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Some Properties Of Cokes Produced From High Pressure Carbonisation Of Coals

by

C. K. MAN

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology June 1990

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ABSTRACT

The British Gas Lurgi slagging gasifier is a counter-current fixed bed gasifier operating at high pressure. Coal descending the gasifier is pyrolysed to form coke which is then gasified. Properties of such coke affect the gasifier in its efficiency of operation. This thesis describes a) the carbonisation of cokes from coal under simulated gasifier conditions, b) the characterisation of the resultant cokes in terms of structure and physical properties and, c) the formulation of relationships between coal thermoplasticity and coke properties.

Three high-volatile bituminous coals (Manton NCB 502, Manvers Barnburgh NCB 702, and Gedling NCB 802) were carbonised in an autoclave under a range of pressures (0.5-8.0 MPa), using two different heating regimes, shock heating to 700 °C and slow heating to 700 °C at 5 °C/min. Physical characterisation of the resultant cokes was carried out using optical and mechanical techniques.

Optical anisotropy and image analysis were used to determine coke structure and porosity respectively. Tensile strength, microstrength and abrasion resistance were measured to establish the cokes' resistance to various forms of breakage. High pressure dilatometry and plastometry were used to measure the effects of pressure and heating rate on coal thermoplastic properties.

Relationships between coal thermoplastic properties and coke properties are very complex. This work has shown that these relationships are highly dependent on carbonisation conditions with heating rate rather than pressure being the more dominant parameter.
I would like to thank my supervisors Drs. J.W. Patrick and K.M. Thomas for their unstinted guidance during this research.

I would also like to thank Drs. A. Walker and D.E. Clarke for their advice and encouragement during the past three years.

I also wish to acknowledge the help given to me by various members of staff at the British Gas London Research Station. I am also grateful for the availability of facilities afforded to me during my stay at L.R.S.

Finally, I would like to thank the Science and Engineering Research Council and British Gas plc for their financial support.
To my wife, Kelly.
When I use a word,
it means just what I choose it to mean,
neither more nor less...

Charles Lutwidge Dodgson

( Lewis Carroll )
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CHAPTER 1.0 INTRODUCTION

1.1 Fossil Fuels

Fossil fuels in the form of coal, oil and gas provide the major source of energy world-wide. Coal is the most abundant of these fossil fuels with reserve estimates varying from hundreds to thousands of years at present rates of consumption (1). Although oil and gas currently supply a large part of the world’s energy needs, the decline of oil production over the next few decades will have to be replaced by an energy source which is plentiful, flexible and relatively easy to extract and utilise, i.e. coal.

1.1.1 Current Situation

At the present time, the UK has large supplies of coal. These reserves fall into 3 categories (2) :-

i) Proven: those reserves which are virtually certain to be technically and economically producible,

ii) Probable: those reserves which are estimated to have better than 50% chance of being technically and economically producible,

iii) Possible: those reserves which at present are estimated to have a significant but <50% chance of being technically and economically producible.

Recoverable UK coal reserves are estimated to be 45000 Mt, while the corresponding figures for North Sea oil and gas are 3700 - 6800 and 2500 Mtce, respectively (3). The relatively low reserves of oil and gas, coupled with their
high consumption (Fig. 1.1) will rapidly deplete these energy resources (4).

1.1.2 Future Supplies

As the world's demand for energy increases, reserves of oil and natural gas will rapidly diminish. At some point in the next century, it will be necessary to supplement and eventually replace oil and natural gas with other sources such as substitute natural gas (SNG) which is produced by coal gasification (2,3). It is difficult to predict when this transition will occur but the major source of hydrocarbon fuels in the medium and long term will be coal.

Coal contains incombustible mineral matter together with a number of undesirable elements such as nitrogen, sulphur and chlorine. It is important that as the future utilisation of coal increases, waste material should be removed and not released into the environment as pollutants. The gasification of coal converts coal into a gaseous fuel of high calorific value and has the advantage of being readily purified.

