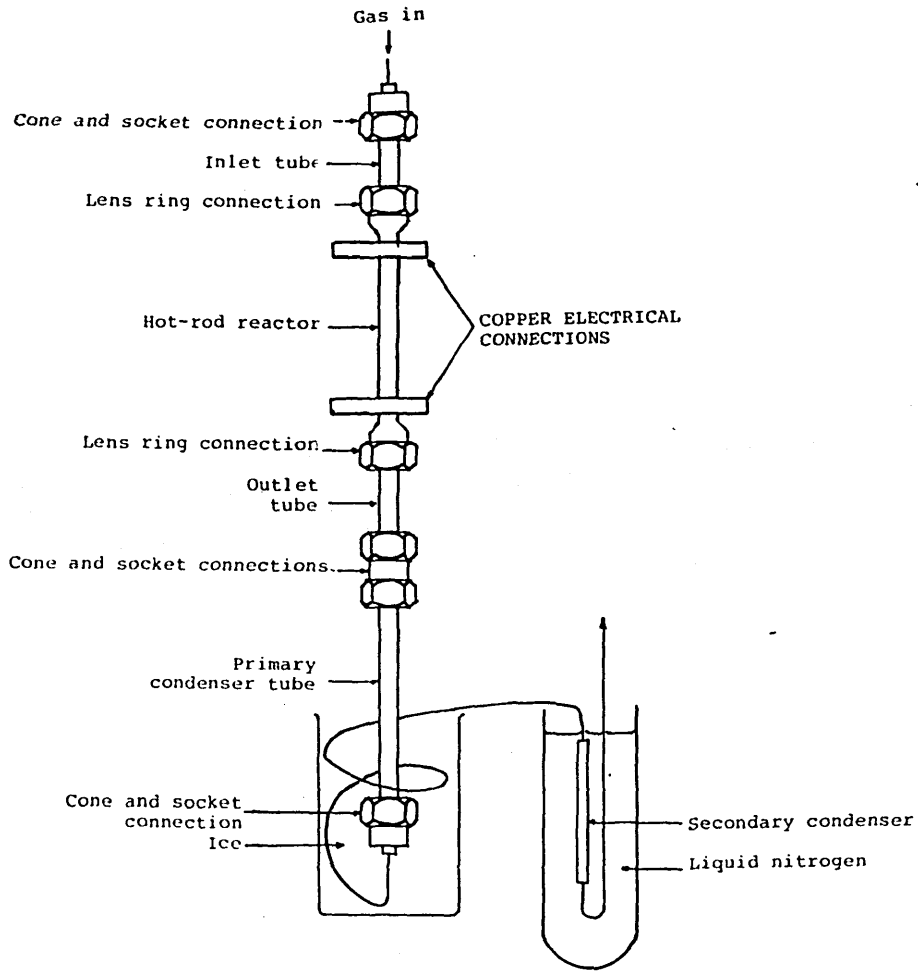


Fig 8.5a

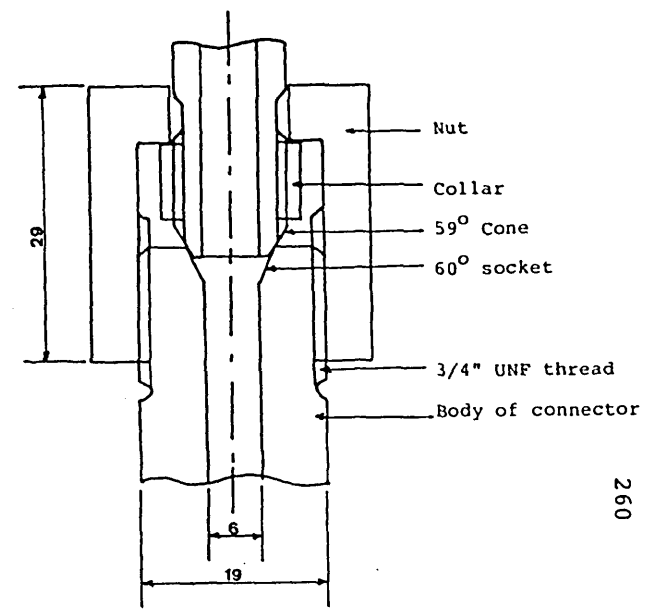


Fig 8.5b

Figure 8.5 (a) Assembled hot-rodd reactor sysem; (b) cone and socket connector

The gas inlet connection is from a 1/8" Swagelok into a 1/8" NPT male tapered thread fitting, which seals into a female thread machined on the gas inlet connector. On the downstream side of this is a "cone and socket" type connection, where a 59^{o} cone is cut on the end of the inlet tube which seals on a 60^{o} socket machined into the inlet connector (see Figure 8.5b). The two components are held together by a nut which screws onto the connector. The force is transmitted from the nut to the tube via a collar which is screwed onto the tube on a left handed thread.

The inlet tube is connected to the "hot-rod" by a lens-ring type seal. This is shown in Figure 8.3 and is described in the previous section. An identical connection seals the outlet tube to the "hot-rod". The short outlet tube is connected to the condenser by the union connector which has cone and socket connections at either end.

The condenser will be described in more detail in the following section, though the connection between the small diameter tubing and the large diameter nimonic is identical to that on the inlet connector.

8.2.5 DESIGN OF CONDENSERS

Figure 8.6 presents a diagram of the condensers. Two stage condensing is used in this apparatus for two reasons: to ensure that all the tar which is produced is

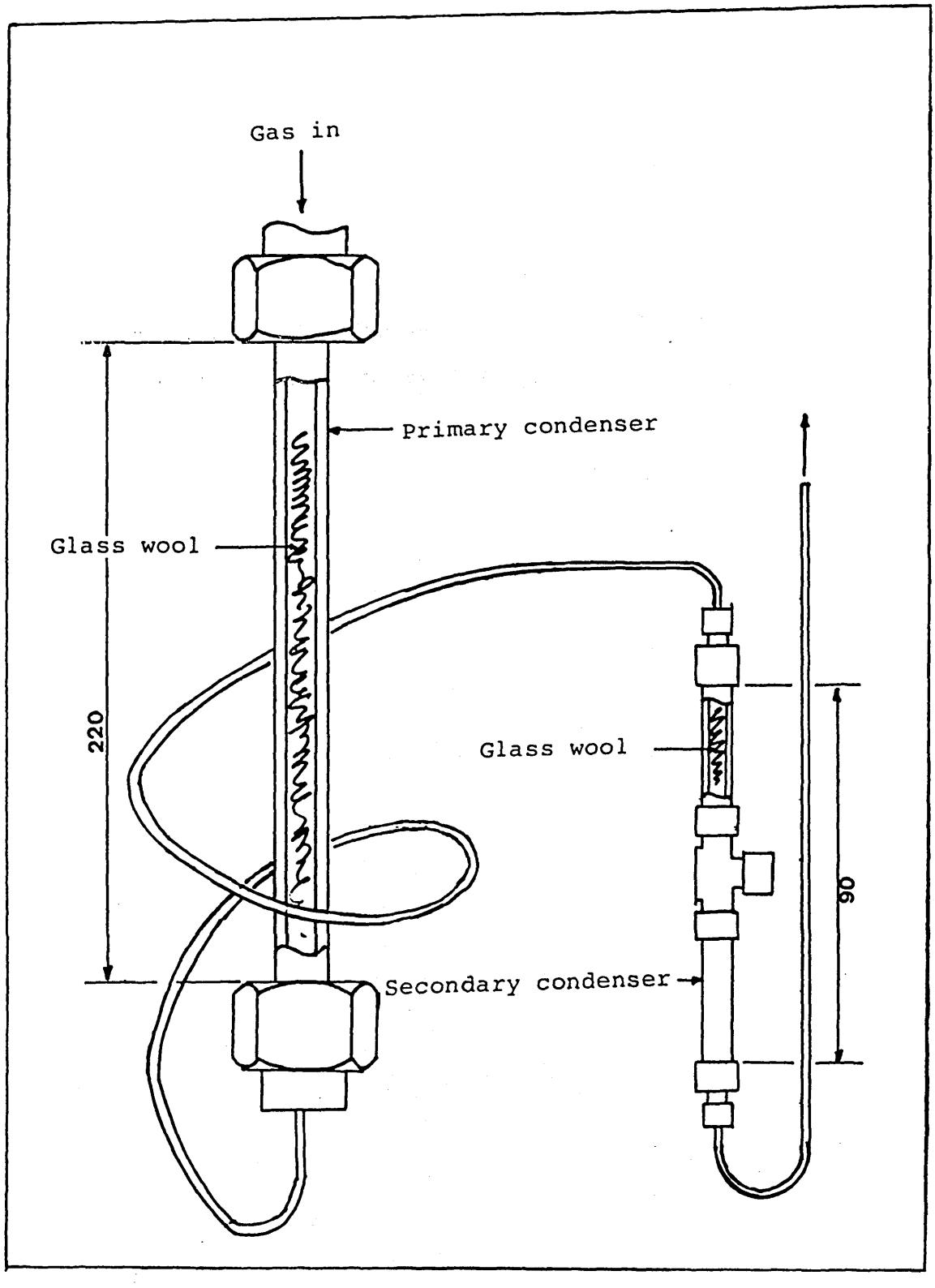


Figure 8.6 Diagram of the condensers for the hot-rod reactor.

all dimensions in mm

trapped, and to prevent blockages by condensing too much material in a narrow diameter pipe. Tests using a third condenser collected no further tar, showing that the two traps efficiently collected all the tar produced.

The primary condenser traps the majority of the tar. It is cooled in an ice/water bath. It consists of a 200 mm long, large diameter tube (6 mm ID, 10 mm OD) formed from Nimonic alloy, which is followed by a 600 mm long coil of smaller diameter (1/8", 3.175 mm OD, 69/1000",1.753 mm ID) type 316 stainless steel tubing. The large diameter pipe is loosely packed with glasswool, as is the large diameter section of the connector. Much of the tar accumulates at this latter location. Most of the water formed in the pyrolysis collects on this glass wool.

The secondary condenser is cooled by liquid nitrogen. Any tar which passes through the first trap is caught in this, along with some gases which condense out, for example hydrogen sulphide. The trap consists of two short lengths (30 mm) of 1/4" (6.35 mm) OD, 3/32" (2.38 mm) ID type 316 stainless steel. These are loosely packed with glasswool and are held together by a Swagelok 3-way Union connector, with a blank nut sealing one hole. The connections at either end were made by Swagelok 1/4" to 1/8" Reducing Unions.

8.3 POWER SUPPLY AND CONTROL

The electrical power for the hot-rod reactor is supplied from a high output current transformer. The input supply to the transformer is upto 240-50 volts with a maximum current of 13 amps, while its output is 2.5 volts providing up to 1000 amps.

Temperature logging and power control is performed by a Newbrain model A microcomputer together with an MFI 1010 intelligent data logger (manufactured by C.I.L) which is linked to the Newbrain by an RS 232 interface.

The signals from the thermocouples attached to the hot-rod are logged directly by the MFI 1010, using the built-in cold junction compensation and linearisation. Interference on the thermocouple signals is reduced by the integration routine built into the logger. One of the 0-5 volt output signals from the MFI 1010 is used as the control signal, operating a proprietary thyristor firing circuit. This in turn controls two high current thyristors which are located on the input to the transformer, and hence control the power supplied to the hot-rod.

The algorithm used in the control program utilises proportional and integral control. The control algorithm was tuned by trial and error. The control program, which is run on the Newbrain, updates the power signal, which is sent by the MFI 1010, once per second, timing being

provided from the logger. The temperature of the hot-rod is plotted in real time on the screen of the Newbrain to facilitate monitoring of the experiment.

Table 8.1 Typical values for the control and experimental parameters used in the hot-rod control progam

Control Parameters	
Heating rate	5°C/s
Peak temperature	485°C
Hold time	200 s
Experimental Parameters	
Offset for ramp cut-off	28°C
Initial power for ramp[a]	2.05 volts
Initial power for hold[a]	1.5 volts

a - the value given is the voltage sent from the logger to the control circuitry.

In order to achieve the best time-temperature profile, ie. a linear ramp followed by a sharp tranformation into an isothermal hold, a number of control parameters are set in the control program, prior to each experiment, these being the initial power set for the ramp, the initial power set for the isothermal hold and the number of °C below the peak temperature at which the power is

cut to that required in the hold. The optimum values for these control parameters vary depending on the experimental parameters set, these being: the heating rate and the peak temperature. A typical set of values for the control and experimental parameters is given in Table 8.1.

8.4 DESIGN OF HIGH PRESSURE GAS CIRCUIT

The objectives in the design of the gas circuit were as follows:

(i) To be able to maintain and measure a specified stable gas pressure during pyrolysis.

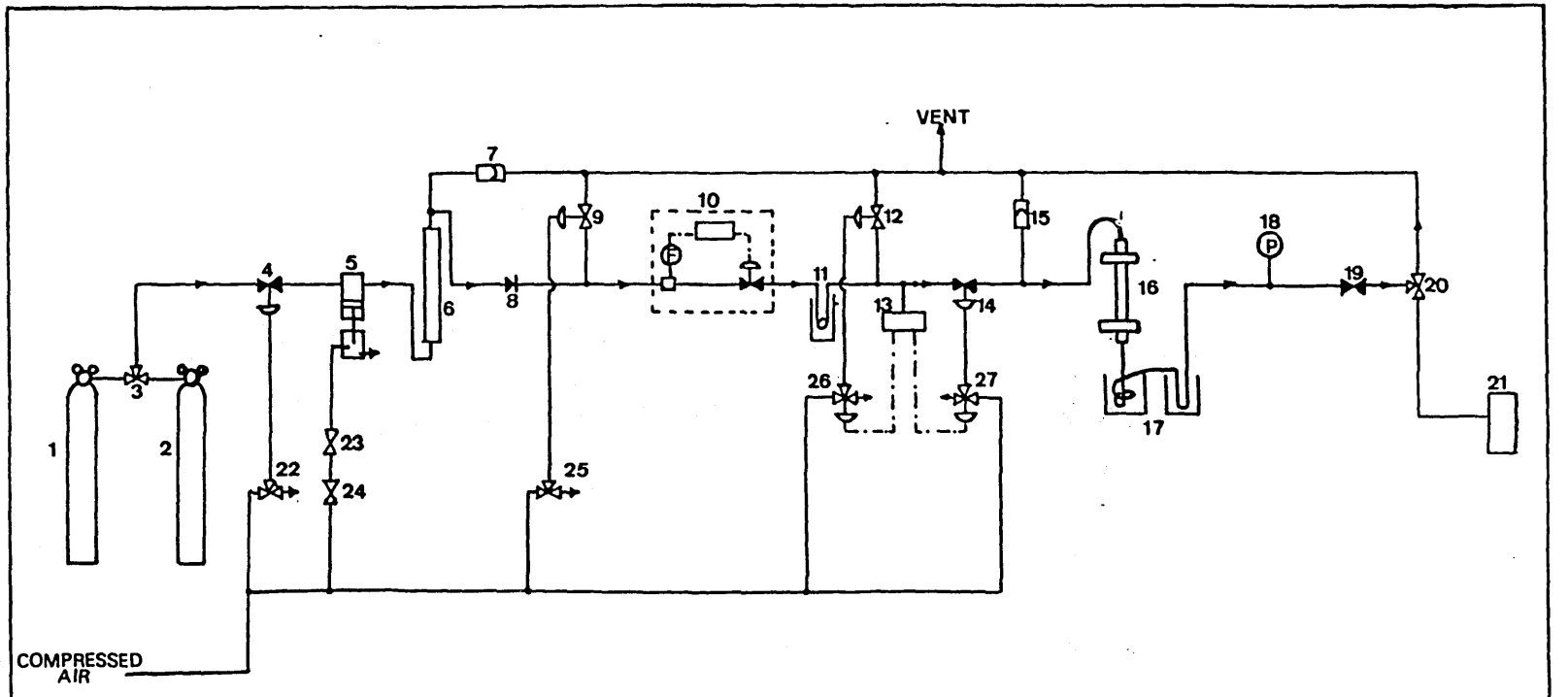
(ii) To be able to maintain and measure a specified stable gas flowrate during the pyrolysis.

(iii) To be able to operate safely in a laboratory environment within the specifications of The High Pressure Safety Code (1977).

A diagram of the gas circuit which was constructed is shown in Figure 8.7.

The maximum working pressure of the system is 150 bar. Gas is supplied at up to this pressure from cylinders (Nos.1 & 2 on diagram). In order to extend the life of gas cylinders, a compressor is installed (No.5). This a compressed-air driven gas booster, type AG-75 made by Haskel Energy Systems. The reciprocating nature of the output from the compressor is smoothed by the surge control volume (No.6), a (--) cc tank which was also

Figure 8.7 High pressure gas supply system for hot-rod reactor



1. Hydrogen cylinder
2. Helium cylinder
3. 3 way ball valve
4. Manual Gas shut-off valve
5. Air driven gas booster
6. Surge control volume
7. Bursting disc
8. One-way valve
9. Manual Gas vent valve
10. Flow controller
11. Water trap
12. Automatic gas vent valve
13. Pressure Transducer
14. Automatic shut-off valve
15. Bursting disc
16. Hot-rod reactor
17. Condenser
18. Pressure gauge
19. Let-down valve
20. 3 way valve
21. Gas collection bag
22. 3 way valve controls 4
23. Ball Valve
24. Flow control valve
25. 3 way valve controls 9
26. 3 way valve controls 12
27. 3 way valve controls 14

made by Haskel. The gas flowrate is monitored and controlled by the mass flowmeter (No.10) which was supplied by Brookes Instruments (Units 5810P,5835P and 5871). This unit can control flows up to 3 standard litres/minute (evaluated at atmospheric pressure and 25^{o}C) of hydrogen.

Pressure is monitored by the transducer (No. 13) which is an A-10, 0-3000 psi transducer, with a digital monitor E307-2, supplied by RDP Electronics. This is located sufficiently close to the reactor to be considered to be the reactor pressure. Pressure is controlled by the let-down needle valve (No.19), which is a 1656 G2Y metering valve from Hoke International.

The safety features are extensive in order to provide both manual and automatic flow shut-off and venting.

Automatic devices are provided to protect against an overpressure, and to take suitable action in the event of a reactor rupture. The primary protection is provided from the pressure transducer on which adjustable upper and lower alarm set points can be set. In the event of the pressure straying from between these limits during a run, due to an overpressure or rapid pressure-drop following reactor rupture, the electrical alarm circuit is closed. This is transmitted through a relay box to switch off the power to two Solenoid valves (Nos.27 & 28)supplied by Ivac Ltd (type D320A184). These valves control the compressed air supply to two fast acting

pneumatic valves (Nos 12 & 14) which were supplied by Autoclave Engineers (types 6V71 M4OL & 6V71 M4CL). The loss of power causes the the air pressure to these valves to be vented with the result that the valves act accordingly, the shut-off valve (No.14) shutting off the gas flow, and the relief valve (No.12) venting the high pressure gas upstream of the reactor.

As a back-up to the relief valves, two bursting disc assemblies are fitted to the system. One disc (No.15) immediately preceding the reactor (No. 16), the other disc (No.7) following immediately after the compressor (No.5) to protect the surge control volume (No.6). Both have inconel bursting discs rated at 220 bar fitted, as supplied by Autoclave Engineers. If the bursting disc on the surge control volume ruptures, then the one-way check valve (No.8) prevents the entire contents of the system being vented, and also protects devices upstream of the reactor from being contaminated by the hot effluent from the hot-rod.

Additionally two manual remotely operated pneumatically actuated ball valves (supplied by Hoke) are provided. One (No. 4) can shut off the gas supply at an early stage in the circuit, while the other (No.9) can vent the entire system when required.

8.5 LIMITATIONS OF THE HOT-ROD REACTOR

8.5.1 LIMITATIONS TO HEATING RATE

As has been reported in chapter 3, several of the workers who have previously used hot-rod type reactor have heated the tube at high heating rates up to 650°C/s (Graff and co-workers, 1976). Heating rates up to 100°C/s have been reported by several workers (Kershaw and Barrass, 1979; Stangeby and Sears, 1980). The heating rates which are reported are the heating rates of thermocouples attached on the exterior of the heated tubes, which do not necessarily record the temperature on the inside of the tube, nor do they take account of radial temperature profiles which may develop in the coal cylinder as a result of the use of high heating rates at the boundary.

To determine whether significant radial temperature profiles are likely to develop, and how these are affected by heating rate, a calculation of the heat transfer in the coal was performed. The mathematical expression used was taken from Carslaw and Jaeger (1957) and is given below in equation (8.1).

$$T(r) = K\left[t-\left(\frac{R^2-r^2}{4c}\right)\right] + \frac{2K}{Rc}\sum_{n=1}^{\infty}\frac{J_o(r\alpha_n)\, e^{-c\alpha_n^2 t}}{J_1(R\alpha_n)\,\alpha_n^3} \qquad (8.1)$$

T(r) is the temperature at radius r, R being the external radius of the coal plug. K is the linear

heating rate ($^{o}C/s$) and t is time. C is a constant defined in equation (8.2). C_p is the heat capacity for coal, estimated as 1300 J/Kg K, k is the thermal conductivity of coal estimated at 0.186 W/m^2 K, while p is its density measured as 860 kg/m^3.

$$c = k / (C_p.p) \qquad (8.2)$$

The terms $J_o(r\alpha_n)$ and $J_1(R\alpha_n)$ are the zeroth and first order Bessel functions of $r\alpha_n$ and $R\alpha_n$ respectively. α_n is the nth solution of the equation 8.3.

$$J_o(\alpha) = 0 \qquad (8.3)$$

The values used for α were those tabulated by Carslaw and Jaeger (1957).

In the evaluation of equation (8.1), the series were summed to the sixth term of alpha. Equation (8.1) assumes that the only mode of heat transfer is conduction and that the only source of heat is from the walls. The model therefore underestimates the heat transfer coefficient, and overestimates temperature profiles. However, the results it produces give a reasonable approximation as to the effect of heating rate on the radial temperature profile. The results of computed solutions of the equation at different heating rates are shown in Figure 8.8. The temperature shown, as a function of radius, is that achieved at the moment that the outside of the coal plug, ie. the wall, reaches

the peak temperature.

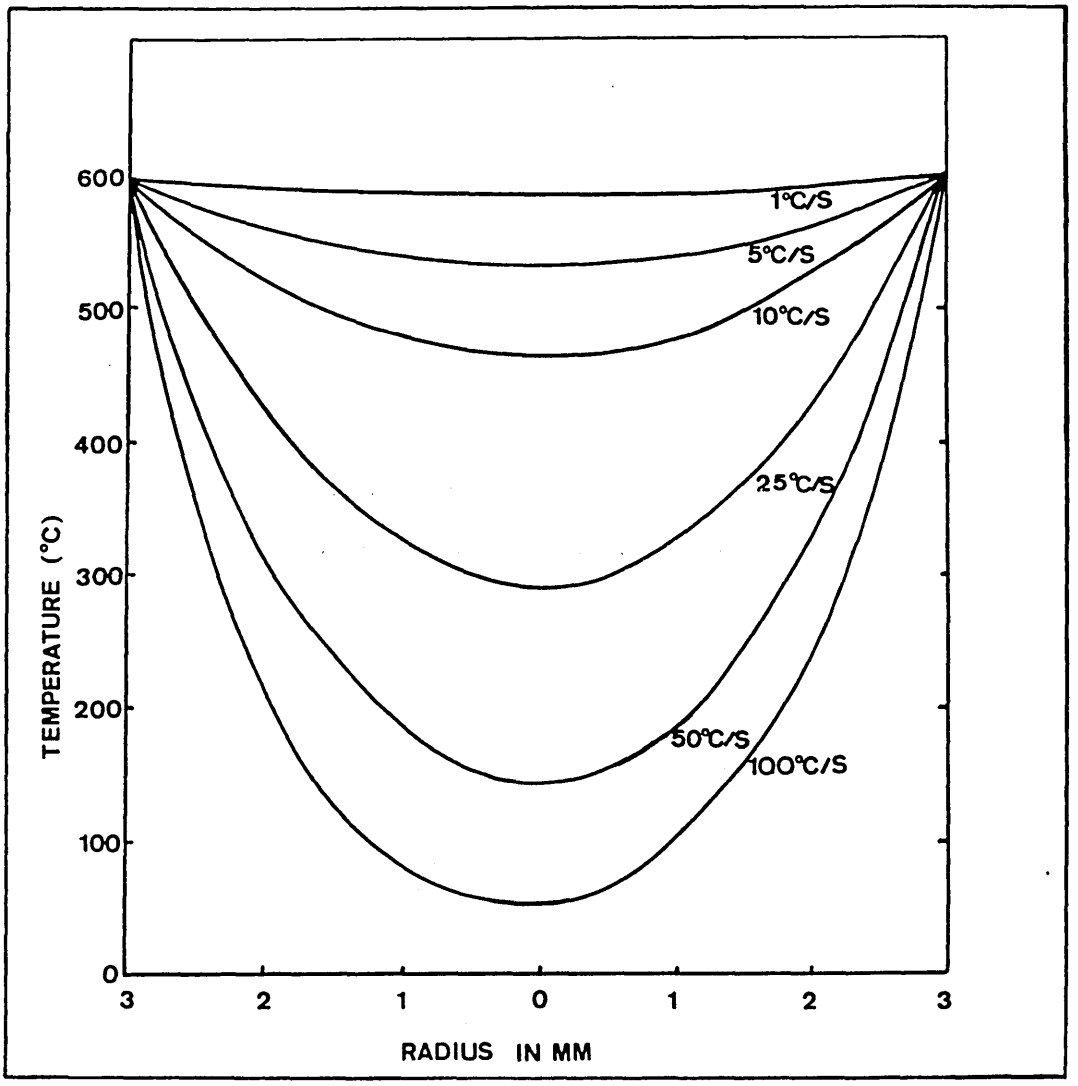


Figure 8.8 Solutions of equation 8.1 showing calculated radial temperature profiles in the coal plug in the hot-rod reactor, for a range of heating rates.