One of the best-developed coal gasification process aimed at the production of SNG is the British Gas-Lurgi slagging gasifier (2). The output gases from this gasifier (60% carbon monoxide and 28% hydrogen) are converted into methane via catalytic methanation. Current gasifiers are capable of gasifying 500 tonnes/day of coal. The output gases can be treated by standard separation processes to remove acid gases e.g. hydrogen sulphide, sulphur dioxide etc. which are believed to be the cause of 'acid rain'. Although any carbonaceous feedstock can be converted into methane, the
only economically viable feedstock, due to its high carbon content, is coal. For this reason, the remainder of this chapter will concentrate on coal, covering both its primary and secondary structures.

1.2 Coal Origins

Coal is a very complex heterogeneous substance and has been given several descriptions (5,6). It can be described as a combustible sedimentary rock consisting of a mixture of organic chemical substances principally carbon, hydrogen, and oxygen, together with smaller amounts of nitrogen, sulphur and mineral matter. It is black or brown in colour and its surface may be dull or have a bright lustre. These and other properties depend on the processes of coal formation.

Coal formation occurred mainly in two geological eras. The first extended from the Lower Carboniferous to the Permian (Table 1.1) and the abundant coal resources in North America and Europe were deposited during this age. The second era began in the late Cretaceous and peaked in the Tertiary. Nearly all lignites and brown coals date back to this era.

Coal basins have chiefly formed in subsided areas or geosynclines. As the rate of subsidence slowed down, sedimentation resulted in shallow lagoons which favoured aquatic plant growth and the extensive formation of swamps. Apart from a few rivers traversing the swamp, the water was nearly stagnant and plant debris continued to accumulate. The plant material settled on the swamp bottom and was converted into peat by microbiological processes.
The accumulation of peat continued until the rate of subsidence of the geosyncline increased again. Sedimentation occurred and a new future coal seam formed. The cycle may be repeated, and this sequence accounts for the formation of the numerous coal seams over millions of years.

1.3 Coalification

Coalification or metamorphic development is the conversion of organic material by heat and pressure and is indicated by a gradual increase in carbon content and decrease in oxygen and hydrogen contents of the organic material during the coal forming process. There are two stages (7,8) :- a) biochemical stage b) geochemical stage. It should be noted that it is not always possible to distinguish between the two stages.

a) The biochemical stage in the formation of coal involves the transformation of plant tissue into peat. Such decompositions are carried out by enzymes, oxidation, fungi, and bacteria both aerobic and anaerobic. For peat to accumulate, the rate of plant growth must exceed the rate of deposition. This requires a water-logged site with layers of living plants on top, dead plants decaying immediately below the surface and a mass of decayed plant material below. The degree of biochemical decay increases with depth in the deposit.

b) The geochemical stage relates to changes in chemical composition produced by heat and pressure i.e. changes from peat to mature coals. The biochemical stage of coalification is considered to be complete after bacterial and fungal activities have ceased. This is usually when the deposit has
been sealed by an impervious layer of sediment. After this, any physical or chemical changes, including the rate of chemical change, are determined by temperature and pressure.

An increase in temperature causes an increase in the rate of chemical change. For homogeneous first order reactions, the rate is doubled for each rise in temperature of 10°C. The time required to produce bituminous coal has been calculated to be about 8 million years (8), assuming that the "coal-forming reaction" took place at an average temperature of 10°C above ambient. The temperature of the strata depends upon the temperature gradient which in turn varies with depth. Generally, this gradient (which is not constant) is about 3-5°C per 100m (7). Extremes of heat e.g. contact with igneous intrusions cause destructive distillation and do not follow the course of the normal metamorphic changes resulting from small temperature rises but lead to changes similar to those in commercial coking. This effect is only regionally significant and does not have any appreciable effect on coalification in general.

Pressure is less important than temperature in coalification. The effects of pressure are: - i) to bring reacting insoluble compounds or groups into sufficient proximity for them to react, ii) to reduce the rate of reactions resulting in the evolution of volatile products. Pressure also has an effect on the compactness and porosity as well as the moisture content of coal. Strong tectonic pressures have little effect on coalification and it has been shown that coalification was already complete before the start of folding (7).
1.4 Coal Petrography

Coal is a very heterogeneous material and petrography is the study of the microscopic components (macerals) which make up coal. The Stopes-Heerlen System uses reflected-light microscopy to characterise coals into four rock types called 'lithotypes': vitrain, clarain, durain, and fusain.

In the USA, the Thiessen - Bureau of Mines system, based on transmitted-light microscopy was adopted. Lithotypes are composed of a number of distinct organic components which each have a distinct set of physical and chemical properties.

Today, these constituents are called macerals by analogy with minerals occurring in inorganic rocks and have the suffix 'inite' (vitrinite, liptinite, inertinite). Macerals evolve from the different organs or tissues of the initial coal-forming plant materials during the course of the first stage of carbonification. They are microscopically recognisable and control the chemical, physical, and technological properties of a coal (Table 1.2). The standard method of determining the maceral composition of a coal sample is a petrographic point-count with an incident-light microscope, of a pellet of crushed particles (9-11).

1.5 Coal Rank

A general progression exists in the metamorphism of plant material to coal. The terms which have been applied classically to this sequence are: peat --> lignite --> sub-bituminous --> bituminous --> semi-bituminous --> semi-anthracite --> anthracite --> meta-anthracite.
Many changes take place throughout the above sequence and it is the measurement of these changes, or the parameters which are used to measure these changes, that is known as rank.

Principal changes with increase of rank (8) are:

i) Increase in carbon, progressively and uniformly.

ii) Decrease in hydrogen, gradually at first until the carbon content reaches about 89 wt.% and then more rapidly.

iii) Decrease in the proportion of volatile matter evolved on destructive distillation, progressively and uniformly within each series of organic compounds.

iv) Increase in calorific value until the hydrogen has decreased to below 4.5 wt.% . This change is related to the change in elementary composition.

v) Decrease in moisture content, particularly in the inherent or 'hydroscopic' moisture, until anthracititous rank is reached.

vi) Increase in absolute density.

vii) Development of coking properties over a certain range of rank and type (15-35 wt.% volatile matter, dmmf basis).

viii) Decrease in solubility in alkaline solutions.

ix) Increase in depth of colour, lustre and importantly reflectivity (Fig. 1.2) (12).

x) Decrease in reactivity towards oxidising or hydrogen-ating agents.
1.6 Coal Composition and Analysis

The classical analytical methods for coal are called a) 'ultimate' and b) 'proximate'. Ultimate analysis (9, 13) gives the precise proportion of the main elements contained in the coal substance, i.e. carbon, hydrogen, nitrogen, sulphur and oxygen. The oxygen may be determined chemically but is usually estimated by difference. The analysis may be presented on an as-received basis, a dry basis, or most commonly, a dry mineral matter free basis. The proximate analysis (9, 15) is less precise and gives the amount of moisture, ash, volatile matter and (by difference) fixed carbon.

Based on ultimate analysis, Van Krevelen's 'atomic H/C vs. O/C diagram' (Fig.1.3) shows the coalification series graphically by plotting their H/C and O/C ratios. This graphical representation has the advantage of showing simple reaction processes as straight lines e.g. dehydration, decarboxylation and demethanation.

Being relatively quick and easily carried out in the average laboratory, proximate analysis is the most widely used method for analysing coals.

Moisture is determined by drying a weighed sample of the coal at a temperature between 104 - 110°C. The moisture content varies with factors such as the mine from which the coal was extracted, the coal seam, and the extent to which the coal has been weathered. High moisture content is undesirable because for example part of the heat of combustion of the coal is consumed in its evaporation.
Volatile matter is the portion converted into volatile products when coal is heated in the absence of air. Since the proportion volatilised varies with temperature and time of heating, the conditions of the test are standardised and rigidly adhered to give comparative results (9,16) (Fig.1.4).

Ash is the residue derived from the mineral matter during complete combustion of coal in excess air. It is quantitatively different from the mineral matter originally present in the coal because of the various changes that occur e.g. loss of water from silicate minerals, loss of carbon dioxide from carbonate minerals, oxidation of iron pyrite to iron oxide and fixation of oxides of sulphur by bases such as calcium and magnesium. The amount of ash is usually determined by burning a sample of the coal in an adequately ventilated muffle furnace at a temperature range 700-950°C.

Fixed carbon is the material remaining after the determination of moisture, volatile matter and mineral matter. Fixed carbon and ash represents the approximate yield of coke from coal. The amount of fixed carbon is calculated by difference.