These results suggest that even at moderate heating rates of 20-30^{o}C/s, a substantial fraction of the coal plug is heated at a much lower rate than the walls, or the exterior of the coal plug. As stated above this model overestimates the radial temperature profile, but

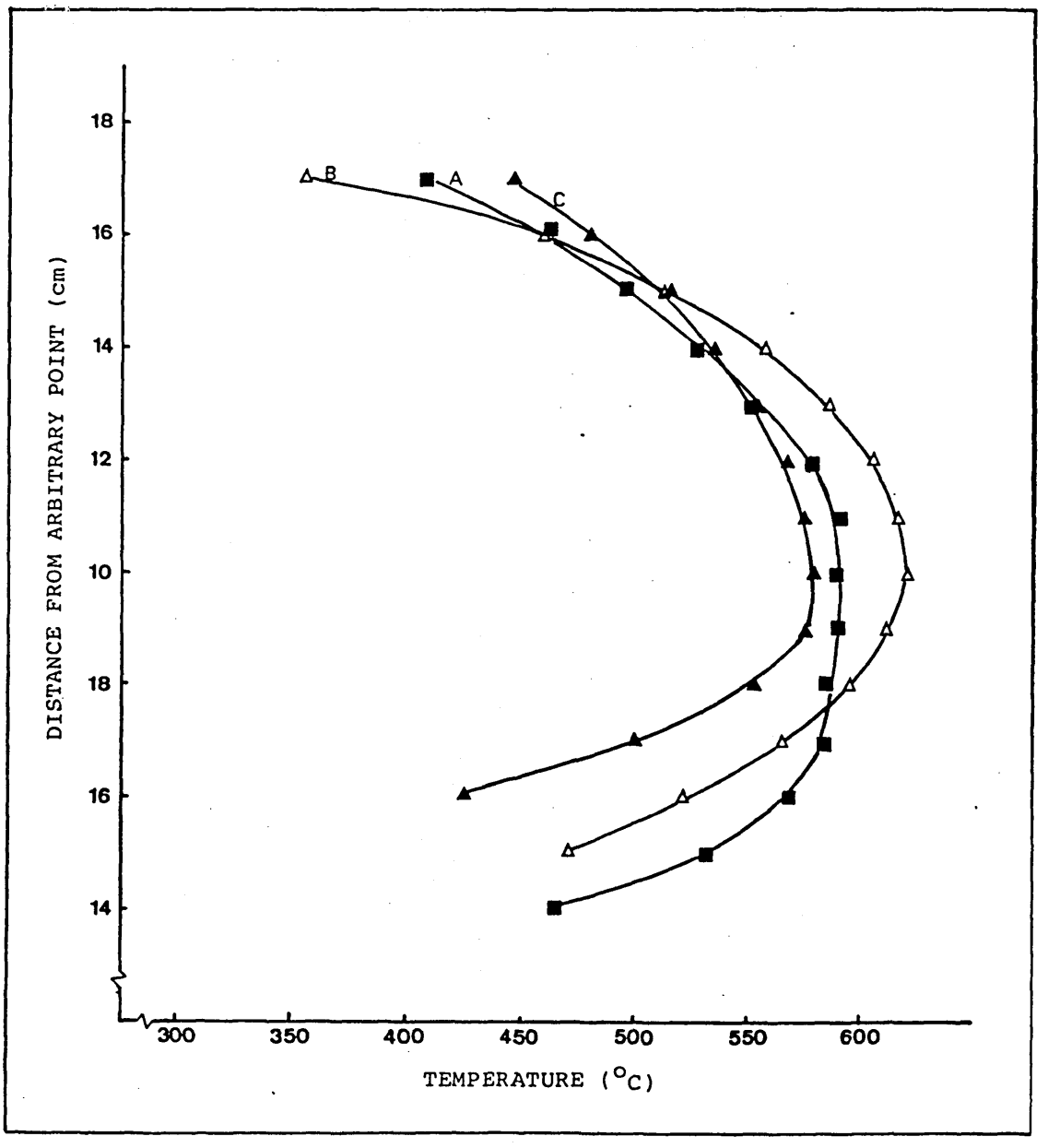
it can be seen that use of heating rates greater than $20^{o}C/s$ is likely to introduce a significant temperature profile across the coal, and render the results less meaningful.

8.5.2 LIMITATIONS TO THE COAL SAMPLE SIZE

The major limitation on the size of coal sample which can be pyrolysed in the hot-rod reactor, is the axial temperature profile. The length of the isothermal zone in the profile limits the amount of coal which can be heated to the required temperature in pyrolysis. Some examples of measured profiles are shown in Figure 8.9. The profiles were measured internally when the hot-rod had reached a constant temperature, using a Type K thermocouple, above a plug of wire-wool, ensuring that the thermocouple measured the temperature a solid would experience. Internal temperatures profiles were not measured when coal was present in the reactor, nor were they measured when the reactor was under pressure. Although these measurements would ultimately be desirable, they have not been achieved to date. In the measured profiles, the temperature of the hot-rod was considered to be isothermal in a region where the temperature was within $10^{o}C$ of a set value.

The non-isothermal nature of the axial temperature profile results from conduction of heat away from the heated section. The major contribution to this conduction is down the copper electrodes due to their

Figure 8.9 Axial temperature profile in the hot-rod reactor:
A - 5% helium flow with no insulation around hot-rod
B - 50% helium flow with no insulation around hot-rod
C - 50% helium flow with insulation around top of hot-rod



large thermal mass in comparison to the reactor tube. At high gas flowrates, the asymmetry of the profile suggest that at high flowrates, significant amounts of heat is removed by the gas stream, which enter cold.

There is very little that can be done to limit the non-isothermal nature of the profile, or to extend the isothermal zone other than to lengthen heated section, and to use the lowest flowrate allowable by other factors. When this heated length is extended to the maximum, use of a low flowrate (5%) of helium produces an isothermal zone 55 mm long, which is sufficient to hold one gram of coal, using a measured density of 860 kg/m^3. This is sufficient to produce a enough tar for analysis. When the pressure is increased, the profile is assumed to remain constant as the linear velocity of the gas is maintained at approximately the same level. The effect of the presence of the coal on the temperature profile is difficult to quantify, though it is unlikely to make the profile less isothermal.

In this design, the internal temperature cannot be measured while the reactor is under pressure.

8.6 EXPERIMENTAL PROCEDURE

The experimental procedure can be divided into three sections: assembly, pyrolysis/hydropyrolysis and product recovery. Coal samples were prepared using the procedures described in Chapter 6.

8.6.1 ASSEMBLY OF THE SYSTEM

Prior to all experiments, the hot-rod was washed through with methanol and dichloromethane and then dried. The condensers were similarly washed and dried. To ensure that the narrow bore tubing (1/8" OD) was dry, the washed sections were dried in a vacuum oven. The condenser was then assembled. The required amounts of glass wool were pushed into the relevant sections of the condensers as described in section 8.2.5, and all joints tightened sufficiently to produce a good seal.

Two wire wool plugs each approximately 5-10 mm long were formed from pre-washed wire wool (fine grade from Brillo). These were weighed and then one was pushed into the hot-rod from the top, and placed at the required location. A weighed quantity of coal, between 0.3 and 0.5 g, was loaded into the hot rod via a narrow necked glass funnel (3mm OD). This coal was held in place by the other wire wool plug which was pushed in place above the coal. The inlet gas connector was then attached and the joint sealed.

The condenser was then attached below the hot-rod and the joints at either end tightened to produce a pressure tight seal. The pressure transducer, solenoid valves and mass flowmeter were then switched on, and the compressed air flow iniated. The manual pneumatic valves and the automatic pneumatic valves were set to allow gas flow.

The valve on the gas cylinder was then opened allowing gas to flow. The gas flow was sustained at a moderate level (50%) for five minutes to purge the system of air.

The gas circuit was then leak tested. This was performed by closing the outlet valve and raising the pressure supplied from the cylinder to 50 bar. The system was then allowed to reach an equilibrium pressure. The gas flow through the mass flowmeter at this equilibrium represented leakages downstream of this point. If this was greater than 5% (of the maximum flow), then it was concluded that the system was not sufficiently leak tight for an experiment. In this case the pressure in the system was vented and all the connections checked. If the flow was less than 5%, the system was considered to be adequately sealed for performing an experiment.

Prior to an experiment, the ice/water and liquid nitrogen containers were placed in position around the condensers. If the experiment was to be performed at 20 bar or higher, or if hydrogen was used, 1/8" thick steel guard plates were fixed in position around the hot-rod.

The required gas flowrate and pressure were set as follows. The flowrate was set on the mass flowmeter according to the required residence time or gas velocity. The set-point on the controller was set as a percentage of the maximum allowed flowrate of hydrogen which was 3 standard litres/minute (evaluated at 1 atmosphere and 25^{o}C). This mass flow continued to be fed

as the pressure increased, though the actual volumetric flow was reduced. When helium was used the actual flow which the mass flowmeter allowed to flow was equal to the ratio of the heat capacities of hydrogen and helium multiplied by the mass flow evaluated for hydrogen. In calculating residence times and velocities, the gas were assumed to behave as perfect gases. The pressure was set by fine adjustment of the let-down valve.

The apparatus was then ready for the experiment.

8.6.2 PYROLYSIS PROCEDURE

To run the experiment the control computer program was run in the Newbrain microcomputer as described in section 8.3. The experimental parameters (see section 8.3) were set, as were the control parameters. These latter parameters were set at values which gave the "best" time-temperature profile, the best being a constant linear heating rate, followed by an isothermal hold. These values were determined by performing a series of blank experiments without coal or gas pressure varying the values of the control parameters to give the "best" time-temperature profile. Typical values for control parameters corresponding to a set of experimental parameters are given in Table 8.1, while a typical time-temperature profile is shown in Figure 8.10.

When the parameters had been set, the power supply unit

was switched on and the hot-rod heated. During the pyrolysis, the pressure in the system was carefully monitored and controlled at a fixed level. This was important as increases in pressure drop represented decreases in the gas flowrate through the hot-rod, which would increase volatiles residence time and would also decrease mass transfer coefficients in the pyrolysing coal, leading to lower tar yields.

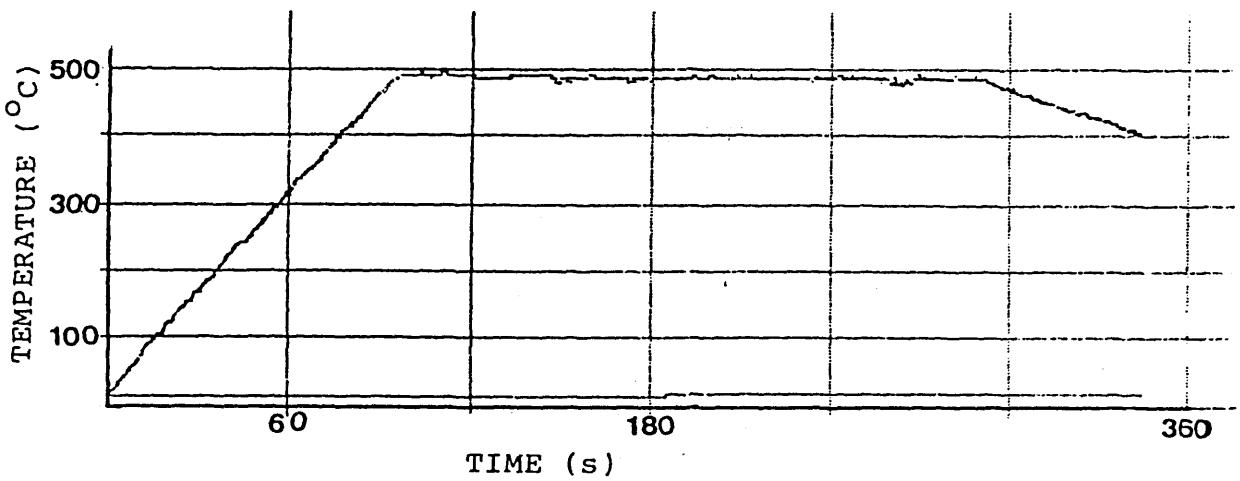


Figure 8.10 Typical time-temperature profile obtained for an experiment on the hot-rod reactor.

When the pyrolysis experiment was complete, the reactor was allowed to cool to <200°C. The system was then depressurised, and disassembled for product recovery.

8.6.3 PRODUCT RECOVERY

In this product recovery, the char was not mixed with the tar and so could be weighed directly. The tar was isolated by washing the condensers. No gas collection was attempted.

The char was recovered as follows. The condenser was removed from below the hot-rod and the inlet gas connection detached. The char and the wire-wool plugs were then pushed downwards out of the hot-rod into a pre-weighed beaker, which was then re-weighed to determine the weight of char. During pyrolysis under most conditions, the char formed a pencil, which was easy to remove from the hot-rod. When the coal did not form a pencil, more force was required to push the char out of the hot-rod. However, the wire wool plug above the coal ensured that very little char adhered to the walls of the reactor.

The tar was recovered in the following manner. The glasswool was removed from the condensers and washed with dichloromethane and methanol repeatedly to remove the tar. The tar solution was collected in a round bottomed flask. The condenser tubes were also washed successively with the two solvents to remove any tar adhering to the walls. Additionally, the solvents were passed down the hot rod to remove tar remaining on the walls.

The tar solution was filtered through Whatmans No.1 filter paper into a weighed 100 ml round bottomed flask. The residue on the filter paper consisted principally of glasswool, although very small quantities of insoluble coal/char were also observed. The solvents were removed by distillation in the same manner as in the fluidised

bed experimental procedure. The flask was then reweighed to determine the tar yield.

The possible presence of extractable material in the char was examined in preliminary experiments, by extracting the char with warm tetrahydrofuran (THF) and with methanol in an ultrasonic bath for one hour. Very little extractable material was noted in either solvent, showing that all the volatiles formed had either evaporated, or had repolymerised forming insoluble char-like material.

8.7 EXPERIMENTAL PROGRAMME

The experiments undertaken using the hot-rod reactor were performed to firstly examine the effect of pressure on pyrolysis under both helium and hydrogen, and secondly to investigate the effect of chloroform extraction and impregnation with catalysts on coal hydropyrolysis.

Following preliminary experiments to characterise the reactor, the effect of pressure on the pyrolysis of Linby coal was examined. Experiments were performed at pressures between 1 and 50 bar in both helium and hydrogen, using two gas flow regimes. In regime 1 the calculated superficial gas velocity was maintained at a constant level as the pressure was increased, and in regime 2 the mass flowrate of the gas was held constant.

The effect of impregnation with catalysts on the hydropyrolysis of Linby coal was then studied. The effects of zinc chloride and tin (II) chloride were considered in the range 1-50 bar.

The influence of chloroform extraction on the pyrolysis of Linby coal at elevated pressure under both helium and hydrogen was investigated. Experiments were performed in the range 1-50 bar for 25 hour extracted coal. In a secondary study the effect of the extent of extraction was considered on pyrolysis at 50 bar in He and H_2. Additionally, the hydropyrolysis of 25 hour extracted Linby, subsequently impregnated with 5% zinc chloride, was examined.

The effect of hydrogen pressure on the pyrolysis of the range of coals was then considered. Experiments were performed at 1 bar under helium and at 50 bar under hydrogen. The coals studied were Cortonwood Silkstone, and Taff Merthyr, together with the lignite Canakkale Can.

In addition to experiments on the untreated coals, the hydropyrolysis of both 25 hour chloroform extracted samples and 5% $ZnCl_2$-impregnated coals was investigated at 50 bar pressure.

The results of these experiments are described and discussed in the next chapter.

LIST OF SYMBOLS USED

C - Constant

C_p - Specific heat capacity of coal

$J_0(z)$ - Zeroth order Bessel function of z

$J_1(z)$ - First order Bessel function of z

k - Thermal conductivity of coal

K - Heating rate

n - Numerical counter

p - Density of coal

r - radius

R - Outside radius of coal

t - Time

$T(r)$ - Temperature at radius r

$_n$ - Constants as defined in text

CHAPTER 9 PYROLYSIS AT ELEVATED PRESSURE - RESULTS AND DISCUSSION

Experiments to determine the effect of pressure on coal pyrolysis were performed in the "hot-rod" hydropyrolysis reactor, which was described in Chapter 8. The results of these experiments are presented and discussed in the following sections. Detailed results not given in this chapter are presented in Appendix III, tables III.1 to III.7.

9.1 EFFECT OF PRESSURE ON THE PYROLYSIS OF LINBY COAL

9.1.1 PRELIMINARY EXPERIMENTS

Preliminary experiments were performed at 1 bar (gauge) pressure under helium to determine the temperature at which the maximum tar yield from Linby coal occurred. The time-temperature programme used was a linear ramp at 5^{o}C/s up to the required temperature, followed by a 200 second isothermal hold. The heating rate used in this programme is within the range allowable for the hot-rod (see Chapter 8). Further extensions of the hold time at peak temperature did not produce any additional tar. This heating programme was used for all subsequent experiments. The gas flowrate used in the preliminary experiments was set to give a superficial velocity in the hot-rod at peak temperature of 0.1 m/s. This corresponds to the velocity used by the National Coal Board in their hydropyrolysis reactor (Fynes and

co-workers, 1984). The peak temperatures quoted in these results are estimated from temperatures at the exterior of the reactor, using measurements made of the internal temperature in the absence of coal.

The results from the preliminary experiments are shown in Figures 9.1 and 9.2, and are presented in detail in Table III.1. The results have a similar form to the results from the fluidised bed flash pyrolysis reactor, in that the tar yield has a maximum in the range 580-600^{o}C, and the yield of char decreases rapidly upto 600^{o}C, and more slowly at higher temperatures.

The absolute values of the tar yield however are considerably smaller than those from the fluidised bed reactor. It would seem that this difference arises as a consequence of the lower heating rate used in the hot-rod reactor. Above 600^{o}C, the tar yield declines more slowly in the hot-rod than in the fluidised bed reactor. In the hot-rod, the lower heating rate, together with a sweep gas, permits tar formed at lower temperatures (<600^{o}C) to escape before the higher temperatures are reached, where the tar is liable to undergo secondary reactions. At higher temperatures, some of the tar fails to escape and undergoes secondary reactions, causing a small decrease in the tar yield. In coal pyrolysis at temperatures greater than 600^{o}C in the fluidised bed, all the tar formed is released into an environment at high temperature, making it more vulnerable to secondary reactions.

Figure 9.1 Tar yield as a function of peak temperature for the pyrolysis of Linby coal in the hot-rod reactor at 1 bar under helium.

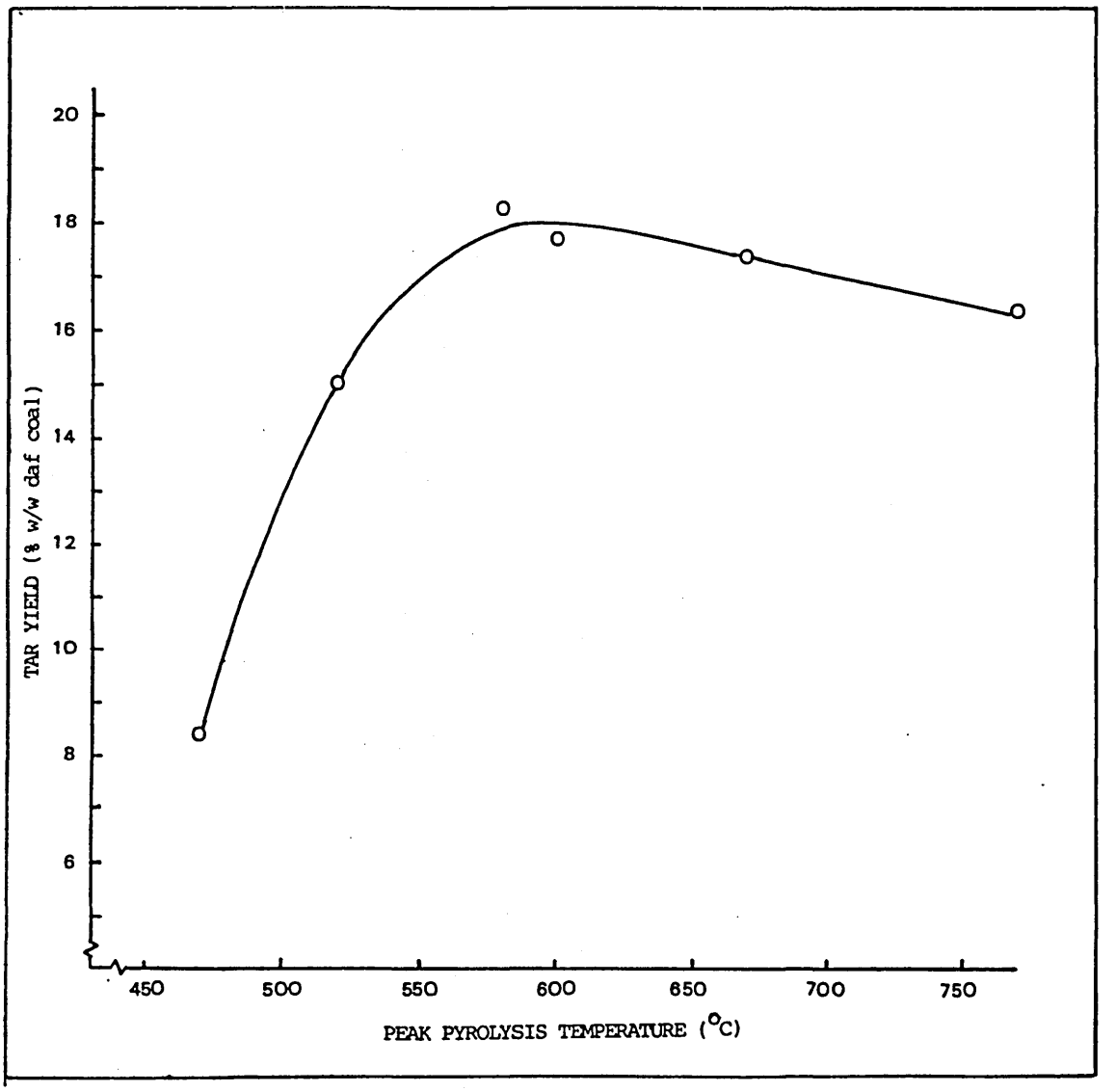
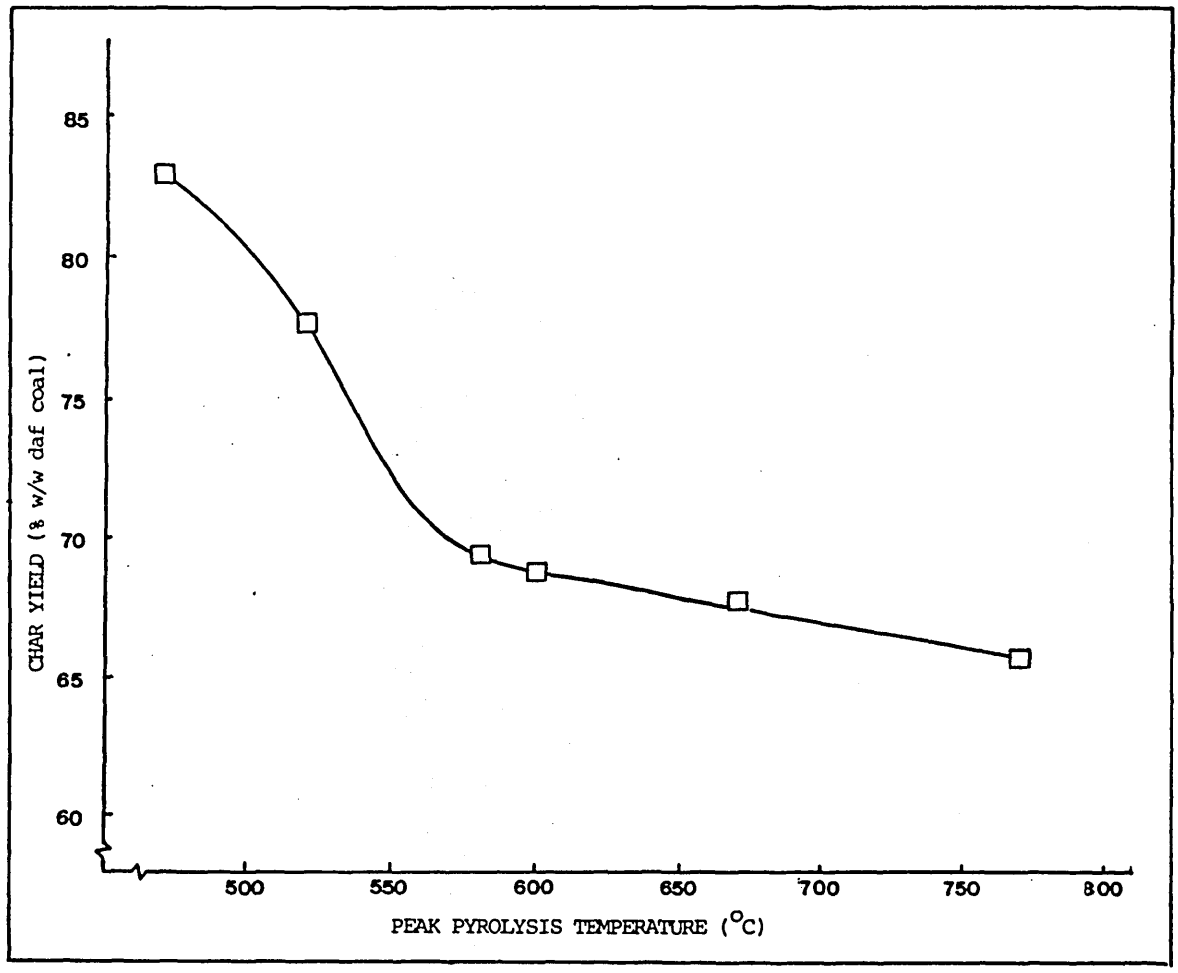


Figure 9.2 Char yield as a function of peak temperature for the pyrolysis of Linby coal in the hot-rod reactor, at 1 bar under helium.



Therefore for pyrolysis at temperatures greater than 600°C the tar yield from the fluidised bed declines more rapidly.

The tars from these preliminary experiments were analysed by ^{1}H NMR and vapour pressure osmometry. The results are shown in Table 9.1. Increases in temperature have much less effect on the structure of the tar than in the case of the fluidised bed. The tar released at 470°C is more aliphatic and of a higher molecular weight than the tars produced at higher temperatures. Above 520°C it appears that temperature has little effect on the structure of the tar. This confirms that most of the tar is removed from the hot-zone before secondary reactions can occur.

Table 9.1 Analyses of the tars from the pyrolysis of Linby coal in the hot-rod reactor at 1 bar pressure.

Peak Temp.(°C)	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
470	22	25	6	30	17	380
520	28	23	5	29	15	nd
590	28	28	7	28	9	330
670	28	26	6	27	13	290

a - ^{1}H-NMR assignments as defined in Appendix I.

b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

All experiments to determine the effect of pressure on the pyrolysis of Linby coal were performed at the temperature of maximum tar yield, that is 580-600°C.

9.1.2 EFFECT OF PRESSURE ON THE PYROLYSIS OF UNTREATED LINBY COAL

Experiments to determine the effect of pressure were performed in the range 1-50 bar. All pressures quoted are gauge pressures. Both inert gas (helium) and hydrogen were used as ambient atmospheres, and two gas flowrate regimes were investigated.

The first set of experiments were performed to examine the effect of of gas pressure while the superficial velocity of the gas stream in the reactor, calculated at the peak temperature, was maintained at a consistent value of 0.1 m/s, for all the pressures investigated. Previous workers have shown that by maintaining the vapour residence time at a consistent value, achieved by holding the superficial velocity at a constant level, the effect of increasing hydrogen pressure is to increase the liquid yields (Dryden and Sparham, 1963, Hiteshue and co-workers, 1964; Fynes and co-workers, 1984).

In the second set of experiments, the mass flowrate of the gas stream was maintained at a constant value of 0.3 standard litres/minute for all pressures used (standard litre measured at 1 atmosphere absolute pressure, and

25°C). These experiments were performed to compare the results obtained in pyrolysis at elevated pressure under conditions of high and low sweep gas flowrates, and to examine whether the hydrogen/coal ratio has any importance in coal hydropyrolysis.

The results from experiments in each of the two regimes are described below. Pressures greater than 50 bar were not used, as the mass flowmeter could not supply sufficient hydrogen to maintain flow regime 1 at pressures greater than 50 bar.

Constant gas velocity regime - Regime 1

The effect of pressure on the tar yield from the pyrolysis of Linby coal under helium and hydrogen is shown in Figure 9.3. The effect on the char yield is shown in Figure 9.4. The data is presented in detail in Table III.2.

Under inert gas pressure, the effect of increasing gas pressure is to reduce the tar yield. This confirms the results obtained by other workers in different reactor geometries as discussed in Chapter 2 (See Figure 2.11). The results show that the mass transfer of volatiles within the coal particle and during the evaporation stage is retarded by the increased pressure, to an extent which allows the tar to undergo secondary reactions reducing the tar yield.

Figure 9.3 Tar yield as a function of gas pressure for the pyrolysis of Linby coal in the hot-rod reactor, with a peak temperature of 580-90°C in gas flow regime 1. Results under helium (▽), and under hydrogen (o).

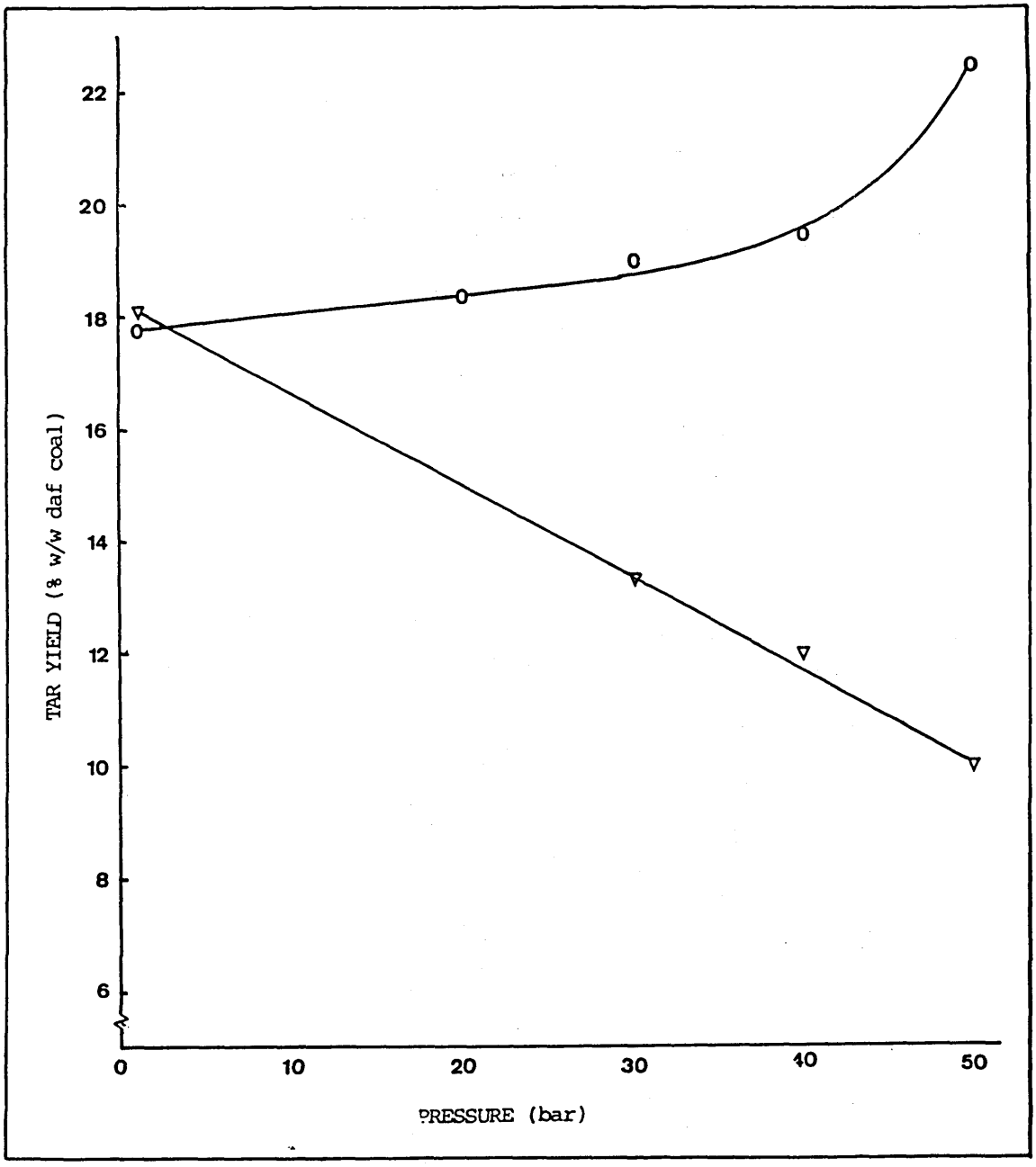
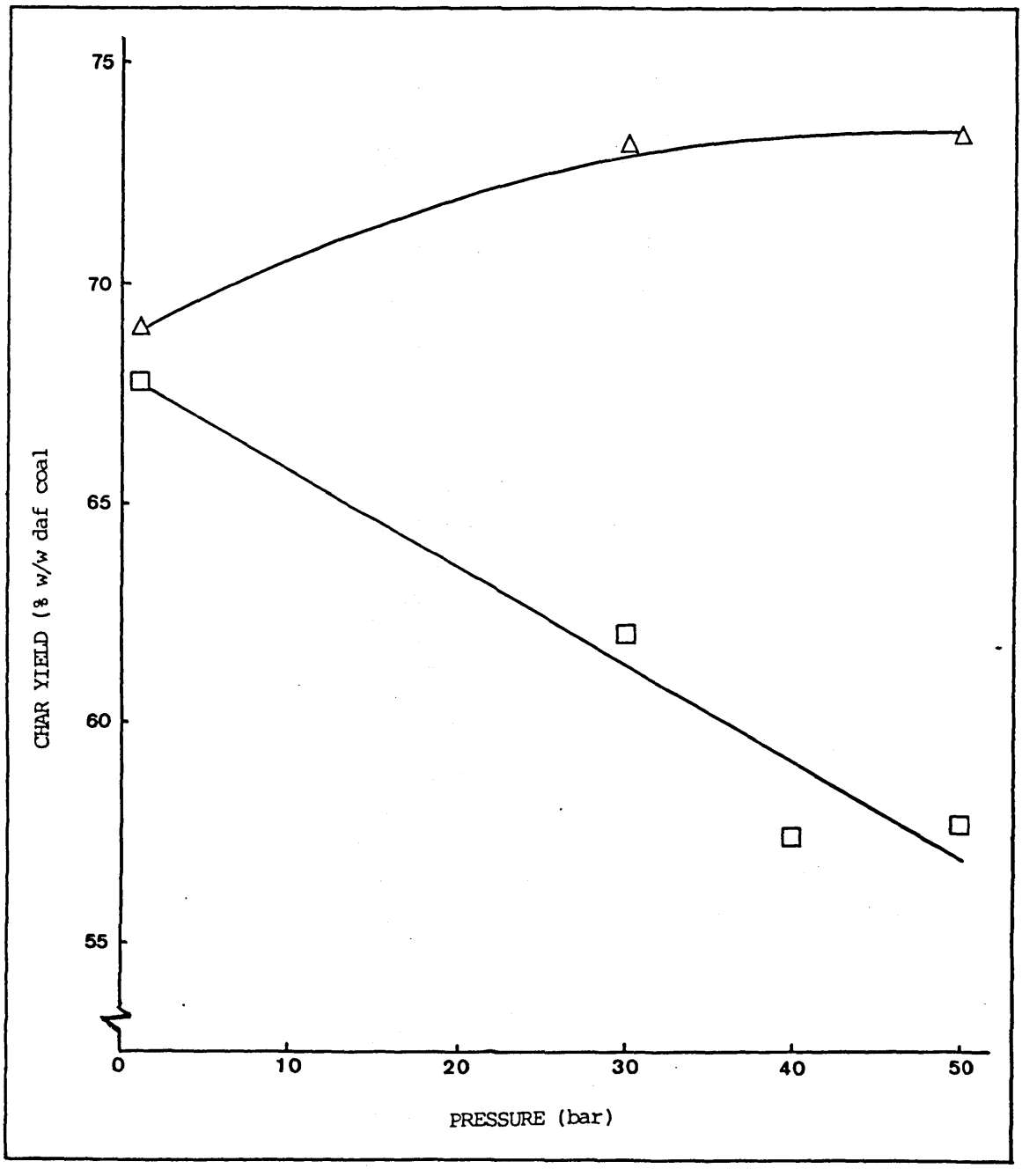


Figure 9.4 Char yield as a function of gas pressure for the pyrolysis of Linby coal in the hot-rod reactor, with a peak temperature of 580-90°C in gas flow regime 1. Results under helium (Δ), and under hydrogen (□).



The nature of the secondary reaction is indicated by the effect of pressure on the char yield. As the helium pressure is increased up to 30 bar, the decrease in the tar yield is approximately balanced by the increase in the char yield, suggesting that the dominant secondary reaction is repolymerisation. At higher pressure though, the char yield does not increase significantly, while the tar yield continues to decline substantially, suggesting that gas-phase cracking is responsible for the further drop in the tar yield.

Under hydrogen pressure, the tar yield increases slowly up to 40 bar and more rapidly up to 50 bar. The result at 50 bar is the mean of two experiments, each within 0.5% of the mean. The increase in the tar yield represents the net result of competition between the effect of the increase in the gas pressure in retarding mass transfer, and the influence of hydrogen in enhancing the yield of tar. The drop in the char yield with hydrogen pressure is larger than the increase in the tar yield, indicating that considerable hydrogasification of the coal/char occurs.
At 1 bar pressure, molecular hydrogen is not chemically active in coal pyrolysis.

Overall, the results obtained under hydrogen are similar to those obtained by Fynes and co-workers (1984) for the same coal under similar condition, using approximately the same gas superficial velocity.

Constant mass flow regime - Regime 2

The results from the experiments where the effect of pressure was studied, whilst the mass flowrate of the sweep gas was maintained at constant level are shown in Figures 9.5 and 9.6 and also in Table III.2. The results are superimposed on those for regime 1, discussed in the previous subsection. As the pressure rises, the superficial gas velocity falls. At 1 bar pressure, the velocity is 0.25 m/s. This falls to 0.016 m/s at 30 bar, and to 0.01 m/s at 50 bar pressure. This has a substantial effect on tar and char yields.

Under inert gas, the drop in the tar yield as the pressure increases is larger than from regime 1, showing that the mass transfer of the volatiles is further hindered by the drop in the flow rate. It is unclear from this result whether this is due to the increase of the volatiles residence time "in-flight", or during the evaporation phase of mass transfer. However, the char yield shows a substantial increase as the pressure rises, of the same magnitude as the decrease in the tar yield. This shows that the dominant secondary reaction occurring to the tar is repolymerisation, suggesting that the effect is due to hindered evaporation, rather than in-flight cracking.

During the experiments under hydrogen, the tar yield also decreases with increasing pressure.

Figure 9.5 Tar yields as a function of gas pressure for the pyrolysis of Linby coal in the hot-rod reactor in gas flow regimes 1 and 2 with a peak temperature of 580-90°C: flow regime 1 - results under He (▽), results under H_2 (○); flow regime 2 - results under He (△), results under H_2 (×).

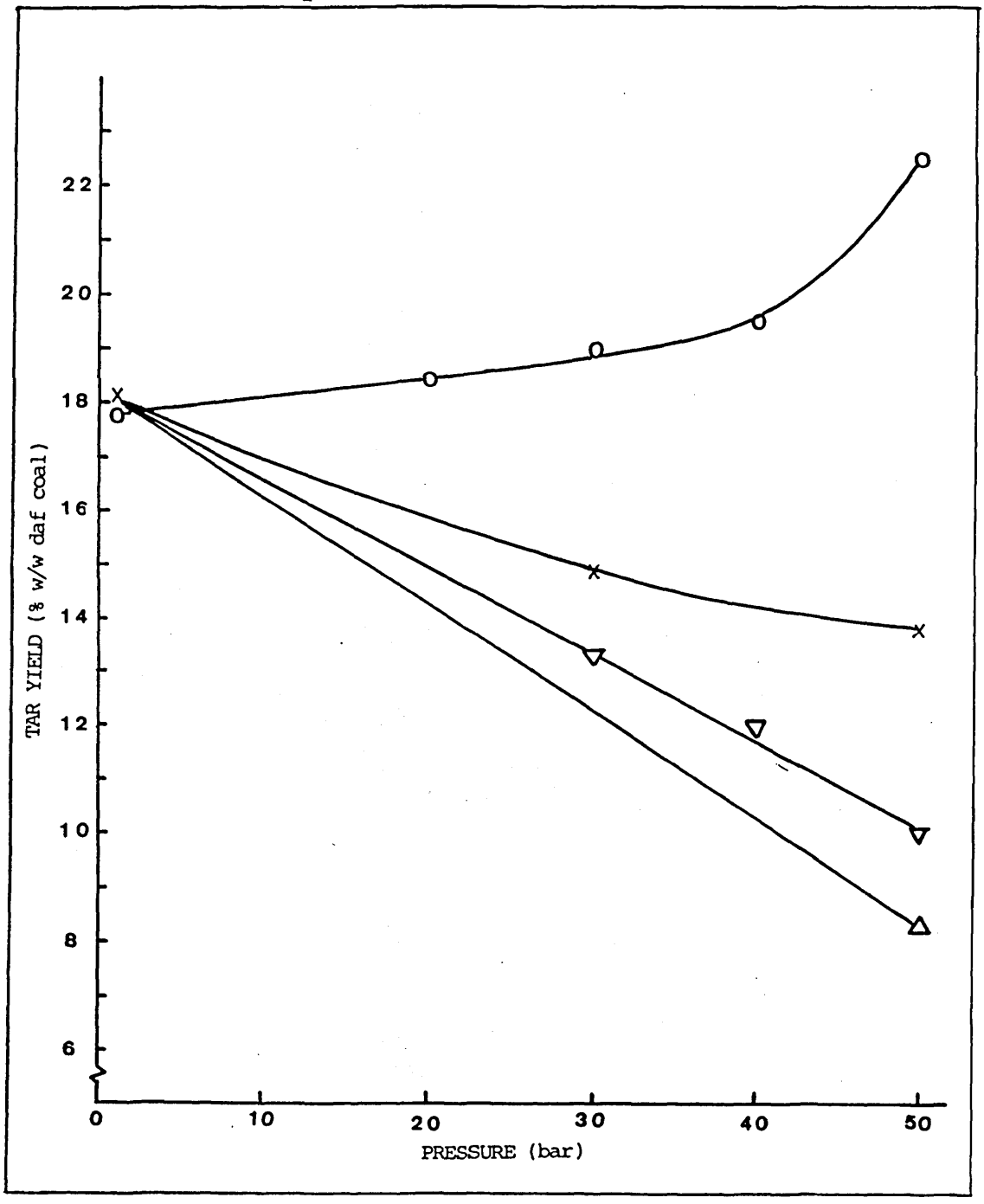
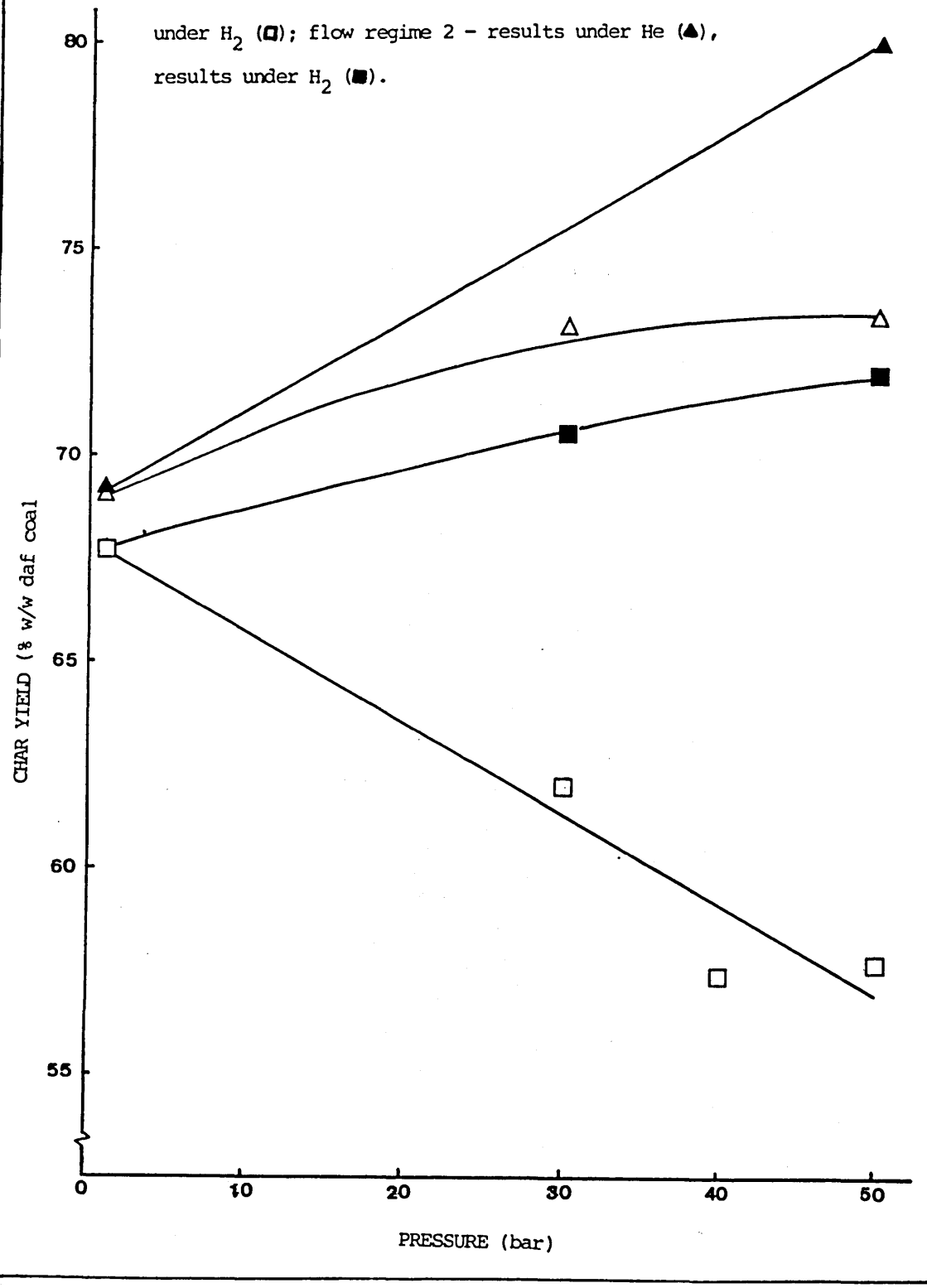


Figure 9.6 Char yields as a function of gas pressure for the pyrolysis of Linby coal in the hot-rod reactor in gas flow regimes 1 and 2, with a peak temperature of 580-90°C: flow regime 1 - results under He (△), results under H_2 (□); flow regime 2 - results under He (▲), results under H_2 (■).



In this flow regime the effect of the gas pressure increasing mass transfer resistances dominates over the activity of the hydrogen in promoting tar formation. The char yield also increases, though by only a small amount as any increase due to repolymerisation is offset by the weight loss due to hydrogasification of the coal/char.

Analysis of the Tars

The results of the analysis of the tars from both flow regimes are presented in Table 9.2. In flow regime 1, increases in gas pressure have a substantial effect on the structure of the tar, but in flow regime 2, the effect is less noticeable.

Under helium, in regime 1, as the tar yield falls with increasing pressure, the hydrogen aromaticity of the tar decreases and the molecular weight increases. Comparing the tar formed at 50 bar in flow regime 2 with that formed at 1 bar in regime 1, the decrease in the aromaticity is of a lower magnitude than the increase observed in regime 1, as is the increase in the mean molecular weight. The reason for these changes is presumably that the more aliphatic molecules are less liable to undergo the secondary polymerisation reactions which result in the decrease in the tar yield and increase in char yield with inert gas pressure.

Table 9.2 Analysis of tars formed in the pyrolysis of Linby Coal in the hot-rod reactor at 590°c over a range of pressures.

Flow Regime 1

Pressure (bar)	Gas	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
1	He	28	28	7	28	9	330
30	He	26	26	5	28	15	340
50	He	19	22	5	36	18	375
1	H_2	28	23	7	30	12	nd[c]
30	H_2	27	31	5	26	11	310
40	H_2	25	26	7	30	12	320
50	H_2	32	23	6	27	12	310
Flow Regime 2							
50	He	23	25	7	32	13	nd[c]
30	H_2	27	25	6	29	13	nd[c]
50	H_2	30	24	5	28	13	nd[c]

a - ^{1}H-NMR assignments as defined in Appendix I.

b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

c - nd- not determined

Under hydrogen, in flow regime 1, the results suggest that as the tar yield increases with hydrogen pressure, the aromaticity of the tar increases, while the mean molecular weight remains approximately constant. Under flow regime 2, although the tar yield falls with pressure, the aromaticity of the tar rises, although to a lesser extent than for flow regime 1, while the mean

molecular weight again remains approximately constant. The rise in the hydrogen aromaticity with hydrogen pressure is the same trend as that observed by Fynes and co-workers (1984). The reason for the changes in structure is either that the additional tar formed by the presence of the hydrogen is highly aromatic, or that the externally applied molecular hydrogen promotes secondary reactions which increase the aromaticity of the tar. The former hypothesis is unfeasible, as it demands that the additional tar formed has a very high aromaticity (80-90%). In the latter theory, the reactions which would cause the modifications to tar structure are dealkylation, ring closure, and dehydrogenation of hydroaromatics. It seems unlikely that high pressure hydrogen would promote dehydrogenation of hydroaromatics or ring closure reactions. Dealkylation seems the most probable reaction. Detailed analyses are are required to confirm this hypothesis.

Discussion - the effect of inert gas pressure

The effect of increases of inert gas pressure in pyrolysis is to decrease the tar yield, and to increase the char yield. The effect in flow regime 2 is that the decline of the tar yield is more pronounced The nature of the secondary reactions responsible for the decline in the tar yield depends on the flowrate. At higher gas velocity (regime 1), both gas phase cracking and repolymerisation occur as shown by increases in gas and

char yields. In regime 2, the dominant secondary reaction is repolymerisation forming additional char. These results show the same trends as observed elsewhere (Howard, 1980; Suuberg, 1985).

The effect of hydrogen pressure

The divergent effects of hydrogen pressure on the tar yield in the two flow regimes results from the differing extent of mass transfer inhibition which result from the different gas flowrates used. The mass transfer of volatiles is inhibited either in the vicinity of the particle (ie, within the particle or during evaporation) or during "in-flight" transport through the hot zone. As transport within the coal particle is unaffected by the gas flowrate, the differences in mass transfer must manifest themselves during either evaporation stage, or during "in-flight" transport.

The results obtained in this study can be compared directly with those obtained by the National Coal Board for the same coal in a similar, though larger scale reactor (Fynes and co-workers, 1984). In the results obtained by the NCB under 50 bar hydrogen, the tar yield is approximately the same as that obtained in gas flow regime 1. The data shows an increase of the tar yield with hydrogen pressure in both cases. The "in-flight" residence time of the volatiles in the NCB reactor was 5 seconds, which matches the volatiles residence time in regime 2 where the tar yield is observed to decline with

hydrogen pressure. However because of the larger scale of the NCB reactor, the superficial velocity of the hydrogen sweep gas was 0.1 m/s, which is the same as the gas velocity used in regime 1, where the tar yield was observed to increase with hydrogen pressure.

This comparison shows that the superficial gas velocity is the parameter which determines the effect of increases in hydrogen pressure on the tar yield. This suggests that evaporation of the tar from the surface of the coal particle to the bulk is the mass transfer step affected to the greatest extent by increases in gas pressure

A sweep gas of sufficient superficial and therefore local velocity enhances convection in the vicinity of coal particles. This enhances the rate of evaporation of volatiles, and so reduces their tendency to undergo secondary reactions. As the gas pressure is increased, gas density and viscosity also rise, which has the effect of inhibiting the evaporation of volatiles. The above results (in flow regime 1) show that this can be overcome by maintaining the sweep gas velocity above a certain level. In the absence of a sweep gas of sufficient velocity (eg in flow regime 2), the rate of evaporation of the volatiles is too slow. The volatiles are therefore liable to undergo secondary reactions in the vicinity of the parent coal particle, which has the effect of reducing the tar yield. This effect is enhanced as the pressure rises.

Suuberg has proposed that in coal pyrolysis in a wire-mesh reactor, in the absence of a sweep gas, evaporation is the limiting step in tar formation (Suuberg and Sezen, 1985; Suuberg, 1985). Under these conditions the effect of an increase of hydrogen pressure is to cause the tar yield to decline. The above results confirm the importance of the evaporation step in coal pyrolysis, and show that in the absence of a sufficient sweep gas stream, increases in hydrogen pressure will cause a decline in the tar yield. The implication of these findings is that is that if a sufficiently strong sweep gas was used in a wire-mesh reactor, the effect of increases of hydrogen pressure might be to increase the tar yield.

9.1.3 THE EFFECT OF CATALYSTS ON THE HYDROPYROLYSIS OF LINBY COAL

The effect of two Lewis acid type catalysts on the hydropyrolysis of Linby coal was considered, these being zinc chloride and tin (II) chloride. Both catalysts have been shown to increase conversion of coal to liquid products under high pressure hydrogen (see Chapter 4), although their effects in coal flash pyrolysis are different (see Chapter 7).

In this study, samples of Linby coal were impregnated with 10% $SnCl_2$ and with 5% $ZnCl_2$ in the manner described in Chapter 6. Hydropyrolysis experiments were performed

between 1 and 50 bar, a heating rate of $5^{o}c/s$ to a peak temperature of 580-600°C. The gas flowrate was adjusted as the pressure was increased to maintain a constant superficial velocity of 0.1 m/s at the peak temperature, as in flow regime 1 (see above).

The results of the experiments are shown in Figures 9.7 and 9.8. The tar and char yields from the catalyst impregnated samples are superimposed on the results from the untreated Linby.

It was shown in the Chapter 7 that in atmospheric pressure pyrolysis at high heating rate, zinc chloride promotes tar formation, but in pyrolysis at a low heating rate, the presence of zinc chloride promotes char formation and reduces the tar yield. In experiments in the hot-rod, the heating rate used is $5^{o}C/s$. As the action of zinc chloride at 1 bar pressure is to enhance char formation, it can be deduced that pyrolysis experiments in the hot-rod reactor are at a low heating rate with respect to the action of the zinc chloride. Neither catalyst shows any ability to utilise externally applied hydrogen at 1 bar pressure.

As the hydrogen pressure is raised, both catalysts cause the tar yield to increase. The presence of zinc chloride also cause a large increase in the gas yield, whereas for tin chloride, the decrease in the char yield is approximately the same as the increase in the tar yield.