Out of the five major elements which make up coal, nitrogen and organic sulphur are always minor components. Nitrogen contents rarely exceed 1% and organic sulphur mostly fall between 0.2 and 1.5% (although the latter can occasionally be as high as 5%). Neither nitrogen or sulphur are related to coal rank but it is possible to use carbon, hydrogen and oxygen contents as rank parameters (Figs. 1.5, 1.6).
1.7 Molecular Structure of Coal

Several analytical techniques have been used in the determination of the molecular structure of coal. These include: a) chemical degradation, b) X-ray diffraction, c) nuclear magnetic resonance, and d) infra-red spectroscopy.

1.7.1 Chemical Degradation

A knowledge of the chemical constitution of coal (C,H,O,N,S) does not give much information of its chemical structure. The structures of coal molecules are highly heterogeneous and complex, and are not identified by ordinary methods of organic analysis. In the classical chemical methods of determining structure, the empirical formula, the molecular weight and degradation / synthesis processes are used. This type of study shows that coal is made up of:

i) small clusters of aromatic rings (typically 1 to 5),
ii) functional groups ( O-H, COOH, >O, C=O, >N:, >N-H ),
iii) bridges ( ether, methylene, -O-C, hydrogen bonds ),
iv) hydroaromatics ( dihydroanthracene, 9,10 dihydrophenanthrene ).

Coal is an assemblage of macromolecules of different size and the average size increases with rank (17). These are crosslinked and are difficult to separate and evaluate.

1.7.2 X-ray Diffraction (XRD)

Since coal is not a crystalline substance, XRD alone cannot determine its molecular structure. It can, however, be used
to establish a carbon skeleton. Coals give diffuse diffraction patterns (compared to graphite) due to imperfections, but the intensity distributions are not totally unrelated (Fig. 1.7).

XRD analysis may be summarised in terms of 3 types of structures (Fig. 1.8) (18) :-

i) in low rank coals, an open structure of small layers randomly orientated and crosslinked,

ii) in medium rank coals, a 'liquid' structure with fewer crosslinks, a moderate degree of orientation and reduced porosity,

iii) in high rank coals, a structure of larger layers with a higher degree of orientation and an orientated pore system.

This work, although completed 30 years ago has stood the test of time.

1.7.3 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance has developed to become an important technique for determining coal structure. Classical proton resonance of solids and coals gives broad lines spectra which have little use. This broadening effect is caused by :-

i) dipole-dipole interaction between neighbouring nuclear spins (\(^1\text{H} - ^1\text{H}\) or \(^1\text{H} - ^{13}\text{C}\) ),
ii) chemical shift anisotropy, where the resonance line position varies according to the orientation of the magnetic field relative to the molecular frame of the solid.

With $^{13}$C resonance, the signal intensity is very weak due to the very long spin-lattice relaxation time.

The value of NMR studies has improved recently with the development of the following techniques:

i) proton decoupling (excitation of the proton resonance simultaneously with the $^{13}$C resonance) which averages out the dipole-dipole interaction between $^1$H and $^{13}$C;

ii) cross polarization (CP) whereby an energy transfer is facilitated between the $^1$H and $^{13}$C nuclei which effectively cools the $^{13}$C spins to a lower temperature, so enhancing the $^{13}$C signal;

iii) magic angle spinning (MAS) involves rotating the sample around an axis at an angle of 54°.7 with the static magnetic field. This rotation averages out the chemical shift anisotropy to zero, but it also generates "side-bands" (corresponding to harmonics of the rotation frequency).

These side-bands can, however, be eliminated electronically by a technique called "total suppression of spinning sidebands" (TOSS).

Solid state $^{13}$C-NMR MAS provides information on the carbon skeleton of organic molecules without destroying the structure. Using a combination of techniques, it is possible
to obtain the quantitative relations of structures present (19-23). The fraction of carbon in aromatic groups (fa) can be directly obtained using CP and CP-MAS $^{13}$C-NMR (24) (Fig. 1.9). Low-rank coals have fa values of 0.4 - 0.5 (25) and anthracites fa values >0.9 (25). The relative aromaticities of coal macerals from a high-volatile bituminous coal are:

fusinite > micrinite = vitrinite > exinite (26).