Figure 9.7 Tar yield as a function of gas pressure for the pyrolysis of Linby coal impregnated with zinc chloride and tin chloride with a peak temperature of 580-90°C: Untreated Linby (o); 5% $ZnCl_2$-impregnated Linby (Δ); 10% $SnCl_2$-impregnated Linby (■).

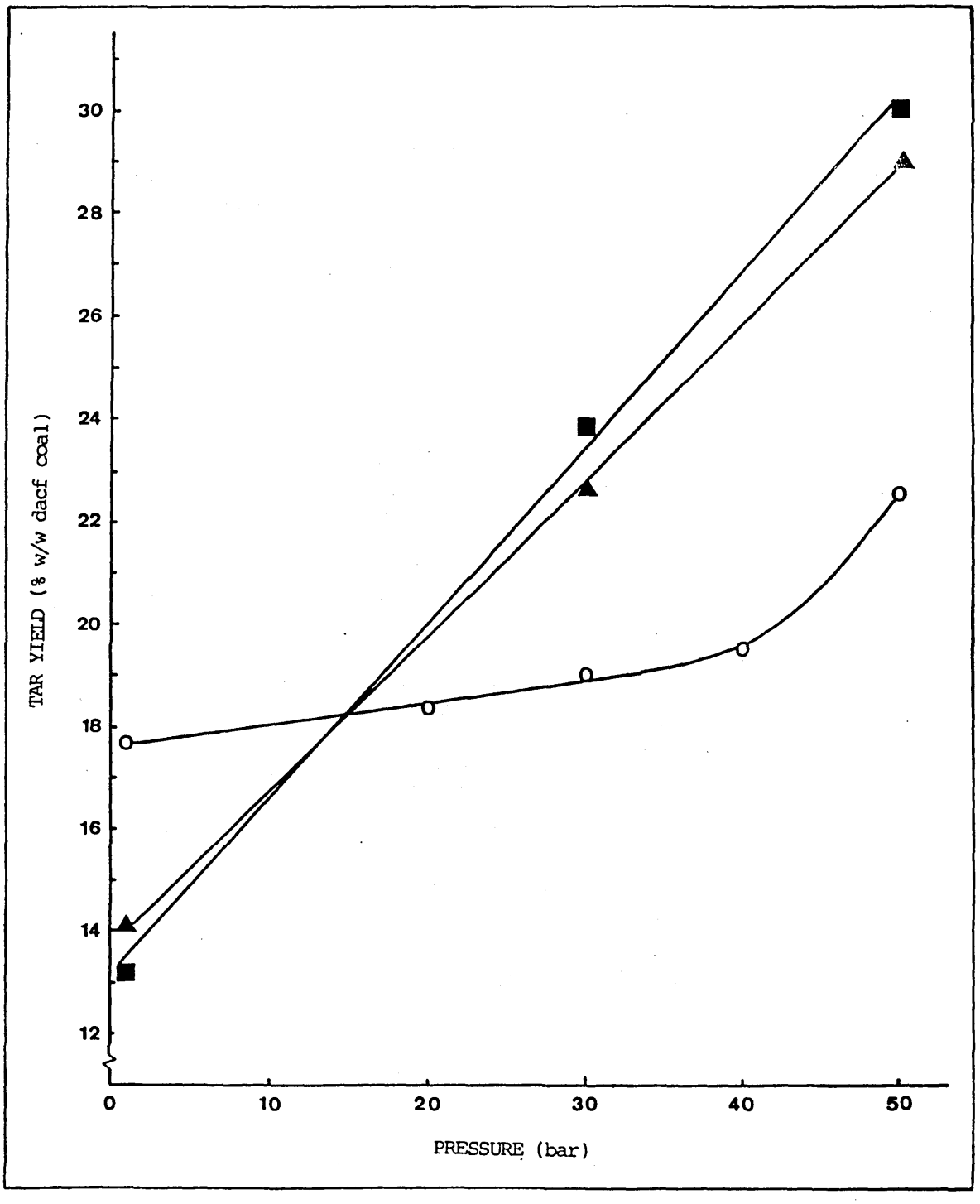
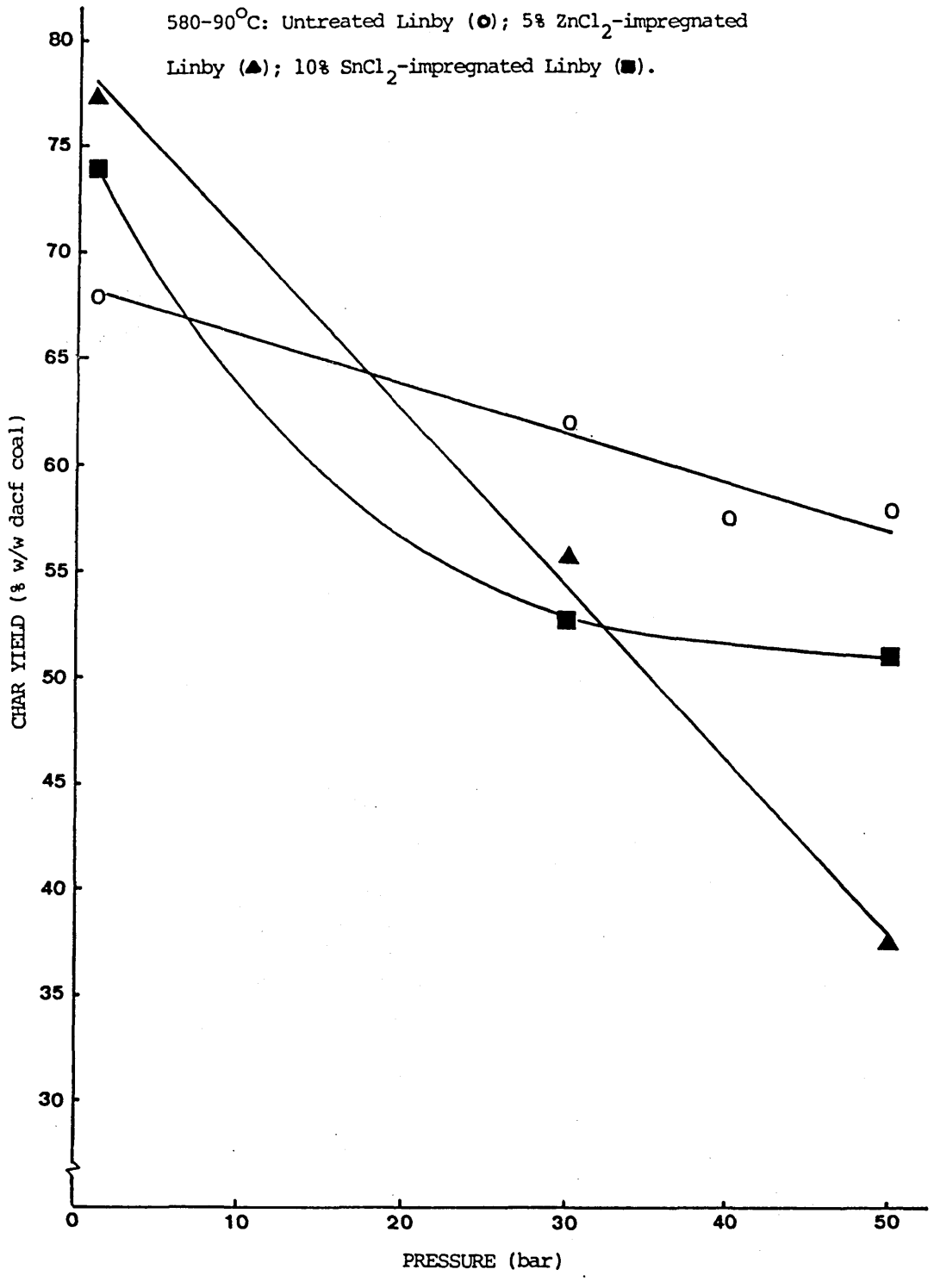


Figure 9.8 Char yield as a function of hydrogen pressure for the pyrolysis of Linby coal impregnated with zinc chloride and tin chloride with a peak temperature of 580-90°C: Untreated Linby (O); 5% $ZnCl_2$-impregnated Linby (▲); 10% $SnCl_2$-impregnated Linby (■).



It appears that tin chloride produces a higher conversion to the liquid product than the zinc chloride, although the tin chloride loading is higher by a factor of 2 on a weight basis and 1.4 on a molar basis. The large increase in the gas yield from zinc chloride suggests that either the catalyst is also active in catalysing secondary cracking of the volatiles, resulting in large gas yields, or that it catalyses hydrogasification reactions.

Analysis of the tars

The results from the analysis of the tars from the catalyst impregnated samples are presented in Table 9.3. The tars from the hydropyrolysis of the zinc chloride impregnated sample at 30 and 50 bar have higher hydrogen aromaticities and higher mean molecular weights than the samples from the untreated Linby formed at the same pressure. The increase in aromaticity may be due to zinc chloride catalysing either the dehydrogenation of hydroaromatics, or the dealkylation of aromatic rings, or both processes. The ^{1}H-NMR spectra (see Table 9.3) suggest that dealkylation reactions occur via beta bond scission, ie the bond between the alpha and beta carbons. Zinc chloride has been shown to promote both dealkylation and dehydrogenation reactions and also condensation reactions in pyrolysis at atmospheric pressure and low heating rates (Bodily and co-workers, 1974; Neuburg and co-workers, in print).

Table 9.3 Analysis of tars from from the pyrolysis of catalyst impregnated Linby coal under hydrogen in the hot-rod reactor over a range of pressures.

Catalyst	Pressure (bar)	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
5% $ZnCl_2$	1	22	26	7	33	12	nd[c]
5% $ZnCl_2$	30	35	29	5	22	9	370
5% $ZnCl_2$	50	38	29	4	21	8	390
10% $SnCl_2$	1	18	19	7	39	17	290
10% $SnCl_2$	30	29	28	6	26	11	330
10% $SnCl_2$	50	35	23	4	26	12	360

a - ^{1}H-NMR assignments as defined in Appendix I.
b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.
c - nd - not determined.

The increase in mean molecular weight may be due to zinc chloride catalysing some condensation reactions, which would increase the size of tar molecules, perhaps in conjunction with dealkylation reactions. Alternatively this may be due to the lack of plasticity shown by catalyst impregnated Linby during hydropyrolysis. Untreated Linby agglomerates during pyrolysis in the hot-rod reactor, whereas the char from $ZnCl_2$-impregnated Linby can be pushed out of the hot-rod as a powder at the end of an experiment. This lack of plasticity would

diminish the extent to which volatiles are liable to undergo secondary reactions following their formation during hydropyrolysis, which may have the result of increasing the mean molecular weight of the tar.

The observed effect of the zinc chloride on tar structure is enhanced as the pressure is increased, showing that either the increase in pressure causes the catalyst to be in contact with the volatiles for a longer time period due to the increases in mass transfer resistances, or that the hydrogen actively participates in the reactions, with a greater effect at higher pressure.

The results of the analyses of the tars from the tin chloride impregnated sample are qualitatively similar to those from the zinc chloride impregnated, although the changes which occur as a result of the presence of the catalyst are of a smaller magnitude than for zinc chloride. This suggests that in hydropyrolysis, the action of tin chloride is similar to the action of zinc chloride.

In pyrolysis at 1 bar pressure, the tars from the catalyst impregnated samples are more aliphatic and of lower molecular weight than the tar from untreated Linby. This confirms that the differing action of both catalysts at low pressure in comparison to their effects under high pressure hydrogen.

Discussion

To summarise, the action of zinc chloride and tin chloride in coal hydropyrolysis is similar. The presence of either catalyst results in an increase in the tar yield relative to the untreated coal at pressures greater than 10-15 bar. Both catalysts also appear to promote dealkylation and condensation reactions, resulting in increases in the aromaticity and mean molecular weight of the tar. The catalysts also appear to promote hydrogasification of the char/coal resulting in large increases in the gas yields.

The mechanism by which the zinc chloride acts under hydrogenation condition was investigated by Bell and co-workers (1981) using the catalyst as a molten salt. The proposed mechanism used Friedel-Crafts chemistry to explain the activity of zinc chloride. A variation of the mechanism is discussed in Chapter 7 (Section 7.4.3.4). In hydropyrolysis, impregnated zinc chloride may promote tar formation via a similar mechanism, with the externally added molecular hydrogen acting as an additional source of hydride ions in the abstraction step. In the absence of the molecular hydrogen or some other source of hydride ions, electrophilic substitution on some other aromatic structure is thought to occur, which would result in a condensation reaction, such as a Scholl condensation, increasing the char yield. This is thought to explain the effect of the catalysts in pyrolysis at atmospheric pressure at low heating rate.

In addition to the effect of the catalyst in increasing the initial formation of tar, the zinc chloride has an effect on the structure of the tar. The nature of the catalysed secondary reaction which cause these changes is unclear, though Friedel-Crafts chemistry is likely to play a role. The catalyst appears to promote dealkylation reactions, primarily via beta-bond scission. Zinc chloride may catalyse some condensation reactions which would result in increases in the mean molecular weight of the tar. The two reactions may be linked: a carbonium ion formed by the dealkylation of a tar molecule may attack another tar molecule, forming a larger tar molecule.

The mechanism by which tin chloride promotes tar formation in hydropyrolysis appears to be similar to the mechanism proposed for zinc chloride.

The mechanism by which zinc chloride promotes gas formation during hydropyrolysis may involve dealkylation of the coal structure in a similar manner to the effect of the catalyst on the tar structure. Zinc chloride has been shown to catalyse dealkylation reactions in the coal structure at low temperatures (300-350^{o}C) at atmospheric pressure (Neuburg and co-workers (in print).

9.1.4 EFFECT OF PRESSURE ON THE PYROLYSIS OF CHLOROFORM EXTRACTED LINBY

Chloroform extraction was shown in Chapter 7 to have a substantial effect on the tar yield from the flash pyrolysis of Linby coal. The effect of extraction on the pyrolysis of Linby coal at elevated pressure under helium and hydrogen was examined in the "hot-rod" reactor. Two sets of experiments were performed, firstly to determine the effect of pressure on 25 hour chloroform extracted coal, and secondly to examine the effect of varying the extent of extraction on the tar yield at 50 bars under hydrogen and helium.

In the following sections the results of these experiments are presented, together with analyses of the tars from the extracted coal. The nature of the mechanism by which the chloroform extractable material acts is then discussed.

9.1.4.1 PYROLYSIS OF 25 HOUR EXTRACTED LINBY

Pyrolysis experiments were performed in the hot-rod reactor on Linby coal which had been Soxhlet extracted for 25 hours with chloroform using the procedure described in Chapter 6. The yield of extract obtained was 1.96.%. The structure of the extract was described and discussed in Chapter 7. Experiments were performed using a heating rate of 5^{o}C/s to a peak temperature of 580^{o}C, over a range of pressures in helium and hydrogen.

The gas flowrate set was that used in flow regime 1 (see above).

The physical behaviour of the extracted Linby in the pyrolysis reactor was different to that of the untreated Linby. Following pyrolysis in the hot-rod under any set of conditions, the untreated Linby formed a coherent "pencil" of char, which could easily be pushed out of the reactor. This behaviour was more pronounced at higher pressure, especially under hydrogen. The extracted Linby showed no tendency to agglomerate and did not form a char pencil under any set of pyrolysis conditions.

The results from the experiments are shown in figures 9.9 and 9.10. The results from the extracted coal are superimposed on those from the untreated Linby. More detailed results are presented in Table III.4.

Under helium, at 1 bar pressure, the tar yield from the extracted Linby, when added to the amount of extract removed, is approximately the same as the tar yield from untreated Linby. It appears that at this heating rate, the extractable material merely acts as a volatile component in pyrolysis, and does not play any other discernable role in tar formation. This trend continues up to 40 bar. However, at 50 bar, the tar yield from the untreated Linby is less than that from the chloroform extracted Linby, without adding the extract removed.

Figure 9.9 Tar yield as a function of gas pressure for the pyrolysis of chloroform extracted Linby coal in the hot-rod reactor, with a peak temperature of 580-90°C: 25 hour chloroform extracted Linby under He (■), under H_2 (▲); Untreated Linby under He (□), under H_2 (△).

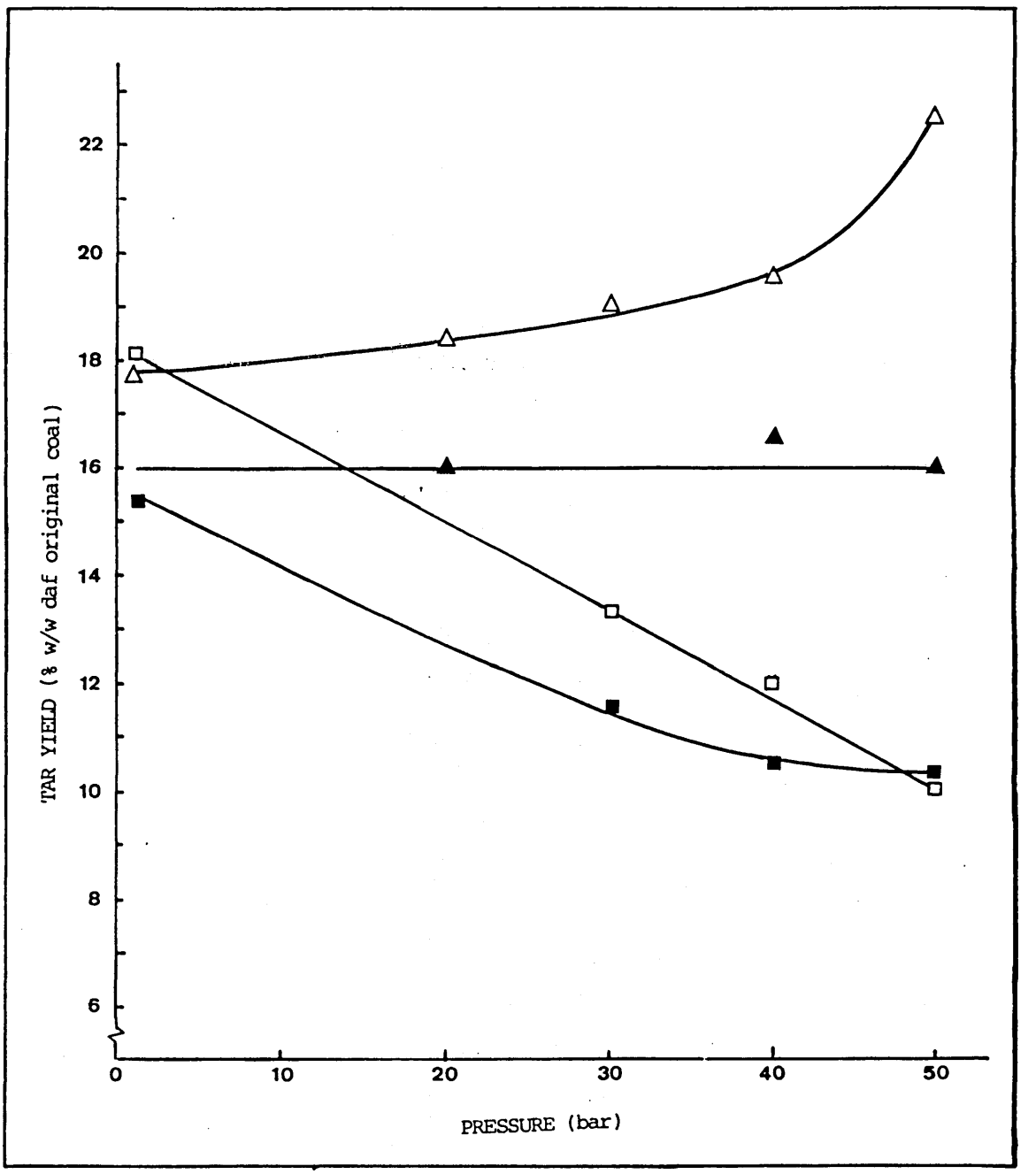
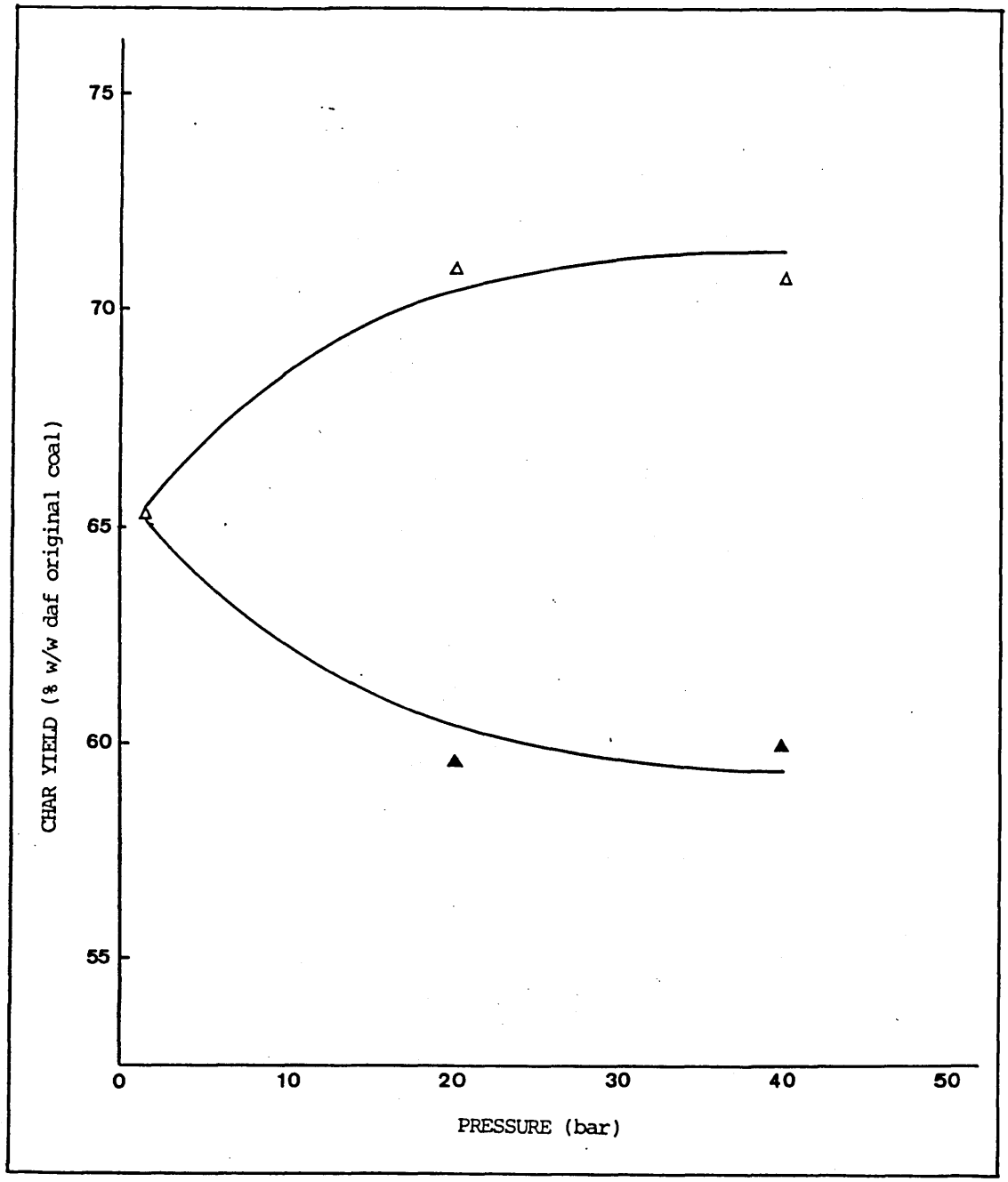


Figure 9.10 Char yield as a function of gas pressure for the pyrolysis of chloroform extracted Linby coal in the hot-rod reactor, with a peak temperature of 580-90°C: 25 hour chloroform extracted Linby under He (Δ), under H_2 (▲);



In addition, over the whole pressure range, the char yield from the untreated Linby is consistently greater than that from the extracted Linby.

The reason for this behaviour could be linked to the lack of plasticity shown by the extracted coal. The additional gas yield from the extracted coal, appears to be due to gas producing reactions occurring to a greater extent. This may be a result of the easier access of the sweep gas to the particles within char from the extracted coal, following the initial pyrolysis. The higher tar yield at 50 bar from the extracted coal can again be explained by invoking the lack of plasticity shown by the extracted coal. The agglomeration of the untreated coal during pyrolysis is more pronounced at this pressure (ie 50 bar), an effect which would tend to hinder the transport of tar out of the parent coal particle and out of the coal bed. In the absence of this plasticity, the mass transfer of tar thought to be less inhibited and so the tar yield is greater from the extracted coal.

Under hydrogen, the effect of chloroform extraction on the pyrolysis of Linby coal is more straightforward. As the hydrogen pressure increases, the tar yield from the extracted coal remains approximately constant at 16%, whereas the tar from the untreated Linby increases to 22.5% at 50 bar. This shows that the extractable material plays a role in promoting tar formation by interacting with the externally applied molecular

hydrogen. The fact that the tar yield from the extracted coal does not decline with increasing pressure, shows that the action of externally applied hydrogen is not solely via the extracted material. This suggests that the externally applied hydrogen may also act directly during the formation of tar or may act via low molecular weight material which is not extracted by the chloroform.

9.1.4.2 EFFECT OF VARIATION OF THE EXTENT OF EXTRACTION

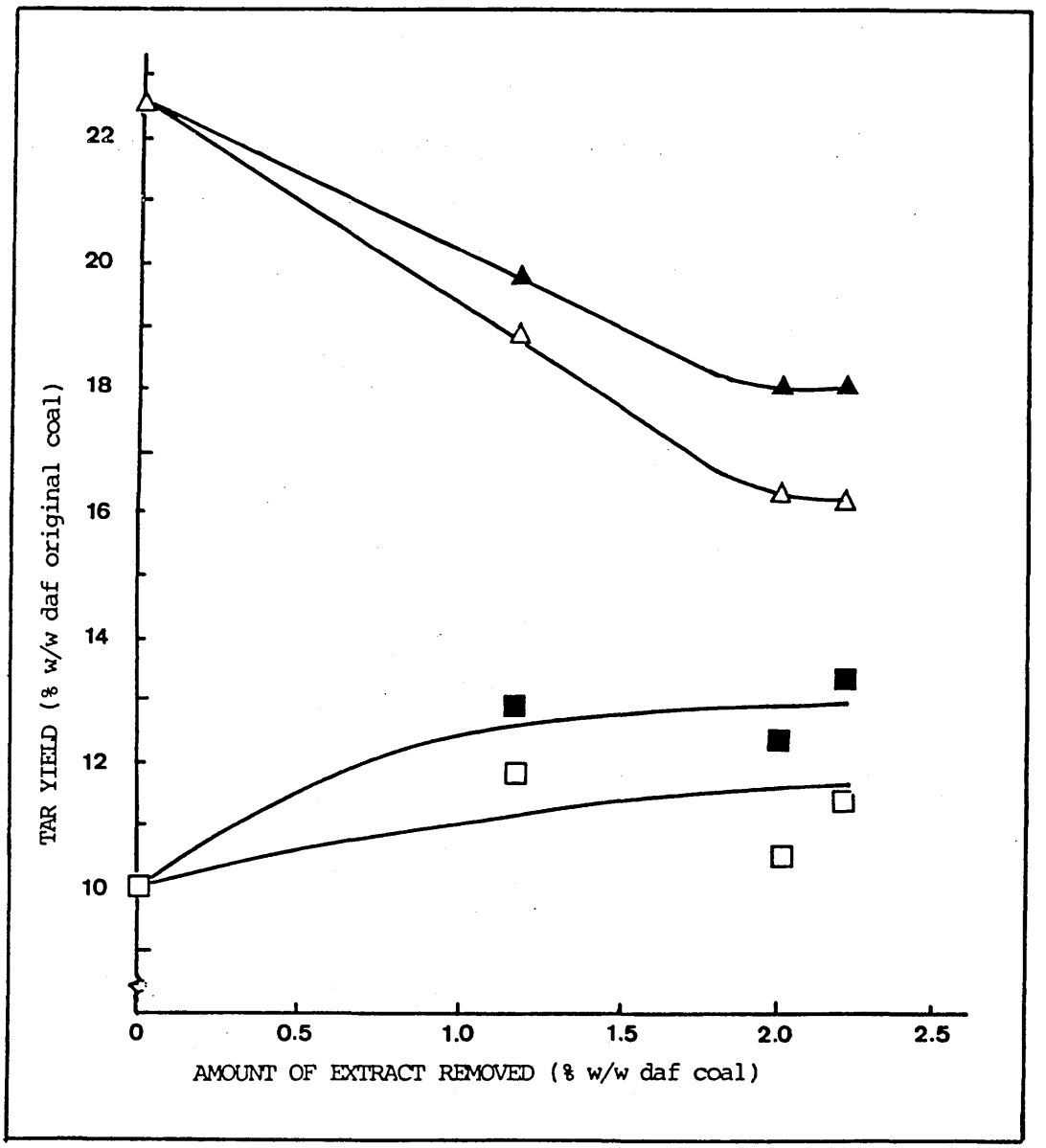
Samples of Linby coal were extracted with chloroform for 4.5 and 72 hours according to the procedures described in Chapter 6. The yields of chloroform soluble material from these extractions are shown in Table 9.4. The extraction residues were pyrolysed under 50 bar hydrogen and 50 bar helium, using a heating rate of 5°C/s to a peak temperature of 580°C. The gas flowrate set was that used in flow regime 1 (see section 9.1.2).

Table 9.4. Chloroform extraction yields from Linby coal as a function of extraction time. Yields on % w/w daf coal.

Extraction Time (hours)	Yield
4.5	1.16
25	1.97
72	2.16

The tar yield from the pyrolysis experiments as a function of the extent of extraction is shown in Figure 9.11.

Figure 9.11 Tar yield as a function of the amount of extract removed for the pyrolysis of Linby coal in the hot-rod reactor at 50 bar with a peak temperature of 580-90°C: Tar yield under H_2 (Δ); Tar yield + extract under H_2 (▲); Tar yield under He (□); Tar yield + extract under He (■).



More detailed results are shown in Table III.4. Under hydrogen, the tar yield declines steadily upto 2% extract removal, with an apparent plateau at the greater extent of extraction. This finding would appear to confirm the role of the extractable material as an intermediate in the action of molecular hydrogen in promoting tar formation during hydropyrolysis.

Under helium, despite the scatter in the data, the tar yield is observed to increase with the amount of extract removed. As the amount of extract removed is increased, the agglomeration of the char is reduced. These results parallel the trend observed for the 25 hour extracted sample and suggest that the effect may be due to the reduced plasticity of the extracted sample.

9.1.4.3 EFFECT OF EXTRACTION ON THE PYROLYSIS TAR STRUCTURE

The results from the analysis of the tars obtained from the pyrolysis of extracted Linby are shown in Table 9.5. Extraction has a noticeable effect on the structure of the tars formed in pyrolysis in both helium and hydrogen.

Under helium, at 1 bar pressure, the tar from the extracted Linby has a higher mean molecular weight and a lower hydrogen aromaticity than the untreated sample. These differences cannot be explained by adding the analyses of the extract to those of the tar from the

extracted coal, and may result from the chemical activity of the extract or its absence, or may be due to the lack of plasticity shown by the extracted Linby.

Table 9.5 Analysis of tars formed in the pyrolysis of chloroform extracted Linby coal in the hot-rod reactor over a range of pressures.

Extract Yield	Press (bar)	Gas	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
1.97[c]	1	He	25	22	7	31	15	380
1.97[c]	30	He	22	22	6	33	17	340
1.97[c]	50	He	22	18	7	35	18	320
1.97[c]	40	H_2	28	30	6	26	10	340
1.97[c]	50	H_2	30	27	5	27	11	320
1.16[d]	50	He	24	27	6	32	11	300
1.16[d]	50	H_2	33	28	6	24	9	340
2.16[e]	50	He	25	25	7	30	13	390
2.16[e]	50	H_2	32	25	5	28	10	370
sample impregnated with 5% $ZnCl_2$								
1.97[c]	50	H_2	35	30	6	19	10	440

a - ^{1}H-NMR assignments as defined in Appendix I.

b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

c - 25 hour extraction

d - 4.5 hour extraction

e - 72 houe extraction

As the helium pressure rises and the tar yield falls,

the aromaticity of the tar from the extracted Linby falls, paralleling the result for the untreated sample, although the rate of decline with pressure is greater for the untreated coal. The tar from the pyrolysis of untreated Linby at 50 bar has a lower aromaticity than the tar from the pyrolysis of the extracted sample under the same conditions. Under these conditions the tar yield from the extracted coal exceeds that from the untreated coal. The samples from the 4.5 and 72 hour extracted Linby confirm this trend, the aromaticity of the tar essentially rising with the extent of extraction, together with the tar yield.

As can be seen from comparison of Tables 9.2 and 9.5, the mean molecular weight of the tar from the extracted Linby appears to decrease with helium pressure, which is opposite to the trend observed for the untreated coal. However, the effect of extent of extraction at 50 bar on the mean molecular weight is unclear and so does not confirm the trend.

The changes in the structure of the tars from the untreated Linby as the helium pressure increases, occur as a result of secondary reactions, the extent of which increase due to the additional mass transfer resistance imposed by the increase in pressure. The secondary reactions also cause changes in the structure of the tars from the extracted Linby. However, due to the lack of plasticity of the extracted Linby during pyrolysis, the nature and extent of these secondary reactions

differ, presumably due to the shorter residence time of the volatiles within the parent coal particle during the pyrolysis of the extracted sample.

Both sets of tars show decreases in aromaticity with increasing pressure, presumably due to the greater vulnerability of more aromatic tar molecules to secondary reactions in the vicinity of coal particles, though this is not the case for in-flight cracking (Collin and co-workers, 1980). The decrease of aromaticity of the tar from the extracted Linby is less pronounced than in the case of the untreated coal.

The effect of pressure on the mean molecular weight of the tar from the two coal samples is appears to be contradictory, though this result is not confirmed by the analyses of tars obtained for the pyrolysis of 4.5 hour and 72 hour extracted Linby under 50 bar helium. The decrease of the mean molecular weight of tar from the extracted sample may be due to secondary cracking which is the extent of which is enhanced because of the lack of plasticity of the extracted Linby. For the untreated Linby, the increase in the molecular weight from the untreated coal is presumably due to repolymerisation reactions.

The differences between the structures of the tar from the untreated and extracted Linby under helium parallel the trend observed for the char/gas yield from the pyrolysis of the two samples as the helium pressure

increases (see Tables III.2 and III.4). For the extracted Linby, gas-phase cracking is the dominant secondary reaction occurring as the pressure rises, shown by a large increase in gas yield. For untreated Linby, a substantial amount of repolymerisation also occurs, indicated by the larger increase in the char yield. As for the differences in the structure of the tar, the difference in behaviour is probably due to the lack of plasticity of the extracted Linby.

Under hydrogen, as the pressure is increased, the aromaticity of the tar from the extracted coal increases, while the mean molecular weight remains approximately constant. This trend, confirmed by the results for the samples from the 4.5 and 72 hour extracted samples, is the same as for untreated Linby, where the increase in aromaticity is appears to be due to dealkylation reactions. The hydrogen aromaticity of the tar from the untreated Linby is consistently higher than the value from the untreated coal suggesting that, although the reactions causing these changes in structure are the same for both the extracted and untreated Linby, these reactions occur to a lesser extent during the pyrolysis of the extracted Linby than for the untreated coal. This may be due to the either the chemical action of the extractable material, or the lack of plasticity exhibited by the extracted coal.

9.1.4.4 HYDROPYROLYSIS OF EXTRACTED LINBY COAL IMPREGNATED WITH 5% ZINC CHLORIDE

Chloroform extraction has been shown to have a substantial effect on the catalytic activity of zinc chloride in the flash pyrolysis of Linby coal. Impregnation of the extracted coal with zinc chloride resulted in a decrease in the tar yield from flash pyrolysis, a reversal of the trend observed for the flash pyrolysis of impregnated but unextracted Linby. The effect of chloroform extraction on the activity of zinc chloride in hydropyrolysis was examined in the hot-rod reactor.

A sample of 25 hour extracted Linby was impregnated with 5% $ZnCl_2$ and pyrolysed under 50 bar hydrogen pressure. A heating rate of $5^{o}C/s$ to a peak temperature of $580-90^{o}C$. The gas flowrate set was that used in gas flow regime 1 (see section 9.1.2).

The tar yield from the extracted catalyst impregnated sample is only 2.1% less than the yield from the untreated, catalysed Linby. This is approximately equal to the amount material removed during the 25 hour extraction with chloroform. The gas yield from the extracted catalysed coal is also similar to that from the untreated catalysed Linby.

Table 9.6. The effect of impregnation with 5% $ZnCl_2$ on the hydropyrolysis at 50 bar of untreated and extracted Linby coal. Yields on % w/w dacf[a] basis of the original coal.

Sample	Catalyst	Tar	Char	Gas[b]
Untreated Linby	--	22.5	57.7	19.8
Extracted Linby	--	16.0	nd	nd
Untreated Linby	5% $ZnCl_2$	29.0	37.3	33.7
Extracted Linby	5% $ZnCl_2$	26.9	41.2	29.9

a - dacf - Dry, ash and catalyst free

b - gas - gas by difference

The results from analysis of the tars from the hydropyrolysis experiments are shown in Table 9.5. The analysis of the tar from the extracted, catalysed sample is very similar to the analysis of the tar from untreated zinc chloride impregnated Linby.

These results suggest that the low molecular weight extractable material does not play a role as an intermediary in the action of zinc chloride under hydropyrolysis conditions. This implies that there are significant differences between the mechanism by which zinc chloride acts in hydropyrolysis and in flash pyrolysis in an inert atmosphere.

9.1.4.5 THE NATURE OF THE ROLE OF THE CHLOROFORM EXTRACTABLE MATERIAL IN PYROLYSIS AT ELEVATED PRESSURE

Low molecular weight extractable material has been shown to play a significant role in coal liquefaction (Larsen and co-workers, 1980), in coke formation (Dryden and Pankhurst, 1955; Brown and Waters, 1966a), in flash pyrolysis and in catalytic flash pyrolysis (see Chapter 7). Three different types of mechanism have been suggested as a means to explain the action of the extractables in these processes, these being: hydrogen donation (Brown and Waters, 1966b; Neaval, 1981), hydrogen shuttling (Larsen and co-workers, 1980; Grint and co-workers, 1984) and a physical solvating effect (Grint and co-workers, 1984; Snape, 1986).

The action of the extractables in flash pyrolysis is discussed in Chapter 7. In the case of Linby coal, it was proposed that the predominant mechanism by which the extractable material acts to promote tar formation is the physical solvating role, with the other mechanisms occurring to lesser extents. However, experiments to determine the effect of pressure on the pyrolysis of Linby coal were performed at a heating rate of $5^{o}C/s$. At 1 bar, and at elevated helium pressures, the extractable material appears to play no role in promoting tar formation. The tar yield from the extracted coal when added to the extract yield is equal to, or greater than the tar yield from untreated Linby. Changes in the tar

structure from the extracted Linby probably result from the lack of plasticity shown by the extracted sample during pyrolysis, and the attendant increase in the ease of mass transfer.

The difference between the effect of the extractables at low heating rate and that in flash pyrolysis is thought to be that in slow pyrolysis at atmospheric pressure, the extractable material either evaporates or undergoes retrograde reactions before it can play a role in promoting tar formation. In flash pyrolysis, the extractables material remains present up to higher temperatures before it is expelled from the parent coal particle, and so is available to play a role during the main phase of tar formation.

In hydropyrolysis at elevated pressure, the extractable material appears able to promote tar formation. However, the results from pyrolysis of extracted Linby coal under helium, at atmospheric and elevated pressure, suggest that the extractable material should not be present to play such a role at the temperature of tar formation at this heating rate. The results obtained under hydrogen suggest that any or all of three processes may be occurring:

(1) The presence of high pressure hydrogen prevents the extractable material from undergoing retrograde reactions which may prevent it from promoting tar formation in experiments at atmospheric pressure and in

inert gas at the same heating rate.

(2) The high pressure hydrogen hydrogenates the coal in some manner at a temperature lower than that at which the chloroform extractable material is lost, utilising the extractable material in this process.

(3) The application of high pressure hydrogen promotes tar formation at a lower temperature than during pyrolysis at atmospheric pressure, at a temperature at which the extractable material remains available in the coal to play a role in promoting tar formation.

Any or all of these processes may be occurring during hydropyrolysis. However, data obtained by the National Coal board indicates that the temperature at the maximum tar yield is abtained in pyrolysis under a hydrogen pressure of 300 bar, is the same as in pyrolysis at 1 bar pressure, that is at 580^{o}C (NCB - Unpublished data). This suggests that the hypothesis (3) is unlikely to be occurring. Both the other theories imply that the externally applied hydrogen interacts with the coal structure (via the extractables) in promoting tar formation, and does not merely act in the gas phase increasing the stability of tar molecules, as has been implied elsewhere (Howard, 1980). The first hypothesis appears to be the more viable, and does not demand any specific mechanism for the role of the extractable material in promoting tar formation. Any one of the mechanisms listed in the first paragraph of this section

adequately fits the hypothesis. As in flash pyrolysis, the predominant mechanism by which the chloroform extractables act is probably the proposed solvating effect, although hydrogen shuttling will probably occur to an appreciable extent, due to the availability of molecular hydrogen.

The second hypothesis demands that the extractable material plays a hydrogen shuttling role in transferring hydrogen from the gas phase to the coal macromolecule.

9.2 HYDROPYROLYSIS OF A RANGE OF COALS

The hydropyrolysis of two other British hard coals, Taff Merthyr and Cortonwood Silkstone, and the Turkish lignite, Canakkale Can, was studied in the hot-rod reactor. A series of preliminary experiments were performed at 1 bar (gauge) pressure. These were to determine the temperature of the tar yield maximum for Can, and to provide "base-case" data for all samples studied.

Following these initial experiments, samples of the coals and the lignite were pyrolysed under 50 bar hydrogen pressure. In addition, the effects of impregnation with 5% zinc chloride, and of 25 hour chloroform extraction on pyrolysis at 50 bar hydrogen pressure were studied.

The following sections describe and discuss the results

of these experiments, and the effect of the parameters studied on the structure of the tars.

9.2.1 PRELIMINARY EXPERIMENTS

Preliminary experiments were performed on Taff Merthyr and Cortonwood Silkstone at 580-600°C under helium at 1 bar (gauge) pressure to determine base case data. The heating programme used was the same as for previous experiments, and the gas flow was set to produce a superficial velocity of 0.1 m/s at peak temperature. For Canakkale Can, flash pyrolysis experiments in the fluidised bed reactor have shown that the maximum for the tar yield occurs at a lower temperature than for the hard coals (See Chapter 7). Preliminary pyrolysis experiments on the Can were performed using a range of peak temperatures to determine whether a similar effect is observed in the hot-rod reactor, and to establish base case data at the temperature of the maximum tar yield.

Pyrolysis of the Can with the tar traps cooled as for previous experiments resulted in a large pressure drop developing during the experiment. This was probably due to the secondary trap, which was cooled by liquid nitrogen, becoming blocked by condensed carbon dioxide. For all subsequent experiments on the lignite, the secondary trap was cooled with a ice/water/salt mixture whose temperature was -15°C. This prevented the second trap from becoming blocked, and appeared to trap all the

tar which was produced.

The effect of peak temperature on the tar and total volatiles yield from Can is shown in Figure 9.12. The results are shown in more detail in Table III.5. As for flash pyrolysis experiments, the maximum for the tar yield is shifted to 520-530°C. This is probably due to the lower thermal stability of the more oxygenated tar formed in the pyrolysis of the lignite. All remaining experiments on the Canakkale Can were performed with a peak temperature of 520-530°C.

The base case tar and total volatiles yield from the hard coals and the lignite are shown in Figure 9.13. More detailed results are shown in Table III.5. Also shown is the tar yield from flash pyrolysis experiments in the fluidised bed. As observed in flash pyrolysis experiments, the tar yield is highest for a coal carbon content of 80-82%. However the tar yields from the pyrolysis in the hot-rod reactor are substantially lower than those from the fluidised bed. This should be expected as the heating rate of the coal in the fluidised bed is thought to be much higher than that in the hot-rod reactor. The largest discrepancy between the tar yield results from the two reactors is for Cortonwood Silkstone. In the case of the hot-rod, the yield is only 8.1%, whereas from the fluidised bed, the tar yield is 26%. The reason for this may be the enhanced plasticity of Cortonwood Silkstone, which is known to be a good coking coal (Analysis given in Table 6.1).

Figure 9.12 Tar yield as a function of peak temperature for the pyrolysis of Canakkale Can in the hot-rod reactor at 1 bar pressure under helium.

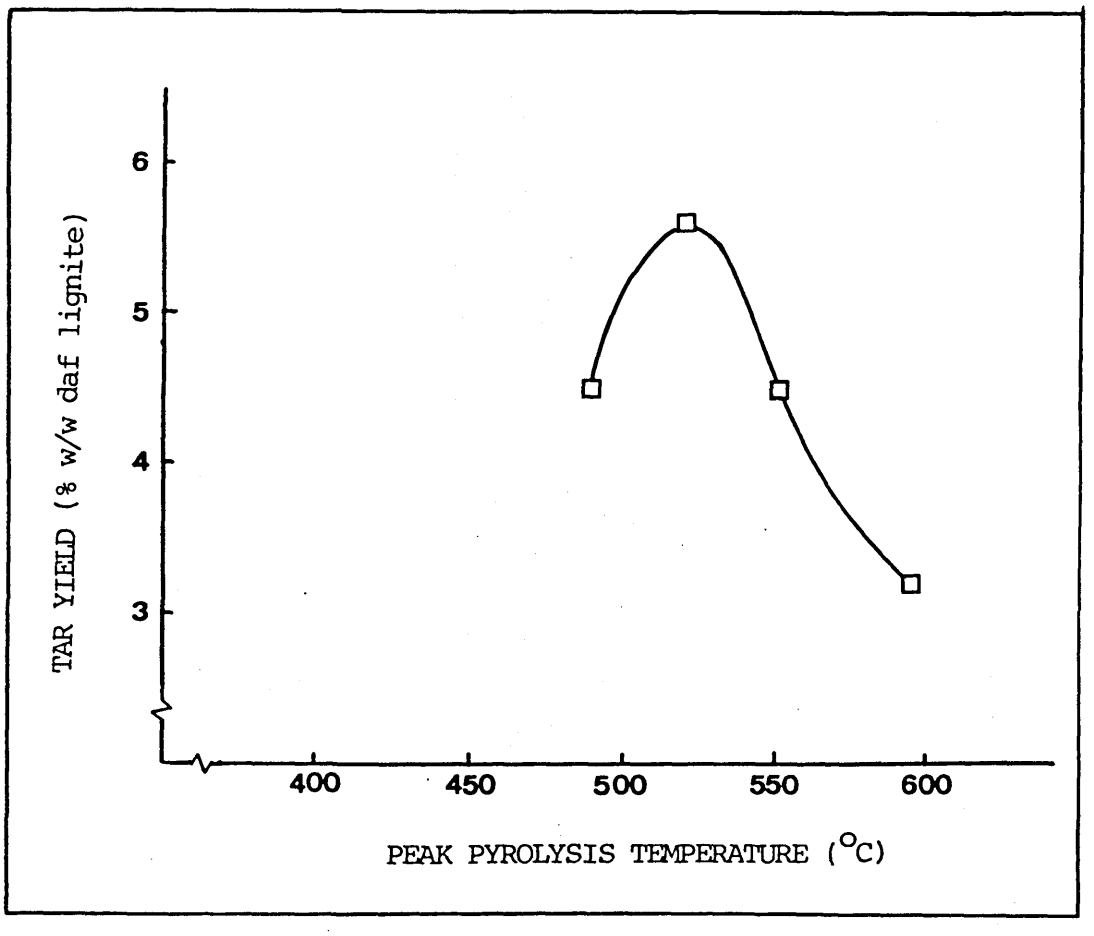
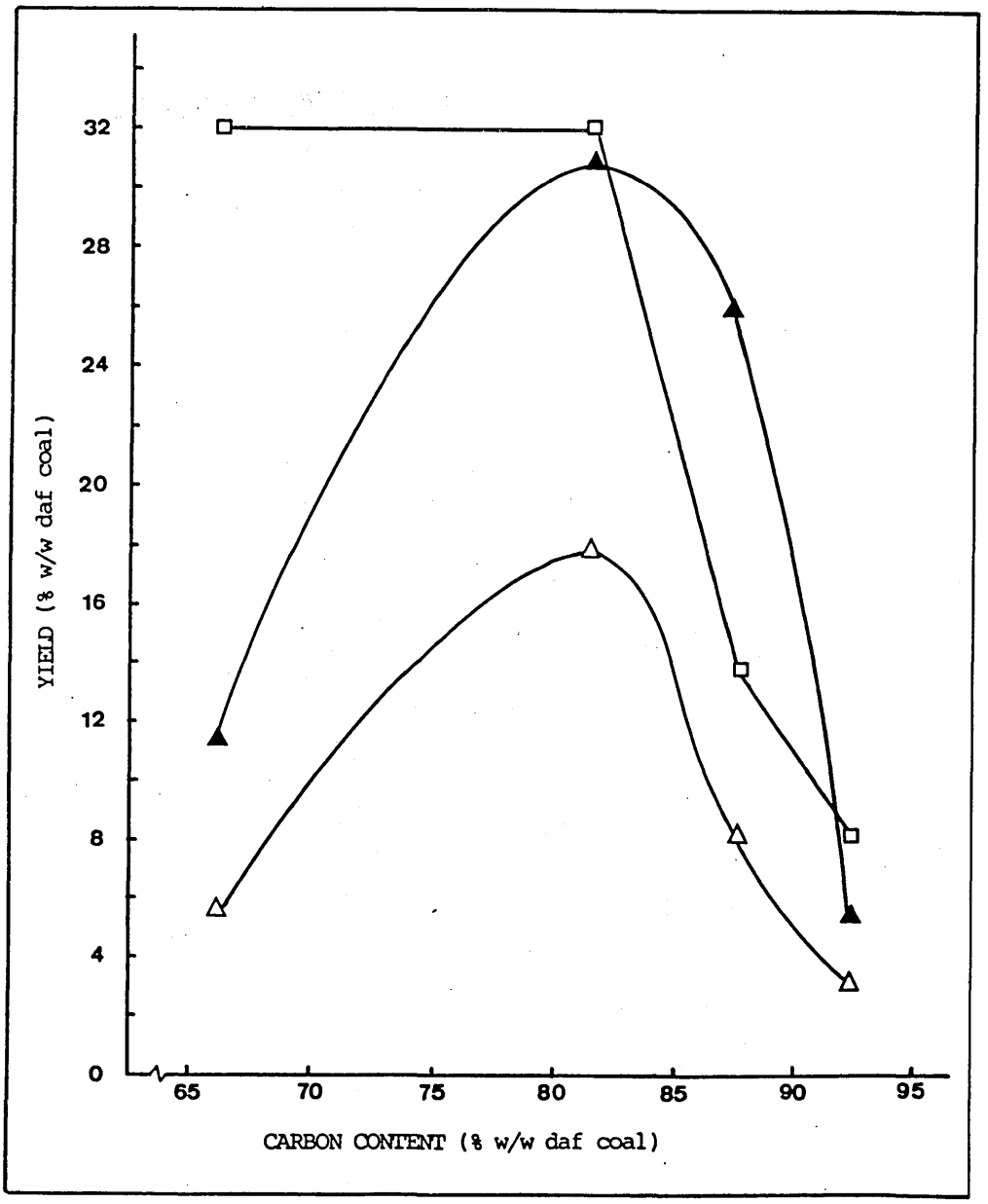


Figure 9.13 Tar and total volatiles yields as a function of carbon content for the pyrolysis of a range of coals in the hot-rod reactor at 1 bar under helium with a peak temperature of 580-90°C: tar yield (Δ); total volatiles yield (□); tar yield from the fluidised bed (▲).



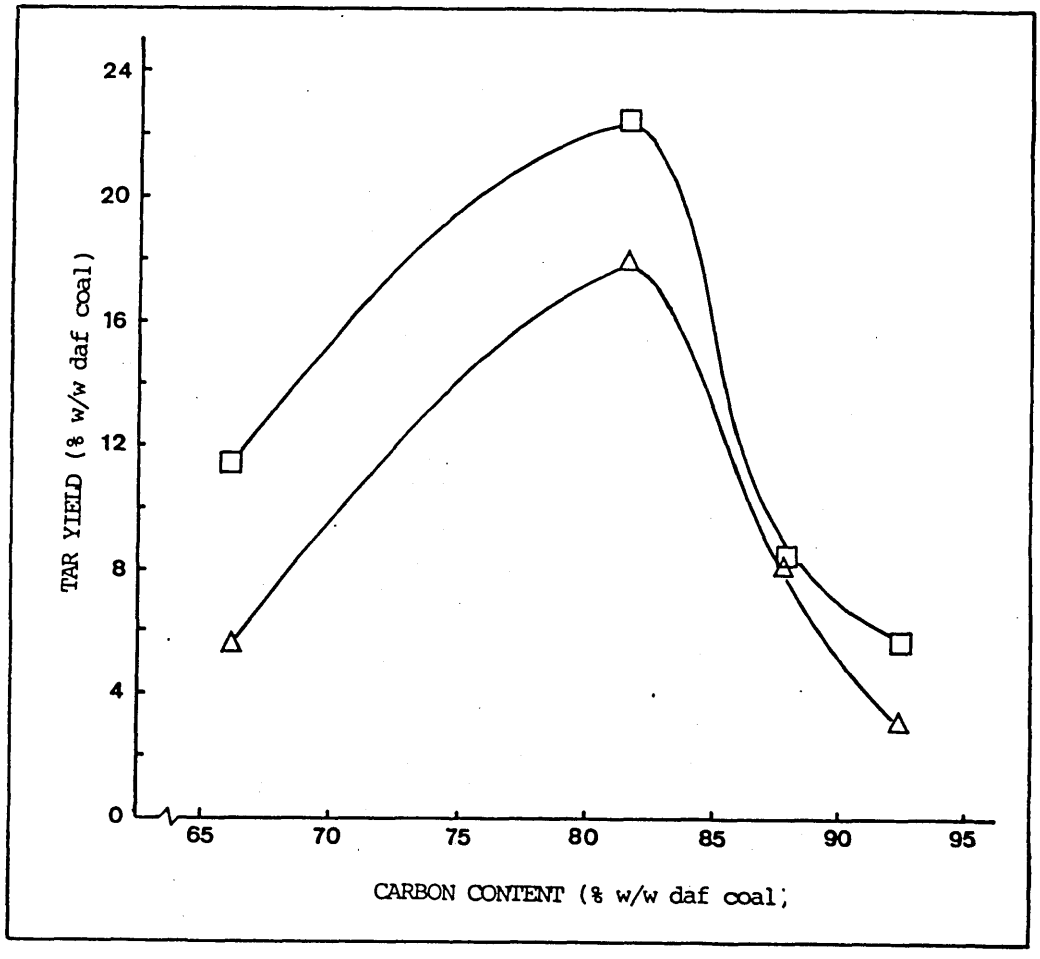
The char from Cortonwood forms into a hard "pencil" during pyrolysis in the hot-rod reactor, suggesting that some of the drop in the tar yield results from secondary reactions, occurring in either the individual coal particles or in the coal mass, the extent of which are promoted by the greater resistance to mass transfer of the volatiles by the plasticity of the coal. Neither Can nor Taff Merthyr samples showed any tendency to agglomerate during pyrolysis.