1.7.4 Infra-red Spectroscopy (I.R.)

This is a useful technique for estimating the aromatic to aliphatic hydrogen ratios ($H_{Ar}/H_{Al}$), hydroxyl and carbonyl concentrations. Hydrogen bonded to aromatic and aliphatic carbons have absorption bands at 3030 cm$^{-1}$ and 2920 cm$^{-1}$ respectively. It has been shown that 80% of the hydrogen in low rank coals is aliphatic and the proportion falls to zero for anthracites (17) (Figs. 1.10, 1.11).

This analytical technique has been improved with the advent of Fourier Transform infra-red spectroscopy (FTIR) (27,28). The aromatic and aliphatic C-H stretching frequencies can be used to determine the aromatic and aliphatic hydrogen content ($H_{Ar}$ and $H_{Al}$) by measuring the integrated intensities of the respective infra-red bands.

FTIR has also been coupled with other instrumental methods for coal analysis e.g. photoacoustic-FTIR (29) and thermogravimetric-FTIR (30).
1.8 Coal Models

The main information required for the construction of a coal model are:

i) size and distribution of macromolecules,
ii) number, type and distribution of functional groups, heteroatoms, aromatics and aliphatics,
iii) nature and distribution of bridging structures between aromatics,
iv) cross linking in the macromolecular structure.

By using chemical, spectroscopic, and crystallographic data, Given (31) constructed a molecular model of coal. This three-dimensional model was based on the XRD of Hirsch (18) and van Krevelen's statistical constitutional analysis (7). It contained one- and two-membered rings linked together by dihydroaromatics, pyridine type rings, quinones, hydroxyl and carbonyl groups (Fig. 1.12).

Pitt (32) proposed similar models for vitrains of 80% and 90% carbon based on 9,10 dihydrophenanthrene type of linkages between aromatic units and suggested that these types of molecules exist in an entangled state in coal (Fig. 1.13). Pitt notes that his models contain slightly more hydrogen than the corresponding coals and suggests that the difference would become smaller if the models were dimerized. The introduction of bridging structures would also reduce the hydrogen content.

The model proposed by Wiser is based on small aromatic rings linked together by a wide variety of bridges e.g. ether and
methylene (Fig. 1.14) (33). The rapid degradation of coal into smaller soluble fragments can be attributed to these relatively weak bonds.

Shinn (34) constructed a model using various liquefaction schemes. A molecular weight of 10 000 a.m.u. was selected as the basis for the model and the distribution of atoms in the model was determined to be $C_{661}H_{561}O_{74}N_{11}S_{6}$. N.m.r. data for a coal of this rank showed a distribution of 70% aromatic carbons and 30% aromatic protons. The aromatic carbons from data by Winans et al. (35-37) are distributed among various aromatic ring systems and there is a relative abundance of single- and two-ring structures. In contrast to Wiser's model (Fig. 1.14), systems containing more than four aromatic rings are absent (Fig. 1.15). Shinn's model (Fig. 1.16) represents the average of several macerals (being approximately 85% vitrinites, 8% liptinites and 7% inerts) (34).

More recently, extended models of coal structures have been put forward. Work by Gundermann et al. (38) involved the synthesis of tryptycene derivatives to investigate the tryptycene unit (Fig. 1.17) which is present in the Given model (Fig. 1.12).

In summary, coal has a macromolecular structure which contains crosslinks and entanglements of heterogeneous macromolecules. The type of crosslinks may vary significantly and could involve, for example, oxygen, carbon and various aliphatic groups. The coal models described above are only guides to possible structures. They represent a statistical average of composition data and not of individual or discrete coal 'molecules'.

15
1.9 Classification of Coal

The properties of coals are extremely varied and necessitate characterisation on the basis of its utilisation. The widespread occurrence of coal and the diversity of its uses requires a classification system which can be used as a means of comparison between different coals world-wide.

The Seyler system is a good scientific system (Fig. 1.18) (Table 1.3) (39) and was based on the carbon and hydrogen contents, which are easier to determine than oxygen content. Coals tended to fall into well-defined bands according to their composition. Although this system has been useful for scientific studies, it is not used in commercial practice because it is too complex and has been superseded by other systems.