9.2.2 EFFECT OF HIGH PRESSURE HYDROGEN

Experiments to determine the effect of high pressure hydrogen on the pyrolysis of the range of coals were performed at 50 bar, using the same conditions as the preliminary experiments. The tar yields from these experiments are shown in Figure 9.14. More detailed results are given in Table III.6.

The tar yields from both Taff and Can are enhanced by the high pressure hydrogen, in a similar manner to Linby. Under hydrogen, the tar yields from both samples exceed the maximum tar yields obtained at 1 atmosphere in the fluidised bed. This is not observed in the case of Linby coal. From Cortonwood Silkstone however, the tar yield from the hydropyrolysis is only 0.2% greater than the yield obtained under helium at 1 bar. Similarly the yield of total volatiles (see Table III.6) from Taff and Can increase substantially as a result of the presence of the high pressure hydrogen, whereas the

Figure 9.14 Tar yield as a function of carbon content for the pyrolysis of a range of coals in the hot-rod reactor at 50 bar under hydrogen with a peak temperature of 580-90°C: result under 50 bar H_2 (□); result under 1 bar He (Δ).



yield from the Cortonwood shows only a small increase as a result of the hydrogen.

The tendency of coals to undergo plasticity and agglomerate during pyrolysis has been shown to be enhanced by the application of high pressure, and by the application of hydrogen (Fynes and co-workers, 1984). In pyrolysis under 50 bar hydrogen pressure, the plasticity of the Cortonwood Silkstone was enhanced, as was to be expected, with the result that the char formed into a hard, coke-like pencil, harder than the char formed at 1 bar helium, or than any of the chars formed from Linby. It would appear that the increase in the bulk plasticity of the coal inhibits the mass transfer of volatiles following their formation in either individual particles or in the coal bed.

In order to test this theory, a hydropyrolysis experiment was performed on a 50:50 w/w mixture of Cortonwood Silkstone with sand (acid washed, 100-40 Mesh obtained from BDH Chemicals). The effect of the sand was to prevent the coal from agglomerating during pyrolysis. Evidence for this was observed when, at the end of the experiment, the char/sand mixture could be pushed out of the hot-rod as a powder. The results from the experiments are shown in Table 9.7. The presence of the sand did not result in an increase in the tar yield. This result would suggest that the bulk plasticity of the coal may not be the cause of the absence of an increase in the tar yield under high pressure hydrogen.

However, the plasticity of individual coal particles may inhibit the mass transfer of volatiles in pyrolysis. This inhibition of mass transfer would render the volatiles more liable to undergo secondary reactions, which would diminish the yield of tar, counteracting the effect of high pressure hydrogen in enhancing tar formation. This will be further discussed in the discussion section.

Table 9.7 Effect of admixing with sand on the hydropyrolysis of Cortonwood Silkstone. Yields on a % w/w daf basis.

Sample	Gas	Pressure	Tar	Gas[a]	Char
Coal	He	1 bar	8.1	5.3	86.6
Coal	H_2	50 bar	8.3	7.7	84.0
Coal + Sand[b]	H_2	50 bar	7.6	5.7	86.7

a - gas - by difference

b - 50/50 w/w mixture of coal + sand

Analysis of the tars

The tars formed in pyrolysis and hydropyrolysis of the untreated coals were analysed by ^{1}H-NMR and vapour pressure osmometry. The result of these analyses are shown in Table 9.8. The aromaticity of the tar formed in the pyrolysis at 1 bar in general increases with rank, with the mean molecular weight remaining approximately constant over the range of carbon contents. The aromaticity of the tar from the pyrolysis of Cortonwood

Silkstone is higher than that of Taff Merthyr. This may be due to the plasticity of the Cortonwood Silkstone which enhances the extent of secondary reactions which increase the aromaticity. The effect of hydrogen pressure is to cause an increase in the hydrogen aromaticity for all samples. There is no apparent effect on the mean molecular weight of the tar, which suggests that circumstances of the evaporation stage of mass transfer of volatiles are similar under both sets of conditions.

Table 9.8 Analysis of the tars form the pyrolysis of a range of coals in a hot-rod reactor at 1 bar helium pressure and under 50 bar hydrogen.

Sample	pressure (bar)	gas	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
Can[c]	1	He	10	19	10	45	16	290
Can[c]	50	H_2	22	25	6	34	13	310
C'wood[d]	1	He	37	23	4	25	11	330
C'wood[d]	50	H_2	45	19	3	22	11	300
Taff[e]	1	He	32	14	8	33	13	290
Taff[e]	50	H_2	35	16	7	30	12	280

a - ^{1}H-NMR assignments as defined in Appendix I.

b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

c - Canakkale Can

d - Cortonwood Silkstone

e - Taff Merthyr

This trend is as observed for Linby. As discussed in Section 9.1.2, an explanation of this is that the hydrogen participates in dealkylation reactions, causing a decrease in the aliphatic content of the tar with the result that the aromaticity rises.

Discussion

To summarise, the effect of high pressure hydrogen on the pyrolysis of Taff Merthyr and Canakkale Can is to cause an increase in the yields of tar and gas. High pressure hydrogen also causes an increase in the hydrogen aromaticity of the tar. These trends are similar to those observed for Linby coal, described in Section 9.1.2. For Cortonwood Silkstone, hydrogen pressure did not cause an increase in the tar yield. This appears not to be due to the bulk agglomeration of the char. The absence of an increase in tar yield from Cortonwood Silkstone with the application of high pressure hydrogen is due to either the inhibition of the mass transfer of volatiles from individual particles due to their plasticity, and the inability of the hydrogen to promote tar formation to the same extent as in the other coals and the lignite.

The enhanced plasticity of individual particles would be expected to inhibit the transport of the volatiles within coal particles and the transport of hydrogen into coal particles. The first effect would make the volatiles more liable to undergo secondary

reactions, with the result that tar would be lost due to repolymerisation, which would occur as the volatiles would still be in contact with the parent coal particle. The inability of hydrogen to penetrate the interior of coal particles would prevent it being able to stabilise free-radicals following their formation during pyrolysis.

It should be noted that the increase in the gas yield from Cortonwood Silkstone, as a result of the application of high pressure hydrogen, is much lower than for Linby or Canakkale Can, and is only equal to that for Taff Merthyr. This also suggests that the hydrogen is unable to gain access to the majority of hydrogasification sites in the coal/char. Hydrogasification is known to occur to a significant extent at these temperatures and pressures. If the hydrogen is unable to gain access to the interior of the coal particle to participate in hydrogasification, it is probable that this is also be the case in the promotion of tar formation in hydropyrolysis.

9.2.3 EFFECT OF IMPREGNATION WITH ZINC CHLORIDE ON HYDROPYROLYSIS

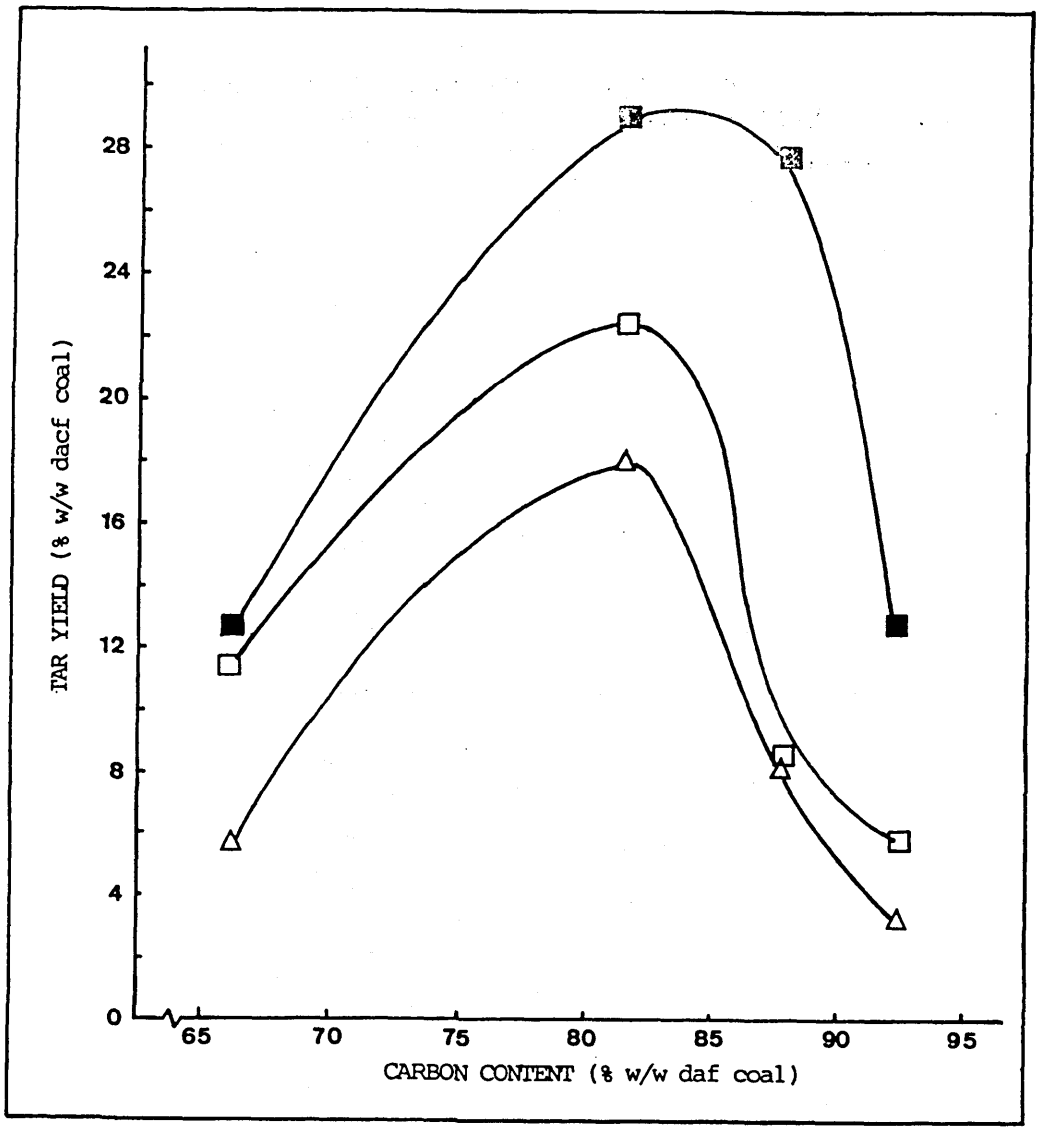
The effect of zinc chloride impregnation on coal pyrolysis product distributions at atmospheric pressure was shown in the previous chapter. The presence of zinc chloride increases the tar yield in the flash pyrolysis of hard coals, a trend which is reversed in slow

pyrolysis. Zinc chloride causes a decrease in the tar yield in the flash pyrolysis of Canakkale Can. Zinc chloride has also been shown to catalyse coal liquefaction, under high pressure hydrogen (See Chapter 4).

The effect of zinc chloride on the hydropyrolysis of Linby coal was shown in section 9.1.3. Zinc chloride was shown to produce large increases in the yields of both tar and total volatiles. This section shows the effect of zinc chloride impregnation on the hydropyrolysis of two other hard coals and the lignite. Samples of Cortonwood Silkstone, Taff Merthyr and Canakkale Can were impregnated with 5% $ZnCl_2$ using the method described in Chapter 6. Hydropyrolysis experiments were performed at 50 bar pressure using the same conditions as in the previous section.

The tar yields from the experiments on the catalyst impregnated samples are shown in Figure 9.15, superimposed on the results for the hydropyrolysis and 1 bar pyrolysis of untreated samples. More complete results are shown in Table III.7. The effect of zinc chloride is to cause an increase in the tar yield for all samples studied. The increase for Can is small although a substantial increase in the gas yield is noted. For Cortonwood Silkstone, the presence of the zinc chloride causes the tar yield to increase dramatically from 8.3 to 27.7%.

Figure 9.15 Tar yield as a function of carbon content for the pyrolysis of a range of coals impregnated with 5% zinc chloride in the hot-rod reactor at 50 bar under hydrogen with a peak temperature of 580-90°C: 5% $ZnCl_2$-impregnated coals under 50 bar H_2 (■); untreated coal 50 bar under H_2 (□); untreated coal under 1 bar He (△).



As was the case for the hydropyrolysis of Linby, the zinc chloride also prevented the coal from agglomerating during the hydropyrolysis, the char being pushed out of the hot-rod as a powder. These two phenomena appear to be linked: the loss of plasticity may facilitate the access of hydrogen to the pyrolysing coal enabling it to further promote tar formation. For Taff Merthyr, a substantial increase in both the tar and gas yield is observed. The apparent lack of activity of the catalyst in the hydropyrolysis of Canakkale Can parallels the results obtained in flash pyrolysis at atmospheric pressure, where impregnation with zinc chloride causes the tar yield to decline.

Analysis of the tars

The tars from the experiments were analysed by ^{1}H NMR and by vapour pressure osmometry. The results of these analyses are shown in Table 9.9. The effect of zinc chloride on the structure of the tars from the hydropyrolysis of Linby was to cause the mean molecular weight and hydrogen aromaticity to increase. However, the effect on the tars from Cortonwood and Taff is somewhat different. In both cases, the effect is to increase the mean molecular weight and to cause a decrease in the hydrogen aromaticity. The tar from the zinc chloride impregnated Can was not analysed.

Table 9.9 Analysis of tars formed in the pyrolysis of 5% zinc chloride impregnated coals in the hot-rod reactor under 50 bar hydrogen.

Coal	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
Cortonwood						
Silkstone	40	25	4	21	10	360
Taff Merthyr	24	13	— 51 —		12	370

a - ^{1}H-NMR assignments as defined in Appendix I.

b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

Discussion

To summarise, the presence of zinc chloride causes an increase in the tar yield in the hydropyrolysis of all the coals studied together with the lignite. For the Cortonwood and the Taff, the tars from the catalyst impregnated coals are less aromatic and have a higher mean molecular weight than tars from the untreated sample obtained under the same conditions.

Effect on Canakkale Can

Impregnation with zinc chloride causes a much smaller increase in the tar yield from Canakkale Can than for the hard coals, although the catalyst does cause a substantial increase in the gas yield. The reason for

this lack of activity of the zinc chloride towards tar production from the lignite under hydrogenation conditions is probably analogous to the behaviour of the catalyst in flash pyrolysis of Can, where the effect of zinc chloride is to cause a decrease in the tar yield, a reversal of the trend observed for hard coals.

The mechanism proposed for the action of zinc chloride under hydrogenation conditions (See section 9.1) is similar to that proposed for flash pyrolysis. The action of the catalyst depends on the formation and stability of carbonium ions and/or radical cations. In discussing the results from the fluidised bed reactor, it was proposed that because the average number of aromatic rings per cluster in the lignite is small (1-2), the carbonium ion formed is insufficiently stable, and therefore liable to undergo Scholl condensation reactions prior to the hydride abstraction step. In the hydropyrolysis of Can, it appears that the availability of hydrogen to act as a source of hydride ions is higher than in pyrolysis at atmospheric pressure, and so carbonium ions formed are more likely to be stabilised by hydride abstraction before condensation reactions can occur. Therefore in hydropyrolysis the impregnation with zinc chloride causes a increase in the tar yield. However it can be hypothesised that due to the lower stability of the carbonium/radical ions formed from the lignite, the increase in the tar yield is smaller than for the hard coals studied.

Effect on Cortonwood Silkstone

The tar yield from Cortonwood Silkstone increases dramatically as a result of the presence of the zinc chloride. The addition of the catalyst also prevented the coal from agglomerating during pyrolysis. The increase in the tar yield probably results from the action in two ways: firstly in enabling the hydrogen to gain access to the interior of coal particles and facilitating the mass transfer of the volatiles out of the particles; and secondly in acting to catalyse the formation of tar in the same manner as for the other coals.

The reason why the zinc chloride reduces the tendency of the coal to agglomerate is unclear, although a similar effect was noted for all the catalysts used in fluidised bed flash pyrolysis experiments on Linby, and was also noted for Linby in hydropyrolysis. The addition of many inorganic materials has been shown to have a detrimental effect on the ability of coals to form cokes (Habermehl and co-workers, 1980), where it was proposed that the inorganic additives interfered with hydrogen transfer during coke formation. This study shows that in both flash pyrolysis and hydropyrolysis, zinc chloride has a substantial effect on hydrogen transfer and utilisation.

The effect of zinc chloride on the structure of the tars from Cortonwood Silkstone is different from its effect on the tar from Linby. In this case, the catalyst

causes a decrease in the aromaticity of the tar compared to the tar produced in the hydropyrolysis of untreated Cortonwood. There are two tentative explanations for this differing behaviour. Firstly, in the case of Cortonwood, zinc chloride may be unable to catalyse the reactions which cause the increase in aromaticity in Linby. The proposed nature of this reaction is dealkylation of aromatic structures at the beta bond position. This would be due to the original absence of sufficient concentrations of longer aliphatic side chains in Cortonwood Silkstone. Zinc chloride may also participate in the hydrogenation of aromatic rings.

Secondly, the lack of plasticity shown by the catalyst impregnated coal may mean that the volatiles are less liable to undergo secondary reaction than those from the untreated coal. The structure of the tar from the untreated coal appears to be dominated by secondary reactions, the hydrogen aromaticity is higher than for the tar obtained from Taff Merthyr. It is probable that both effects play a role to some extent.

Zinc chloride also appear to cause an increase in the mean molecular weight of the tar. This may be due higher mean molecular weight of the additional tar produced as a result of the presence of the catalyst, although the catalyst may also cause condensation reactions. The reduction in the extent of secondary reactions due to the lack of plasticity of zinc chloride-impregnated Cortonwood may also have an effect.

Effect on Taff Merthyr

The effect of impregnation with zinc chloride on the hydropyrolysis of Taff Merthyr is similar to the effect on Linby, that being substantial increases in the yield of both tar and gas. This suggests that in the case of Taff Merthyr, the action of the zinc chloride is very similar to that in the hydropyrolysis of Linby. The catalyst promotes tar formation and also hydrogasification of the char.

The effect on the tar structure is significantly different to the effect on Linby. The catalyst appears to decrease the aromaticity of the tar in comparison with the tar obtained from untreated Taff at both 1 bar helium pressure and under 50 bar hydrogen. This suggests that the zinc chloride is promoting hydrogenation reactions, and is unable to catalyse the dealkyation reactions which appear to occur in the case of Linby. This is probably due to the lower concentration of longer alkyl chains in the case of Taff Merthyr, as was proposed for Cortonwood Silkstone, and the greater ease of hydrogenation of aromatic rings due to the higher aromaticity and more condensed structure of the semi-anthracite.

9.2.4 EFFECT OF EXTRACTION ON THE HYDROPYROLYSIS OF A RANGE OF COALS

It was shown in Chapter 7 that chloroform extraction has

a substantial effect on the tar yield from the flash pyrolysis of hard coals and a lignite. The tar yield from the extraction residue was much less than the tar yield from the untreated sample, the difference being significantly greater than the amount of extract removed. In addition, chloroform extraction causes a substantial decrease in the tar yield from the hydropyrolysis of Linby coal. In this section, the effect of chloroform extraction on the hydropyrolysis of Taff Merthyr, Cortonwood Silkstone and Canakkale Can is considered.

Samples of the two coals and the lignite were extracted with chloroform for 25 hours using the method described in Chapter 6. Extract yields are presented in Table 9.10. Hydropyrolysis experiments were performed at 50 bar using a heating rate of 5^{o}C/s up to a peak temperature of 580^{o}C (530^{o}C in the case of Canakkale Can), with gas flowrates set to the values used in flow regime 1 (see section 1.1.2). The tar yields from the experiments are presented in Figure 9.16. Results are given as a % of the original coal and are superimposed on the results for the hydropyrolysis and 1 bar pyrolysis of the untreated coals. More complete results are shown in Table 9.11.

For all samples studied, the effect of chloroform extraction is to reduce the yield of tar formed in hydropyrolysis.

Figure 9.16 Tar yield as a function of carbon content for the pyrolysis of a range of chloroform extracted coals in the hot-rod reactor at 50 bar under hydrogen with a peak temperature of 580-90°C: 25 hour chloroform extracted coal 50 bar H_2 (▼); untreated coal 50 bar H_2 (□); untreated coal 1 bar He (Δ).

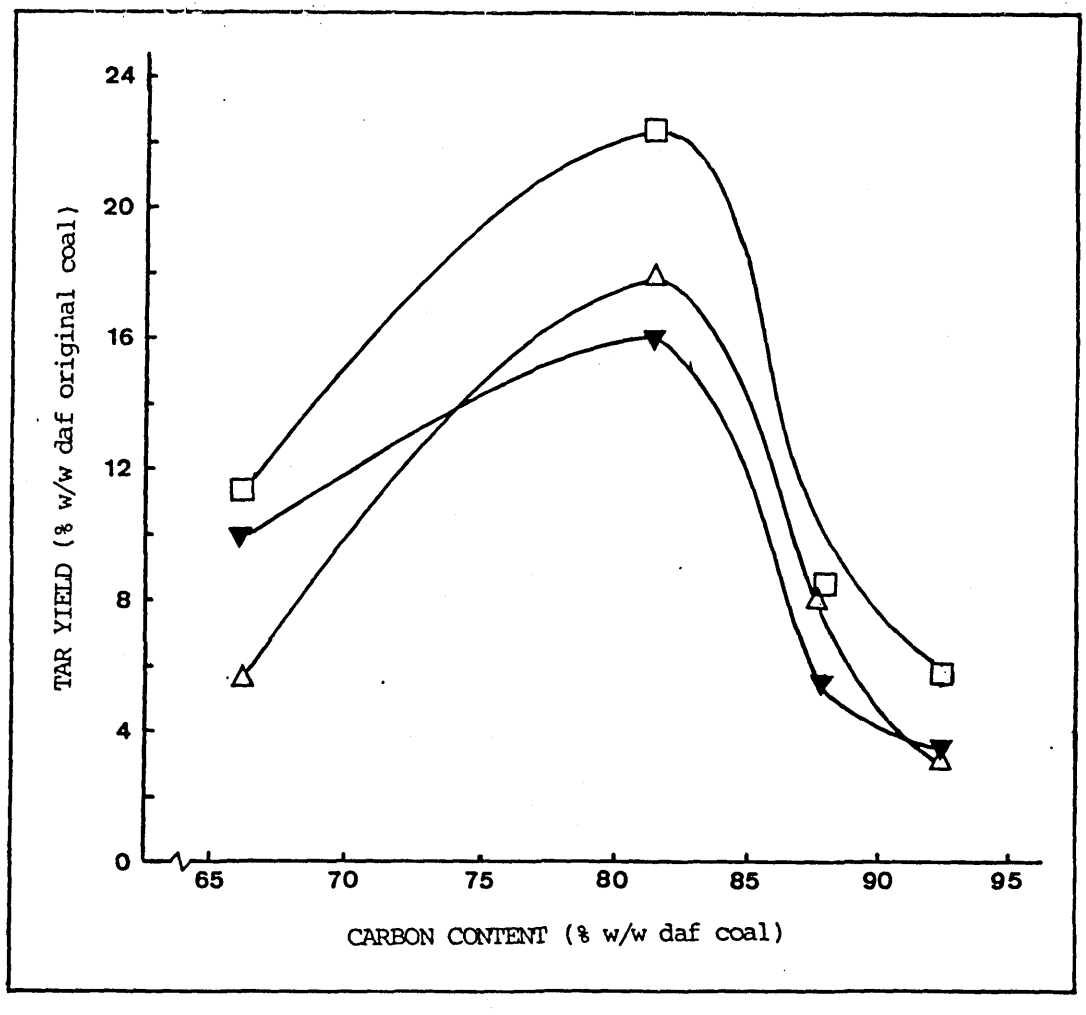


Table 9.10. 25 hour chloroform extraction yields from an array of coals. Yields on a % w/w daf basis.

Coal	Extract Yield	Pentane Soluble Fraction
Canakkale Can	1.17[a]	0.70[a]
Linby	1.97[a]	0.67[a]
Cortonwood Silkstone	0.25	nd[b]
Taff Merthyr	0.11	nd[b]

a - mean value from two different extractions

b - nd - not determined

The effect on Canakkale Can is small, the difference between the results from the untreated and the extracted lignite being 1.5%. Assuming that the 1.2% extract removed is potentially volatile material, the net difference between the extracted and untreated lignite is only 0.3%. This shows that the extractable material does not play a measurable intermediary role in tar formation during the hydropyrolysis of Can lignite, other than acting as a volatile component.

For both Cortonwood Silkstone and Taff Merthyr, extraction reduces the tar yield by an amount much greater than the yield of chloroform extract. It should be noted that extracted Cortonwood formed into a hard, agglomerated pencil, during hydropyrolysis, although the pencil was not so hard that from the untreated coal.

Table 9.11 Effect of extraction on the Hydropyrolysis of a range of coals at 50 bar. Yields on a % w/w daf basis of the original coal.

Sample	Tar	Gas[a]	Char
Untr.[b] Can	11.4	37.8	50.8
Extr.[c] Can	9.9	36.3	52.6
Untr.[b] Cortonwood	8.3	7.7	84.0
Extr.[c] Cortonwood	5.5	1.8	92.4
Untr.[b] Taff	5.8	7.6	86.6
Extr.[c] Taff	3.6	4.4	91.9

a - Gas - by difference

b - Untr. - Untreated coal

c - Extr. - 25 hour chloroform extracted coal

This is different to the trend observed for Linby in hydropyrolysis where the extracted coal showed no tendency to agglomerate, or the behaviour of Cortonwood in flash pyrolysis, where extraction prevented the coal from agglomerating. However, Neuburg and co-workers (in press) have shown that heating Cortonwood Silkstone to temperatures between 300 and 400^{o}C releases a substantial amount of chloroform extractable material (approx. 8% w/w daf coal), which is believed to be present in the original coal. This additional chloroform extractable material is thought to be able to play a role in the development of plasticity (Dryden and Pankhurst, 1955), although it appears that it is unable to play a role in promoting tar formation the flash

pyrolysis or hydropyrolysis of Cortonwood Silkstone.