In general, most coal classification schemes involve two types of parameters. These include i) volatile matter, ii) free swelling index (FSI), iii) calorific value, iv) dilatometry, v) Gray-King assay, and more recently, vi) vitrinite reflectance.

1.9.1 By Volatile Matter Content

Most countries classify coals according to the volatile matter content. This is the percentage loss in weight when a sample of crushed coal is rapidly heated to 900°C under standard conditions in a crucible of specified type, with allowances for moisture and mineral matter in the coal.

Volatile matter is, therefore, a measure of the amount of material driven off under standardised conditions rather
than simple distillation of pre-existing components. This value decreases with increasing rank from around 40% to <5% and in a given coal, exinite has a higher volatile matter content than vitrinite with inertinite having the lowest value.

The use of volatile matter as a parameter in coal classification has special relevance to the carbonisation of coal. It gives a rough measure of tar and gas yields which may be expected when a coal is heated in the absence of oxygen.

1.9.2 British Coal (NCB) Classification, UK

Although volatile matter forms the backbone to coal classification, it is necessary to use at least one more parameter in order to characterise the behaviour of a coal when heated. This is because two coals may have the same volatile content but differ from one another in the extent to which they swell or cake together (Fig. 1.19) (32,40).

The NCB system relies on the coke-forming characteristics of the various coals as well as on the types of coke produced by a standard coking test (the Gray-King carbonisation assay). In this classification system, a three-figure code number is used to describe each particular coal with the lower numbers being assigned to the higher rank coals (Table 1.4) (41).
1.9.3 By Fixed Carbon (ASTM System), US

The fixed carbon (F.C.) of a coal is the solid residue, other than mineral ash, remaining after all the volatile matter has been removed under prescribed conditions. It is often described as the coke-like residue.

% F.C. = 100 - ( %moisture + %volatile matter + %ash )

The American Society for Testing and Materials (ASTM) has devised a method of coal classification which makes use of fixed carbon content as well as other physical properties. Proximate analysis data form the basis in which the coals are grouped. Coals having less than 31 wt% volatile matter, dry-ash-free (d.a.f.) i.e. class II group 4 are classified according to their calorific value (Table 1.5).

The agglomerating characteristics are also used to differentiate between certain adjacent groups. This classification system indicates the degree of coalification via proximate analysis and calorific value, with the lignite coals being classed as low-rank coals and anthracites as high-rank coals. Although coal rank increases with the amount of fixed carbon and decreases with the amount of moisture and volatile matter, it is incorrect to equate coal rank with the proportion of elemental carbon in the coal (42).

1.9.4 By the UN International System

The International System of Coal Classification was developed in 1949 as a result of the greatly increased volume of trade between the various coal-producing and coal-consuming nations (42). In this system, coals are placed
into two major groups: hard coal and brown coal.

Hard coal is defined as a coal with a calorific value greater than 10,260 Btu/pound (23.86 MJ/kg) on a moist, ash-free (m.a.f.) basis. Brown coal is defined as coal with a calorific value of less than 10,260 Btu/pound (23.86 MJ/kg). The hard coals, (based on d.a.f., volatile matter content and m.a.f. calorific value) are divided into groups according to their caking properties. The coal groups are then further subdivided into subgroups according to their coking properties.

A three-figure code is used to express the coal in this classification system e.g. x (class) y (group) z (subgroup). Therefore a 423 coal would be a class 4 coal with a free swelling index of 2.5-4 and a dilatation of between 0 - 50% (Table 1.6).

1.9.5 The New Economic Commission for Europe (ECE) System

The ECE 'classification' system is not hierarchical and 'codification' is a more accurate term (43). The codification (Table 1.7) uses a 14 digit code to represent the eight chosen parameters. These are (in sequence):-

i) mean random vitrinite reflectance (2 digits);

ii) vitrinite reflectogram characteristics (1 digit);

iii) maceral composition (inertinite content 1 digit, lipinite content 1 digit);

iv) crucible swelling number (1 digit);

v) volatile matter (2 digits);

vi) ash (2 digits);

vii) sulphur (2 digits);
viii) gross calorific value (2 digits).