Analysis of Tars

The results of the analyses of the tar formed in the hydropyrolysis of chloroform extracted coals are shown in Table 9.12. The effect on the tar structures observed for both hard coals and for the lignite are similar to those observed for Linby. For both Taff Merthyr and Cortonwood Silkstone, the hydrogen aromaticity of the tar from the extracted coal is lower than that formed in the hydropyrolysis of the untreated coal, while the mean molecular weight is higher than that for the untreated sample.

Table 9.12 Analysis or tars formed in the pyrolysis of 25 hour chloroform extracted coals in the hot-rod reactor under 50 bar hydrogen.

Sample	H_{ar}[a]	H_{α}[a]	H_{β}[a]	H_{n}[a]	H_{γ}[a]	MW[b]
Canakkale Can	22	22	7	35	14	340
Cortonwood Silkstone	37	16	4	29	14	360
Taff Merthyr	22	13	— 49 —		16	310

a - ^{1}H-NMR assignments as defined in Appendix I.
b - MW - number averaged mean molecular weight determined by vapour pressure osmometry, using the technique described in Appendix I.

The hydrogen aromaticity of the tar formed in the

hydropyrolysis of extracted Canakkale Can is approximately the same as that for the untreated lignite, as should be expected if the extractable material plays no discernable intermediary role in tar formation in the hydropyrolysis of Canakkale Can.

Discussion

To summarise, the effect of chloroform extraction on the hydropyrolysis of Taff Merthyr and Cortonwood Silkstone is to diminish the tar yield to an extent greater than the amount of extract removed. For the Can lignite, extraction causes only a small drop in the tar yield, which is approximately balanced by the amount of extract removed.

In the hydropyrolysis of hard coals, the low molecular weight material, extracted by the chloroform, plays a role in the action of molecular hydrogen in promoting tar formation. In the case of Cortonwood, although the application of high pressure hydrogen does not result in an increase in the tar yield, the externally applied hydrogen appears to promote tar formation to an extent which balances the loss of tar due to increased mass transfer resistances. In promoting tar formation, the hydrogen is thought to be acting, at least in part, via the chloroform extractable material, showing that the extractables are acting as an intermediate in the action of high pressure hydrogen.

The mechanism by which the chloroform extractable material acts in the hydropyrolysis of Cortonwood and Taff is probably similar to the mechanism by which they act in flash pyrolysis. The proposed dominant mechanism in that case is hydrogen shuttling. In hydropyrolysis, the hydrogen availability is high and therefore hydrogen shuttling is also likely to be the predominant mechanism by which the chloroform extractable material acts.

In the hydropyrolysis of Canakkale Can, the extractables do not appear to play a substantial role in the action of hydrogen in promoting tar formation. In the flash pyrolysis of Can, chloroform extraction has been shown to substantially reduce the tar yield. It was proposed that the extractable material acts as a hydrogen donor in flash pyrolysis of Can, as it was shown that the chloroform extract was highly aliphatic and contained a substantial quantity of donatable hydrogen held in hydroaromatic groups (see section 7.4.3.3). As discussed above, in the hydropyrolysis of Cortonwood Silkstone and Taff Merthyr, it appears that the chloroform extractable material probably acts as a hydrogen shuttler. However, the low aromaticity of the chloroform extract from the Can would make it a poor hydrogen shuttler. Therefore in the hydropyrolysis of Canakkale Can, the chloroform extract does not play a significant role as an intermediate in action of the hydrogen in promoting tar formation.

The effect of chloroform extraction on the structure of

the tars from the hydropyrolysis of both Taff Merthyr and Cortonwood Silkstone is to decrease the aromaticity and the mean molecular weight, associated with the decrease in the tar yield. This suggests that the removal of chloroform extractable material may facilitate hydrogenation of the tar reducing its hydrogen aromaticity. Alternatively, this change may be due to the condensation of aromatic structures, which would reduce the hydrogen aromaticity, but maintain the carbon aromaticity and increase the degree of condensation. This may occur to a greater extent than for Linby due to the higher aromaticity of Cortonwood and Taff, and hence the higher number of rings per aromatic cluster.

The higher mean molecular weight of the tar from the extracted coal may suggest that the extractable material plays a role in inhibiting repolymerisation reactions. In the absence of the extractables the volatile molecules may be more liable to undergo repolymerisation which would result in an increase in the mean molecular weight. The effect of extraction on the mean molecular weight appears to suggest that the reason for the increase in hydrogen aromaticity is enhanced condensation of aromatic structures.

CHAPTER 10 CONCLUSIONS

This project is an examination of the effect of three parameters on coal pyrolysis, these being:

pressure

catalysts

extraction

This chapter summarises the effect of these parameters as shown by the experiments performed.

10.1 THE EFFECT OF ELEVATED GAS PRESSURE ON PYROLYSIS

Inert gas pressure

The effect of inert gas pressure on the pyrolysis of Linby coal in the hot-rod reactor is to cause the tar yield to decrease, and the char yield to increase. This has been shown to be due to the increased resistances to the mass transfer of volatiles within the parent coal particle during transport from the site of formation to the particle surface, and during "evaporation" from the surface of the particle to the bulk gas phase.

The increased resistance to mass transfer appears to result from increases in gas density and viscosity, and the subsequent decrease in the gas phase diffusivity of tar molecules. The increased resistance causes the residence time of the volatiles in the vicinity of the coal particle to increase, rendering them more liable to undergo secondary reactions, with the result that the

tar yield diminishes.

Under low sweep gas flowrates, as the pressure is increased, the decline in the tar yield is balanced by the increase in the char yield, showing that the dominant secondary reaction reducing the tar yield is repolymerisation. At a higher sweep gas flowrate, as the pressure is increased, both the char and gas yields increase, showing that tar is lost due to both gas-phase cracking and repolymerisation.

This difference in behaviour is due to effect of the increased gas velocity on the transport of volatiles, notably during the evaporation step. The higher gas velocity enhances the rate of evaporation of volatiles. This reduces the residence time of the volatiles whilst they are in contact with the parent coal particle, and so diminishes the extent to which they are liable to undergo repolymerisation.

Hydrogen pressure

The effect of hydrogen pressure on the tar yield from coal pyrolysis in the hot-rod reactor is dependent on the coal pyrolysed, and on the velocity of sweep gas, removing tar from the hot-zone. In the pyrolysis of Linby, a non-coking coal, the effect of elevated hydrogen pressure is to increase the tar yield, provided the sweep gas velocity is sufficiently high.

In the absence of a sweep gas of sufficient velocity,

tar production in coal pyrolysis appears to be limited by the evaporation mass transfer step (Unger and Suuberg, 1981; 1983; 1984). This is confirmed by the results presented, and also by Gibbins (in preparation). As the pressure is increased in the absence of a sufficiently strong sweep gas, the effect of the increased resistance to the evaporation step is greater than the effect of hydrogen in enhancing tar production, and therefore the effect of increased hydrogen pressure is to cause the tar yield to decline.

Use of a higher sweep gas velocity enhances the rate of evaporation of volatiles with the result that the effect of the hydrogen in promoting tar production is greater than the effect of the increased pressure in diminishing the tar yield. The location and mechanism by which hydrogen promotes tar formation is unclear from the results discussed in this section. This will be discussed in further detail in section 10.3.2.

In the pyrolysis of Cortonwood Silkstone, a coking coal, increases of hydrogen gas pressure do not increase the tar yield significantly, even in the presence of a high sweep gas flowrate. This may be due to the enhanced plasticity of the coking coal in comparison to the lower rank coal, which either inhibits the mass transfer of volatiles within coal particles, or prevents hydrogen from gaining access to the interior of coal particles.

In the pyrolysis of Canakkale Can, a lignite, and Taff

Merthyr, a semi-anthracite, hydrogen pressure has been shown to result in an increase in the tar yield, showing that hydrogen is active over a wide range of carbon contents.

High pressure hydrogen also appears to participate in reactions which modify the tar structure. These reactions result in increases in the aromaticity of the tar, and may be due to reactions causing dealkylation of the tar.

10.2 EFFECT OF CATALYSTS ON COAL PYROLYSIS

10.2.1 EFFECT AT ATMOSPHERIC PRESSURE

The effect of impregnation with zinc chloride on coal pyrolysis in an inert gas at atmospheric pressure is known to depend on the heating rate used (Kandiyoti and co-workers, 1984; Kandiyoti and O'Brien, 1985). The effect of zinc chloride on the flash pyrolysis of Linby coal in the fluidised bed reactor is to increase the tar yield. The tar produced is lighter than the tar from the untreated coal, contains more hydrogen, and is less aromatic. Zinc chloride appears to be acting as a hydrogenation catalyst, enhancing the amount of hydrogen native to the coal, which is taken up in the tar. The effect of impregnation with zinc chloride on the tar yield from flash pyrolysis of other hard coal, ranging from a high volatile, low rank bituminous coal to a semi-anthracite, is similar to the effect on Linby, ie

the tar yield is enhanced.

However, in the pyrolysis of a Canakkale Can, a lignite, impregnation with zinc chloride causes the tar yield to decline. This is thought to be due to the different molecular structures of the Can and the hard coals. The action of zinc chloride is thought to involve the formation of carbonium ions via heterolytic bond scission, followed by hydride ion abstraction to stabilise the cation. In the case of Can, it is thought that the carbonium ions formed are insufficiently stable, due to the more aliphatic structure of the Can. The mechanism by which zinc chloride acts is further discussed in section 10.3.

The effect of impregnation with other Lewis acid type catalysts on the flash pyrolysis of Linby coal has also been examined. Zinc bromide and iodide, and aluminium chloride enhance the tar yield from flash pyrolysis, whilst impregnation with other catalysts, notably tin (II) chloride, causes a decrease in the tar yield, and an increase in the char yield. There appears to be no correlation between the known activity of these catalysts in coal hydroliquefaction, and their effect in flash pyrolysis. In many liquefaction studies tin chloride and zinc chloride have been assumed to act via similar mechanisms (Weller and co-workers, 1950; Zielke and co-workers, 1966a; Wood and Wiser, 1976). In flash pyrolysis however, this is not the case. There is also no correlation between Lewis acid strength and the

effect in flash pyrolysis, as ferric chloride, known as a strong Lewis acid, causes the tar yield from flash pyrolysis to diminish, while aluminium chloride, which is also a strong Lewis acid, promotes tar formation.

However, there does appear to be a correlation between the mean molecular weight of the oil and the tar yield. This suggests that there is some type of auto-hydrogenation mechanism occurring in catalytic coal flash pyrolysis, whereby the additional tar formed acts to hydrogenate itself utilising hydrogen native to the coal, and hence reducing the mean molecular weight of the oil fraction.

10.2.2 EFFECT OF CATALYSTS IN PYROLYSIS UNDER HIGH PRESSURE HYDROGEN

The effect of impregnation with zinc chloride on pyrolysis under high pressure hydrogen is to cause an increase in the tar yield for all hard coals studied, and also for the lignite. The increase in the tar yield from the lignite is of a much smaller magnitude than the increase for the hard coals. This may be due to the same reasons which result in the differing effect of zinc chloride on the flash pyrolysis of Can compared to the effect on the flash pyrolysis of hard coals. Zinc chloride also causes a large increase in the gas yield from hydropyrolysis, for all samples studied.

Under hydrogenation conditions, the mechanism by which

zinc chloride acts is thought to be similar to that by which the catalyst acts in flash pyrolysis. However, the gas phase hydrogen acts as an additional source of hydride ion in the abstraction step. The mechanism is further discussed in section 10.3.

Zinc chloride also has a substantial effect on the tar structure. For Linby, the tar from the catalyst impregnated coal is more aromatic than the tar from the untreated coal, probably due to dealkylation reactions, which appear to occur at the beta bond in alkyl side chains. As the effect is enhanced as the hydrogen pressure increases, it would appear that hydrogen participates in the dealkylation reaction. However, for Cortonwood Silkstone and for Taff Merthyr, the tars from the catalyst impregnated coal are less aromatic than the tar from the corresponding untreated coals. In the case of Cortonwood, the tar from the untreated coal is modified considerably by secondary reactions which occur due to the increased resistance to mass transfer caused by the plasticity of coal. As the presence of the catalyst inhibits plasticity, the tar from the $ZnCl_2$-impregnated coal is not liable to secondary reaction to the same extent. In the case of Taff, the catalyst appears to promote hydrogenation of the tar. This may be due to the higher aromaticity of the tar formed from Taff Merthyr, which may facilitate hydrogenation of its structure.

The effect of tin chloride in pyrolysis under high

pressure hydrogen is very similar to the effect of zinc chloride, both in terms of the effect on the tar yield and on the tar structure. Tin chloride does not appear able to utilise the hydrogen native to the coal in flash pyrolysis, but is able to utilise externally applied molecular hydrogen in promoting tar formation.

10.3 EFFECT OF EXTRACTION ON PYOLYSIS

10.3.1 EFFECT OF EXTRACTION ON THE PYROLYSIS AT ATMOSPHERIC PRESSURE

The effect of extraction of coal prior to pyrolysis is to cause a decrease in flash pyrolysis tar yield for all samples studied. The amount of extract removed in 25 hour extraction with chloroform is much less than the reduction in the tar yield. This suggests that the chloroform extractable material plays a role in promoting tar formation in flash pyrolysis. In pyrolysis at low heating rate, it has been shown that the tar yield from extracted coal is greater than or equal to the tar yield from untreated coal (O'Brien and co-workers, 1986; Gibbins, in preparation).

Analyses of the extracts suggest that the nature of the role played by the extractable material in promoting tar formation in flash pyrolysis depends on the rank of the coal. The chloroform extract from the lignite contains substantial quantities of hydroaromatic material, which contains donatable hydrogen. In flash pyrolysis, it is

proposed that the extractable material predominantly plays a hydrogen donating role utilising the hydroaromatic hydrogen.

The extract from Linby contains much less hydroaromatic material, but more aromatic material, apparently consisting largely of 2-3 ring structures. This suggests that in the flash pyrolysis of Linby, the extract may play a physical solvating role, increasing the stability of free-radicals. The extracts from Taff Merthyr and Cortonwood Silkstone are more aromatic than the Linby extract and probably have more aromatic rings present per aromatic cluster. This makes them more able to participate in hydrogen shuttling reactions, which may be the action by which the extractable material acts in promoting tar formation in the flash pyrolysis of Cortonwood and Taff.

10.3.2 EFFECT OF EXTRACTION ON COAL PYROLYSIS UNDER HIGH PRESSURE HYDROGEN

Extraction has no effect on the tar yield from pyrolysis of Linby coal at low pressure or at elevated pressure under inert gas in the hot-rod reactor, other than removing a fraction of the volatile matter. At this heating rate, it is thought that the extractable material either evaporates or undergoes retrograde reactions prior to it being able to fulfil the role which it plays in flash pyrolysis. In the hydropyrolysis of Linby at 50 bar, the tar yield from 25 hour

chloroform extracted Linby is 16% compared to 22.5% for the untreated coal. However, the tar yield from the extracted coal is greater than that obtained from the untreated coal under 50 bar helium. Extraction has a similar effect on the tar yield from the hydropyrolysis of Taff Merthyr and Cortonwood Silkstone. However extraction does not have a significant effect on the tar yield from the hydropyrolysis of Canakkale Can.

These results show that in the hydropyrolysis of hard coals, the extractable material plays a role as an intermediary in the action of hydrogen in promoting tar formation. The hydrogen does not act solely via the chloroform extractable material, but may also act via other low molecular weight material which is not extracted by chloroform, or may react directly with the coal macromolecule. The nature of the role played by the extractable material is probably similar to that played in flash pyrolysis involving hydrogen shuttling and/or radical stabilisation. These results suggest that externally applied molecular hydrogen interacts directly with the coal during hydropyrolysis.

In the hydropyrolysis of Canakkale Can, the chloroform extractable material does not appear to act as an intermediary. This may be because the extractable material is unable to play a role in hydrogen shuttling or radical stabilisation due to its highly aliphatic nature.

10.3.3 EFFECT OF EXTRACTION ON THE PYROLYSIS OF $ZNCL_2$ IMPREGNATED COAL

The effect of impregnation with zinc chloride on the flash pyrolysis of chloroform extracted Linby coal was to cause a decrease in the tar yield, which is opposite to the effect observed for untreated Linby.

This suggests that the extractable material is acting as an intermediate in the action of zinc chloride in flash pyrolysis. In this intermediary role, the extractable material may act as a source of hydride ions, or may act to stabilise the carbonium ion formed during heterolytic bond scission, assuming that the zinc chloride acts via Friedel-Crafts chemistry as has been assumed by previous workers (Zielke and co-workers, 1966a; Kawa and co-workers, 1970; Wood and Wiser, 1976; Bell and co-workers, 1981; Kandiyoti and co-workers, 1984).

In pyrolysis under high pressure hydrogen, the action of zinc chloride is not affected by chloroform extraction. The difference between the tar yield from the extracted coal impregnated with zinc chloride, and that from the untreated coal impregnated with zinc chloride, is approximately equal to the amount of material removed during 25 chloroform extraction. This suggests that in hydropyrolysis, the action of tha catalyst is not dependent on the presence of the extractable material to act as an intermediary.

This tends to confirm the theory that in catalytic flash pyrolysis, the extractable material either serves as a source of hydride ions, or serves to stabilise carbonium ions. In catalytic hydropyrolysis, the higher availability of hydrogen serves as a source of hydride ions, and makes the stability of carbonium ions less crucial as they can be stabilised more easily.

APPENDIX I. ANALYTICAL TECHNIQUES EMPLOYED

I.1 Analysis of coal derived liquids

I.1.1 Separation techniques

I.1.2 Nuclear magnetic resonance

I.1.3 Vapour pressure osmometry

I.1.4 Phenolic hydroxyl titration

I.1.5 Size exclusion chromatography

I.1.6 Gas chromatography - mass spectrometry

I.1.7 Structural analysis

I.2 Analysis of coals and chars

APPENDIX I. ANALYTICAL TECHNIQUES EMPLOYED

The analytical techniques described below have been employed in this study to examine the structure of the liquid products of pyrolysis and of coal extracts, and to examine the distribution of catalysts in coal and char.

I.1 ANALYSIS OF COAL DERIVED LIQUIDS

I.1.1 SEPARATION TECHNIQUES

Analysis of coal derived liquids is facilitated by separating the liquids into various fractions. Primary separations can be performed by simple solubility differences, while secondary separations can be achieved by preparative chromatography.

Primary Separation

The usual primary separation employed by workers investigating coal derived liquids is as follows:

(1) the oil fraction - soluble in a straight chain alkane (eg. n-pentane), sometimes known as maltenes

(2) the asphaltene fraction - soluble in benzene or toluene (sometimes CH_2Cl_2), but insoluble in n-alkane used in (1)

(3) the pre-asphaltene fraction - insoluble in benzene or toluene, but defined as coal derived liquid, sometimes known as asphaltols, usually included as converted coal.

In the present study, the above separation was employed when sufficient tar was available to produce a quantitative separation (>300mg). This limited the separation to tars from the fluidised bed reactor, and to coal extracts. The oil was defined as being the n-pentane soluble material, the asphaltene as toluene soluble, n-pentane insoluble material and the pre-asphaltene as the toluene insoluble residue.

Procedure

The tar from the fluidised bed was redissolved in a methanol/dichloromethane mixture. The pre-asphaltene fraction was precipitated out by the addition of ten times the volume of toluene. The solution was then warmed and filtered to separate the preasphaltene. Following this the volume was reduced by evaporating 80% of the toluene using a nitrogen jet and gentle warming using a hair dryer. The asphaltene was then precipitated by diluting the toluene with ten times its volume of n-pentane. The pentane was warmed and filtered to separate the asphaltene. The n-pentane was then evaporated using a nitrogen jet and gentle warming to isolate the oil fraction. All fractions were dried in a vacuum oven, before being weighed to determine the yields.

Secondary Separation

Secondary separations are performed chromatographically. Such separations have been extensively used in the analysis of coal liquids. (Dooley and co-workers, 1978;

Bartle and co-workers, 1979; Farcasiu, 1979; Allen and co-workers, 1984; Baltisberger and co-workers, 1984; Seshadri and co-workers, 1985; Grint and co-workers, 1985). The preparative column is usually 20-25 mm diameter, and 1-1.5 m in length. The most common packing materials are silica and alumina, though this depends on the nature of the liquids which are being separated. The solvents used to elute the coal liquids also depend on the nature of the liquid and the separation required. A typical separation of an oil fraction produces three sub-fractions: the aliphatics, the aromatics, and the polars. Analysis of these fractions by NMR and mass spectrometry confirms the nature of the subfractions. Typical separations of asphaltenes produce two sub-fractions: an aromatic fraction and a polar fraction.

In this study, secondary separations were performed only when a sufficiently large sample was available. This was limited to the separation of the oil fraction of coal extracts, which were separated to facilitate mass spectrometry (see section I.1.6). The technique used was that developed by Grint and co-workers (1985). The column used was a 1.5m long, 25mm diameter glass tube packed with 190 g of silica. The silica was packed in a slurry with n-pentane. The sample under investigation was injected onto the top of the column, and eluted with 1 litre of n-pentane, under a positive nitrogen pressure (0.5 bar gauge). The pentane eluant from the column was divided into four fractions. The first fraction was that

eluted which produced no signal on the ultra-violet detector located at the outlet of the column. This was defined as the aliphatic fraction. The remainder of the eluted pentane had a strong U.V absorption. This was divided into two 250 ml fraction with the remainder forming the fourth fraction. These latter fractions were described as the aromatic fractions. The remainder of the material on the column was then eluted with 250 ml of tetrahydrofuran (THF). The fraction eluted with the THF was termed the polar fraction. The solvents were removed using a rotary evaporator and the sub-fractions were further dried in a vacuum oven.

I.1.2 NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance (NMR) has been used for many years to characterise coal derived liquids. The initial studies in the field used high resolution ^{1}H NMR of tar solutions to produce structural parameters of these tars (Brown and co-workers, 1959a; 1959b). More sophisticated techniques have been developed in recent years. Fourier Transformed ^{1}H and ^{13}C NMR spectroscopy of coal liquids are commonplace (Retcofsky and co-workers, 1977; Dereppe and co-workers, 1978; Ladner and Snape, 1978; Saito and co-workers, 1979; Collin and co-workers, 1980a; 1980b; Joseph and Wong, 1980; Barron and co-workers, 1981; Allen and co-workers, 1984). Furthermore, solid state ^{13}C NMR of coal itself is being increasingly used to characterise coal structure (Retcofsky and Link, 1978; Maciel and co-workers, 1979;

Calkins and co-workers, 1984; Yoshida and Maekawa, 1986).

In the course of this study, ^{1}H NMR spectroscopy has been used to characterise coal tars and tar fractions. Oils and asphaltenes have been been studied, but preasphaltenes were not sufficiently soluble to be analysed. Spectra were obtained in a variety of NMR machines, a Bruker WM 250 producing spectra at 250 MHz, a Bruker WH 400 measuring spectra at 400 MHz, a Jeol JX 270 measuring at 270 MHz, and a Jeol JX 400 operating at 400 MHz.

Typical spectra are shown in Figure I.1. Spectra of the oil fractions were obtained in solution in deuterated dichloromethane (CD_2Cl_2), while those of asphaltene fractions were measured in deuterated pyridine (C_5D_5N). Spectra for tars from the high pressure reactor, which were not separated were measured in a mixture of deuterated methanol (CD_3OD) and deuterated dichloromethane. The peaks for the residual un-deuterated compound present in the solvents were subtracted from the integrals supplied on the spectra. The peaks on the spectra can be assigned to hydrogen atoms in present in different functional groups, the chemical shift of those peaks being a characteristic of the type of functional groups responsible for the peak. The chemical shift assignments are given in Table I.1 and are the same as those used by Bartle and co-workers (1979).

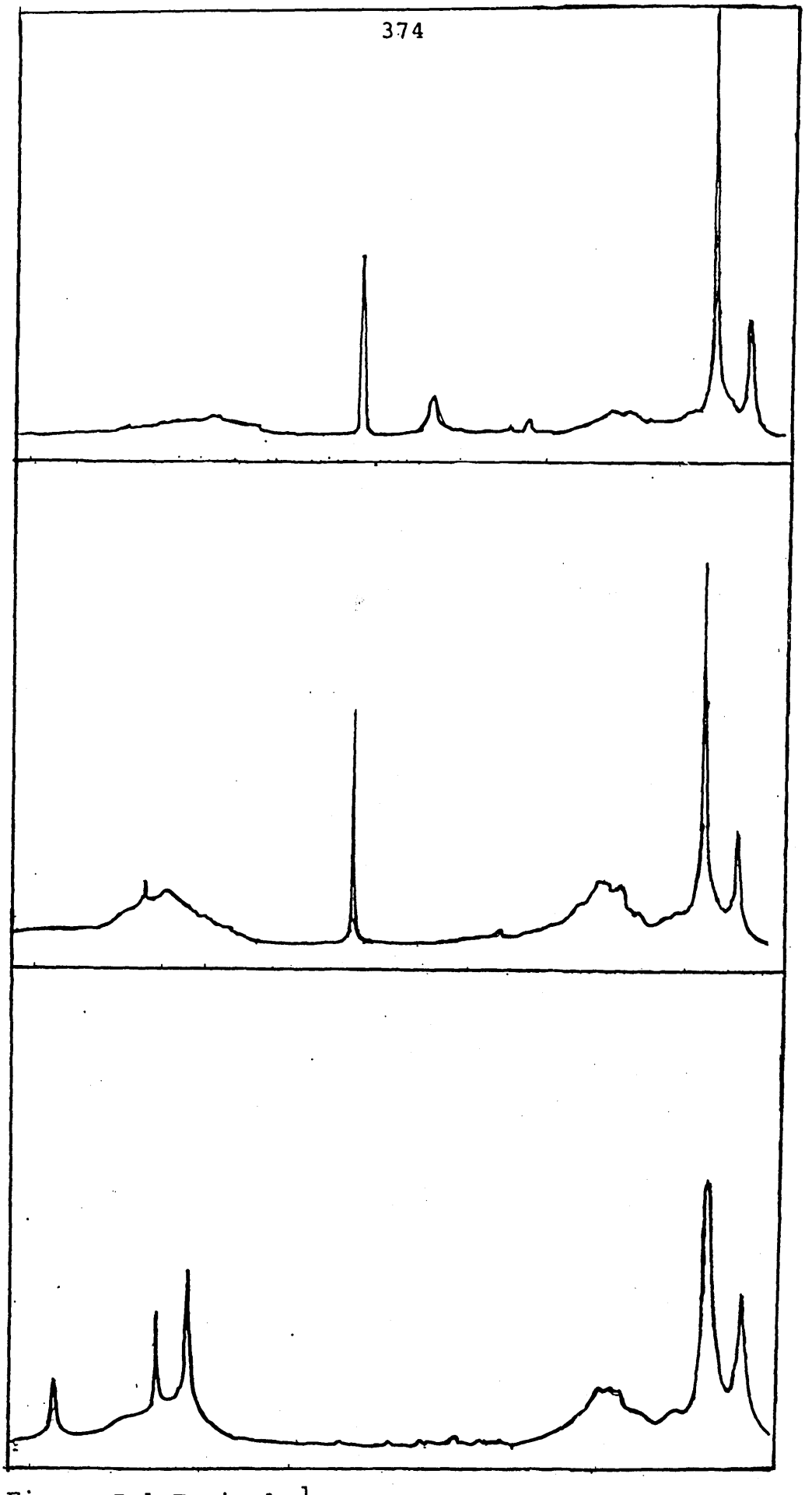


Figure I.1 Typical ^{1}H-NMR spectra of coal tars and tar fractions. (a) Tar from hot-rod experiment; (b) Oil fraction from fluidised bed; (c) asphaltene fraction

from fluidised bed.

Table I.1 Chemical shift assignments for ^1H NMR spectra of coal tars.

Hydrogen Type	Abbreviation	Chemical Shift (ppm)
Aromatic + Phenolic	H_{ar}	5.0-9.0
Ring-joining Methylene	$H_{\alpha,2}$	3.3-4.5
CH_3, CH_2 & CH α to aromatic rings	H_α	1.9-3.0
CH_2 & CH β to aromatic rings[a]	H_β	1.6-1.9
β-CH_3, CH_2 & CH γ or further from aromatic ring[b]	H_n	1.0-1.6
CH_3 γ or further from aromatic rings[c]	H_γ	0.5-1.0

[a] includes hydrogen in light hydroaromatics and saturated rings

[b] includes aliphatic CH_2 and CH

[c] includes aliphatic CH_3

The assignments given in the table were not rigidly adhered to in analysing the spectra, but were varied within +/- 0.5 ppm to ensure that the divisions occurred between peaks. The fraction of hydrogen responsible for each peak was equal to the area of that peak divided by the total area of the peaks. Line integrals were marked on the spectra to facilitate calculation of the distribution of hydrogen atoms.

Carbon-13 NMR spectroscopy was not used in this study

for reasons of sample size, and availability of this type of analysis. To obtain good ^{13}C NMR spectra, samples sizes of 0.5 to 1 gram are required. Additionally, it is necessary to acquire spectra over a long time period, eg 12 hours, with the result that it was difficult to obtain this service on a regular basis.

I.1.3 VAPOUR PRESSURE OSMOMETRY

Vapour pressure osmometry is used widely technique which is used to measure number averaged molecular weights of coal derived liquids (Farcasiu, 1977; Kershaw and Bagnell, 1984; Unger and Suuberg, 1984; Nomura and co-workers, 1985). The principle of the technique is based on the difference of vapour pressure between a tar solution and pure solvent. Two thermistor beads are held in an atmosphere of solvent vapour. One bead is loaded with a drop of pure solvent while the other is loaded with a drop of a known concentration of tar solution. The difference of vapour pressure between the drops results in a temperature difference developing between the beads. Control of drop size was important to ensure that results were reproducible.

In this study, the Vapour Pressure Osmometer used was a Knauer Osmometer type 06.00, with a digital meter type 11.00. The solvent used for all samples was THF. Molecular weights were measured at 45^{o}C, with a concentration of tar in the solvent between 0.01-0.05 mol/litre. The osmometer was calibrated using

phenanthrene.

Molecular weights were measured for tars, oils and asphaltene fractions, but not for pre-asphaltene fractions. The samples of tar were dried thoroughly prior to measurement. The required weight of tar was then weighed into a small (2ml or 3ml) volumetric flask where it was dissolved in the required amount of solvent. Prior to each measurement, drops of pure solvent were injected to reset the zero of the osmometer. The sample solution was then injected. At least two injections were made, to ensure that the result were reproducible. Molecular weights were calculated according to the following formula:

$$M_W = \frac{m\ K_{cal}}{v\ R_{meas}} \qquad (I.1)$$

Where M_W is the mean molecular weight of the sample, m is the weight of the sample in the solution which has a volume v. R_{meas} is the reading measured on the osmometer. K_{cal} is the calibration constant, measured for a solution of known concentration of phenanthrene, and defined by the following formula:

$$K_{cal} = \frac{M_{w,cal}\ v_{cal}\ R_{cal}}{m_{cal}} \qquad (I.2)$$

where m_{cal}, v_{cal}, and R_{cal} have the same meaning as in equation (I.1), evaluated for the calibration solution of phenanthrene. $M_{w,cal}$ is the molecular weight of phenanthrene.

This technique measures the molecular weight of tar and

tar fractions with an accuracy of +/- 30 amu for low molecular weight (<400), and an accuracy of +/- 50 amu for higher molecular weights.

I.1.4 PHENOLIC HYDROXYL MEASUREMENT

The phenolic hydroxyl (-OH) content of coal tars and tar fractions was measured using the technique developed by Vaughan and Swithenbank, 1965; 1970). This method has been extensively in the characterisation of coal tars (Bartle and co-workers, 1979; Fynes and co-workers, 1984; Kershaw and Bagnell, 1984).

In this method the concentration of phenolic hydroxyl is determined by a calorimetric titration of the tar solution dissolved in acetone, against a known concentration of potassium hydroxide in propan-2-ol. The added KOH reacts is neutralised by the phenolic groups in the tar. When the end point is reached, the KOH reacts with the acetone to form diacetone alcohol. This latter reaction is exothermic and causes a rapid temperature rise, which acts as the indicator of the end point. The details of the method are given below.

An accurately weighed quantity of tar (4-5 mg) was dissolved in 5 ml of dry acetone. A thermocouple was placed in the beaker, the contents of which were stirred magnetically. A high concentration solution of potassium hydroxide in dry propan-2-ol (2-3 molar) was then injected into the solution in amounts of 0.5 or 1

microlitres. Following each injection, any temperature change of the solution was noted. By this method the end point was easily determined corresponding to a rapid temperature rise of 1-1.5°C. Prior to the measurement of the phenolic -OH content of a sample, the molarity of the alkali solution was determined by titration against a known weight of benzoic acid. The inherent acidity of the acetone was also measured by a blank titration of 5ml of acetone.

Following the titration of a sample solution, the concentration of phenolic hydroxyl groups in the tar sample was calculated using the following formulae.

$$\% \text{ Phenolic -OH} = \frac{A_{OH}\ (V-V_o)\ M_{w,OH}}{m} \qquad (I.3)$$

In equation (I.3), m is the weight of the sample of tar, $M_{w,OH}$ is the molecular weight of the hydroxyl group (=17 amu), V is the titration volume (ie the volume of KOH solution required to reach the end point) of the tar sample while V_o is the titration volume of 5ml of acetone. A_{OH} is the molarity of the potassium hydroxide solution, measured by titration against benzoic acid, and calculated by the following formula.

$$M_{OH} = \frac{m_{cal}}{M_{w,cal}\ (V_{cal}-V_o)} \qquad (I.4)$$

In equation (I.4), m_{cal} is the weight of the calibrant, benzoic acid used, $M_{w,cal}$ is the molecular weight of benzoic acid, and V_{cal} is the titration volume of the benzoic acid.

This technique measures the % w/w of phenolic hydroxyl groups in a tar sample to an accuracy of +/- 0.3%.

I.1.4 SIZE EXCLUSION CHROMATOGRAPHY

Size exclusion chromatography (SEC), also known as gel permeation chromatography, is a technique which has been used by several workers to provide information about the distribution of molecular weights in coal derived liquids (Richards and co-workers, 1983; Bartle and co-workers, 1984; Unger and Suuberg, 1984). The method utilised in this study on selected samples was that developed by Richards and co-workers (1983) and Bartle and co-workers (1984).

The technique was carried out with a 600 mm long, 7.7 mm inside diameter polystyrene microsphere column ("PL gel" obtained from Polymer laboratories Ltd), with a particle size of 10 um, and a 50 nm pore diameter. Detection on the outlet from the column was ultra-violet absorption at 254 nm. Samples were introduced through a 15 ulitre loop injection valve. The solvent used was tetrahydrofuran (THF) with a flowrate of 1 ml/min.

Calibration of molecular weight versus retention times, and absorption coefficients versus molecular weight was performed against model compounds and polymers, and against fractions of a coal extract of known molecular weight separated on a preparative column of the same packing material (Bartle and co-workers, 1984).

Following this calibration, the molecular weight distribution for a sample could be calculated using the on-line computer. The sensitivity factors which relate absorption coefficient to molecular weight were calculated for coal extracts and therefore maybe inappropriate for coal tars. The molecular weight distributions for the tars were calculated without the use of these factors.

Using the appropriate calibrations, quantitative molecular weight distributions can be measured. Additionally light polar compounds, such as phenols, in the tar may form adducts with the THF solvent. These adducts would be elute with the higher molecular weight material, producing a biased molecular weight distribution. This effect has been noted by Ladner and Snape (1985).

I.1.6 GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Gas chromatography-mass spectrometry (GC-MS) is a method which can be used to give direct structural information about the components present in coal derived liquids. The technique involves the gas phase chromatography followed by mass spectrometry of the effluent from the column. If the chromatography is successful in separating the sample into individual components, then these components can be identified by their mass spectra. The method can only be applied to lighter

fractions of coal tars and extracts, that is those which can be separated on a g.c. column, that is for molecular weights less than 500. This is limited to oil fractions, ie. n-pentane soluble material. Additionally, the results are more easily analysed if the oil fraction is further separated as described in section I.1.1.

In this study, GC-mass spectra were obtained on a Kratos MS 25, operated in electron impact (e.i.) mode. The gas chromatography column was a 25 m long, 0.2 mm inside diameter, fused vitreous silica open tubular column with a Bonded Phase I (methyl silicone) coating, obtained from Scientific Glass Engineering. The temperature profile for the column following injection was a hold at a constant temperature of 110^{o}C for 2 minutes, followed by heating of the column at 5^{o}C/min. up to 285^{o}C, when the temperature was held constant until all material had eluted off the column. Spectra were identified using the Eight Peak Index of Mass Spectra (MSDC, 1983).

I.1.7 STRUCTURAL PARAMETERS

The data provided by NMR spectroscopy (both ^{1}H and ^{13}C) of coal derived liquids are most easily interpreted in conjunction with other analytical data. They can be used to calculate a number of descriptive structural parameters. These structural parameters can be defined and calculated to describe the nature of the structure of an "average" tar molecule, such that changes in experimental conditions and coals can be evaluated in

terms of their effect on these parameters.

Many workers have devised structural analysis schemes for coal liquids. The first NMR based scheme was developed by Brown and co-workers (1959) and most schemes developed since then have been modification of that scheme (Brown and Waters, 1966; Dereppe and co-workers, 1978; Bartle and co-workers, 1979; Collin and co-workers, 1980; Herod and co-workers, 1981). The initial scheme derived by Brown and co-workers was formulated for describing the carbon skeleton of samples, from information about the hydrogen distribution. The most notable calculated parameter was the carbon aromaticity. By assuming the ratio of hydrogen to carbon atoms in the aliphatic groups present in coal derived liquids, the fraction of aliphatic carbons can be estimated and hence the fraction of aromatic carbon. The equation used to calculate the aromaticity, the Brown-Ladner formula, is given below.

$$F_a = \frac{C/H - H_a/x - H_o/y}{C/H} \qquad (I.5)$$

In the above equation C is the carbon content (%), H is the hydrogen content (%), H_a is the fraction of hydrogen alpha to an aromatic ring, and H_o the remainder of the aliphatic hydrogen. The parameters x and y are estimated constants, both lying in the region of 2.0-2.5.

The introduction of ^{13}C NMR has provided a method to test the Brown-Ladner formula. Several studies have

since shown the accuracy of this equation in calculating aromaticities (Retcofsky and co-workers, 1977; Lang and Hajek, 1985).

Other equations were also developed to describe the degree of substitution of the average molecule (s), and the atomic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic material (H_{aru}/C_{ar}), which is a measure of the condensation of aromatic nuclei. These equations are shown below:

$$s = \frac{H_a/x + O/H}{H_a/x + O/H + H_{ar}} \qquad (I.4)$$

$$\frac{H_{aru}}{C_{ar}} = \frac{H_a/x + H_{ar} + O/H}{C/H - H_a/x - H_o/y} \qquad (I.5)$$

In equation (I.4) and (I.5) H_a, H_o, C and H have the same same meanings as in equation (I.3), O is the oxygen content, while H_{ar} is the fraction of aromatic hydrogen.

Since this study other workers have further developed the scheme to describe average structures. Addition of molecular weight determination, together with phenolic hydroxyl measurement provides a reasonably complete description of the sample. Phenolic hydroxyl measurements are required to discriminate between aromatic and phenolic protons which occur in the same in ^{1}H NMR spectra. However the nature of the aliphatic substituents on the aromatic nucleus cannot be determined without the use of ^{13}C NMR (Snape and

co-workers, 1985). When this is utilised, it is possible to discriminate between aliphatic side chains and hydroaromatic groups and so to provide a near complete description of the average structure.

It should be noted that these schemes are best applied when the nature of the sample being studied is well defined, such as an asphaltene fraction. Structural parameters are most appropriate when applied to a comparatively small sub-fractions where the variation in the structure and size of molecules is small.

In this study, since the use of ^{13}C NMR was limited, the aromaticity of samples was calculated using a modified version of the Brown-Ladner formula as given below:

$$F_a = 1 - H/C\ (H_{\alpha,2}/a - H_{\alpha}/b - H_{\beta}/c - H_{\wedge}/d - H_{\gamma}/e) \quad (I.5)$$

where F_a is the carbon aromaticity, H/C is the hydrogen to carbon atomic ratio, and $H_{,2}$, H , H , H , and H are as defined in section I.1.2. The constants a, b, c, d and e are constants whose values were set in the range suggested by Bartle and co-workers (1979). The actual value used for these constants is given below:

a=2, b=2.3, c=1.9, d=2.2, e=3

Further parameters were not derived for the samples studied.

I.2 ANALYSIS OF COALS AND CHARS

The principle aspect from which the coals and chars were analysed in this study was examination of catalyst distribution, chemical form and mobility. The influence of catalyst distribution on coal liquefaction and pyrolysis has been discussed in section 4.5. In that discussion previous studies of catalyst distribution were described. Several studies utilised electron microprobe analysis to determine catalyst concentrations across coal and char particles (Shibaoka and co-workers, Shabtai and co-workers). This process involves use of a conventional scanning electron microscope (sem). Florescent X-rays produced from heavier elements (Atomic number greater than 22) are collected and analysed. The frequency of the X-rays is characteristic of the particular element from which they are produced. Slow scanning of a sample particle by the electron beam along with analysis of the X-rays by a suitable detector connected to a computer, can be used to produce maps of the concentration of specified elements across the particle.

In this study the electron microscope used was a Jeol JSM 35 CF sem operated at 20 KV. Operating with a beam current of 2×10^{-9} amps. Acquisition of x-rays was by a Link Systems energy dispersive spectrometer (EDS) detector, with a take-off angle of 35^{o}. Collection of the data was performed by a Link Systems 860 series II

system 500 computer using a Digimap program. The magification used was x300, which produced a Digimap scanned area of 280 um x 300 um. The spectral peaks used for analysis of elements were as follows: for sulphur the K line at 2.3 Kev, for chlorine the K line at 2.62 Kev, for tin the L line at 3.44 Kev, and for zinc the K line at 8.6 Kev.

Samples for analysis were set in 25 mm diameter, 15 mm thick epoxy resin blocks (Epofix resin obtained from Struers). The surface of the block was polished to produce sections through sample particles. The polishing was a two stage process, the resin blocks were first polished with sequentially three grades of silicon carbide on glass plates. This was followed by successive polishing with two grades of diamonds: 6 um followed by 3um.

Samples were analysed to determine the effect of impregnation in terms of the distribution of catalyst across the coal particle. Additionally the effect of mild heating on catalyst distribution was examined. The catalyst distributions in chars from flash pyrolysis in the fluidised bed were also studied.

Symbols Used in this Section

a - Numerical constant

A_{OH} - Molarity of alkali solution

b - Numerical constant

c - Numerical constant

C - Carbon content of a sample % w/w

d - Numerical constant

e - Numerical constant

F_a - Carbon aromaticity - the fraction of carbon atoms in aromatic groups

H - Hydrogen content of a sample % w/w

H_x - Fraction of hydrogen in a particular group, as defined by subscript x

K_{cal} - Calibration constant for VPO

m - Mass of a tar sample

m_{cal} - Mass of calibration compound

M_w - Mean molecular weight of tar sample

$M_{w,cal}$ - Molecular weight of calibration compound

$M_{w,OH}$ - Molecular weight of hydroxyl group

O - Oxygen content of sample % w/w

R_{cal} - VPO reading for calibration solution

R_{meas} - VPO reading for tar sample solution

S - Degree of substitution of aromatic rings

v - Volume of tar solution

v_{cal} - Volume of calibration solution

V - Titration volume of tar solution

V_{cal} - Titration volume of calibration solution

V_o - Titration volume of acetone

x - Numerical constant

y - Numerical constant

APPENDIX II. RESULTS FOR FLASH PYROLYSIS EXPERIMENTS

Table II.1 Results from the flash pyrolysis of untreated Linby coal

Table II.2 Results from the flash pyrolysis of 5% $ZnCl_2$-impregnated Linby coal

Table II.3 Results from the flash pyrolysis of Canakkale Can

Table II.4 Results from the flash pyrolysis of 5% $ZnCl_2$-impregnated Canakkale Can

Table II.5 Results from the flash pyrolysis of a range of untreated and 5% $ZnCl_2$-impregnated coals

APPENDIX II. RESULTS FOR FLASH PYROLYSIS EXPERIMENTS

Table II.1 Results from the flash pyrolysis of untreated Linby coal. Yields on % w/w daf basis.

Temp. (°C)	Char	Gas[a]	Tar	Oil	Asph.	Preas.
397	90.7	1.0	8.3	2.3	4.0	2.0
500	80.9	6.4	12.7	5.0	4.5	3.2
580	57.0	12.0	31.0	10.1	13.8	7.1
650	57.1	18.4	24.5	5.1	10.2	9.2
700	55.1	28.6	16.3	1.9	9.8	4.6
800	48.3	37.5	14.2	5.6	3.7	4.9

a - gas by difference

Table II.2 Results from the flash pyrolysis of Linby coal impregnated with zinc chloride. Yields on % w/w dacf basis.

$ZnCl_2$ Loading	Temp. (°C)	Char	Gas[a]	Tar	Oil	Asph.	Preas.
5%	397	88.1	1.2	10.7	5.8	2.5	2.4
5%	500	71.8	9.5	18.7	7.0	5.9	5.8
5%	580	51.3	11.9	36.8	15.2	16.8	4.8
5%	650	49.8	22.3	27.9	5.8	12.3	9.8
5%	700	50.7	27.5	21.8	2.5	7.5	11.8
5%	800	46.2	34.5	19.3	3.9	2.2	13.2
2.75%	580	54.8	10.8	34.4	10.1	13.8	7.1
10.0%	580	42.1	15.3	42.6	17.4	22.3	2.9
15.0%	580	42.6	15.4	42.0	18.5	19.2	4.3
20.0%	580	40.4	16.0	43.6	19.3	16.6	7.7

a - gas by difference

Table II.3 Results of the flash pyrolysis of Canakkale Can. Yields on % w/w daf basis.

Temp. (°C)	Char	Gas[a]	Tar	Oil	Asph.	Preas.
465	74.1	20.4	5.5	1.4	2.0	2.1
511	72.5	20.4	7.1	2.5	2.7	1.9
530	68.3	20.1	11.6	6.8	2.4	2.4
545	63.0	27.9	9.1	4.4	2.3	2.4
575	57.7	35.5	7.0	2.2	2.2	2.6
620	56.0	37.0	6.6	2.6	2.2	1.8
710	49.0	44.2	6.8	3.0	2.0	1.8

a - gas by difference

Table II.4 Results of the flash pyrolysis of Canakkale Can impregnated with zinc chloride. Yields on % w/w dacf basis.

$ZnCl_2$ loading	Temp. (°C)	Char	Gas[a]	Tar	Oil	Asph.	Preas.
5%	515	67.3	27.3	5.4	1.8	1.9	1.7
5%	530	64.5	28.3	7.2	1.7	2.5	3.0
5%	545	62.1	31.6	6.3	1.5	1.8	3.0
20%	530	74.0	19.1	6.0	1.1	3.0	2.8

a - gas by difference

Table II.5 Results of the flash pyrolysis at 580°C of a range of untreated coals and 5% $ZnCl_2$-impregnated coals. Yields on % w/w dacf basis.

Sample	Char	Gas[a]	Tar	Oil	Asph.	Preas.
Daw Mill	58.1	11.7	30.2	7.5	15.1	7.6
Daw Mill+$ZnCl_2$	53.8	10.5	35.7	12.2	16.3	7.2
C´wood[b]	55.4	18.7	25.9	7.1	9.3	9.5
C´wood[b]+$ZnCl_2$	53.8	16.4	29.8	6.0	14.8	9.0
Taff[c]	83.5	11.0	5.4	1.5	3.4	0.5
Taff[c]+$ZnCl_2$	83.0	9.5	7.5	1.5	2.3	3.7

a - gas by difference

b - Cortonwood Silkstone

c - Taff Merthyr

APPENDIX III. RESULTS OF EXPERIMENTS ON THE HOT-ROD REACTOR

Table III.1 Results from the pyrolysis of Linby coal at 1 bar pressure

Table III.2 Results from the pyrolysis of Linby coal at a range of pressures in hydrogen and helium

Table III.3 Results from the hydropyrolysis of catalyst impregnated Linby coal

Table III.4 Results from the pyrolysis of chloroform extracted Linby coal at a range of pressures

Table III.5 Results from the pyrolysis of two hard coals and a lignite at 1 bar pressure

Table III.6 Results from the hydropyrolysis of two hard coals and a lignite

Table III.7 Results from the hydropyrolysis of $ZnCl_2$ impregnated coals

APPENDIX III. RESULTS OF EXPERIMENTS ON THE HOT-ROD REACTOR

Table III.1 Results from the pyrolysis of Linby coal in the hot-rod reactor at 1 bar pressure under helium, with a range of peak temperatures. Yields on % w/w daf basis.

Peak Temp. (°C)	Char	Tar	Gas[a]
470	82.9	8.4	8.7
520	77.6	15.0	7.4
580	69.3	18.3	12.4
600	68.9	17.8	12.8
670	67.7	17.4	14.9
770	65.7	16.5	17.8

a - gas by difference

Table III.2 Results from experiments on the pyrolysis of Linby coal in the hot-rod with a peak temperature of 580°C, showing the effect of gas pressure for hydrogen and helium, in gas flow regimes 1 and 2. Yields on % w/w daf basis.

Atmosphere	Flow Regime	Pressure (bar)	Char	Tar	Gas[a]
He	1	1	69.3	18.3	12.4
He	1	30	73.2	13.3	13.5
He	1	40	nd[b]	12.0	nd[b]
He	1	50	73.3[c]	10.0[c]	16.7[c]
He	2	50	80.0	8.3	11.7
H_2	1	1	67.7	17.7	14.6
H_2	1	20	nd[b]	18.4	nd[b]
H_2	1	30	62.0	19.0	19.0
H_2	1	40	57.4	19.5	23.1
H_2	1	50	57.7[c]	22.5[c]	19.8[c]
H_2	2	1	71.0	18.1	10.9
H_2	2	30	70.6	14.9	14.5
H_2	2	50	72.0	13.7	14.3

a - gas by difference

b - nd - not determined

c - mean of two determinations each within +/- 0.5%.

Table III.3 Results from the hydropyrolysis of 10% $SnCl_2$-impregnated and 5% $ZnCl_2$-impregnated Linby coal in the hot-rod reactor with a peak temperature of 580°C, over a range of pressures. Yields on % w/w dacf basis.

Catalyst	Pressure (bar)	Char	Tar	Gas[a]
$ZnCl_2$	1	77.3	14.1	8.6
$ZnCl_2$	30	55.8	22.6	21.6
$ZnCl_2$	50	37.3	29.0	33.7
$SnCl_2$	1	73.9	13.2	12.9
$SnCl_2$	30	52.6	23.8	23.6
$SnCl_2$	50	51.0	30.0	19.0

a - gas by difference

Table III.4 Results from the pyrolysis of chloroform extracted Linby in the hot-rod reactor with a peak temperature of 580°C. Yields on % w/w daf basis of the original coal.

Extraction time (hrs)	Atmosphere	Pressure (bar)	Char	Tar	Gas[a]
25	He	1	63.8	15.3	18.9
25	He	30	71.7	11.5	14.8
25	He	40	nd[b]	10.5	nd[b]
25	He	50	70.8	10.3	16.9
4.5	He	50	nd[b]	11.8	nd[b]
72	He	50	68.8	11.4	17.6
25	H_2	20	nd[b]	16.0	nd[b]
25	H_2	30	59.7	15.0	23.3
25	H_2	40	59.0	16.5	22.5
25	H_2	50	60.5[c]	16.0[c]	21.5[c]
4.5	H_2	50	60.8	18.7	19.3
72	H_2	50	62.0	16.1	19.7

a - gas by difference

b - nd - not determined

c - mean of two determination each within +/- 0.5%.

Table III.5 Results from the pyrolysis of two hard coals, Taff Merthyr and Cortonwood Silkstone, and a lignite Canakkale Can in the hot-rod reactor at 1 bar pressure under helium. Yields on % w/w daf basis.

Sample	Peak Temp.(°C)	Char	Tar	Gas[a]
Canakkale Can	490	71.0	4.5	24.5
Canakkale Can	520	68.0	5.6	26.4
Canakkale Can	550	nd[b]	4.5	nd[b]
Canakkale Can	590	nd[b]	3.2	nd[b]
Cortonwood S´stone	580	86.6	8.1	5.3
Taff Merthyr	580	91.9	3.2	4.9

a - gas by difference

b - nd - not determined

Table III.6 Results of the hydropyrolysis of a range of coals in the hot-rod reactor at 50 bar with a peak temperature of 580°C (520°C for the lignite). Yields on % w/w daf basis.

Sample	Char	Tar	Gas[a]
Canakkale Can	50.8	11.4	37.8
Cortonwood Silkstone	84.0	8.3	7.7
Taff Merthyr	86.6	5.8	7.6

a - gas by difference

Table III.7 Results from the hydropyrolysis of a range of coals impregnated with 5% zinc chloride at 50 bar with a peak temperature of 580°C (520°C for the lignite). Yields on % w/w daf basis.

Sample	Char	Tar	Gas[a]
Canakkale Can	42.7	12.7	44.6
Cortonwood Silkstone	nd[b]	27.7	nd[b]
Taff Merthyr	73.7	12.9	13.4

a - gas by difference

b - nd - not determined

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