This system has the advantage of reducing ambiguities often encountered with descriptive systems e.g. ASTM. However, it can be criticised for being complicated and requires decoding.

1.10 Summary

Coal is a general term used to describe a wide spectrum of rocks of organic origin. The heterogeneous nature of coal makes it difficult to create an accurate model. Although several coal models have been proposed, these only represent statistical averages and not of discrete coal 'molecules'.

These models have been formulated from characteristics which are repeated in coals. These include: size distribution of the macromolecules, functional groups, bridges, average size of aromatic rings, types of cross-links, degree of cross-linking, and carbon aromaticity.

Coal generally appears to consist of crosslinks and entanglements of heterogeneous macromolecules. Despite containing definable units and features which have distinct chemical and physical properties, the heterogeneous nature of coal is a major obstacle in finding its macromolecular structure (since the structure will vary for different macerals). It is clear that the molecules found in coal are very large but their precise structure is still unknown.

The chemical and physical properties of these structures are important in obtaining an understanding of coal behaviour during processes such as carbonisation, gasification and combustion.
Table 1.1 Classification of Geological Strata and Age of Coals (7)

<table>
<thead>
<tr>
<th>Mean age of coals (10^6 years)</th>
<th>Stratigraphic Period</th>
<th>Principal Coal Formations</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>Holocene</td>
<td>Moorland peats in Europe.</td>
</tr>
<tr>
<td>&lt;1</td>
<td>Pleistocene</td>
<td>Forest peats in N. America.</td>
</tr>
<tr>
<td>2</td>
<td>Pliocene</td>
<td>Lignites in Eastern Europe, Japan, New Zealand, Alaska.</td>
</tr>
<tr>
<td>15</td>
<td>Miocene</td>
<td>Lignites in Western Europe, Asia, Australia, Mexico, Greenland.</td>
</tr>
<tr>
<td>60</td>
<td>Eocene</td>
<td>Lignites &amp; subbit. coal in Germany, Hungary, N. America, Burma.</td>
</tr>
<tr>
<td>120</td>
<td>Cretaceous</td>
<td>Lignites, subbit. &amp; bit. coals in N. America, Mexico, Chile, Peru, France, Germany, Austria, Bulgaria, Japan, Australia, New Zealand.</td>
</tr>
<tr>
<td>160</td>
<td>Jurassic</td>
<td>Coals in Sweden, Hungary, Rumania, Russia, China, Australia, New Zealand.</td>
</tr>
<tr>
<td>200</td>
<td>Triassic</td>
<td>Coals in Poland, Austria, N. America, Mexico, Australia.</td>
</tr>
<tr>
<td>245</td>
<td>Permian</td>
<td>Coals in France, Russia, China, India, Africa, Australia, USA.</td>
</tr>
<tr>
<td>300</td>
<td>Carboniferous</td>
<td>Coals in France, Germany, France, Holland, U.K., Poland, Russia, N. &amp; S. America.</td>
</tr>
<tr>
<td>380</td>
<td>Devonian</td>
<td>Coals in Bear Island, Cannel coals in Arctic Islands, Halserite coal.</td>
</tr>
<tr>
<td>450</td>
<td>Silurian</td>
<td>Shungite in NW Russia.</td>
</tr>
<tr>
<td>500</td>
<td>Cambrian</td>
<td></td>
</tr>
<tr>
<td>PROPERTY</td>
<td>MACERAL</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vitrite</td>
<td>Exinite</td>
</tr>
<tr>
<td>Origin</td>
<td>derived from cell wall material or the woody tissue of plants</td>
<td>from waxy &amp; resinous parts of plants e.g. spores, cuticles &amp; wound resins</td>
</tr>
<tr>
<td>Abundance</td>
<td>most abundant, 50 - 90%</td>
<td>varies from &lt; 5 - 15%</td>
</tr>
<tr>
<td>Density</td>
<td>1.3 - 1.8g/ml</td>
<td>1.18 - 1.28g/ml</td>
</tr>
<tr>
<td>Coking ability</td>
<td>important for carbonisation, forms the bulk of the coke mass</td>
<td>some devolatilise as gases &amp; tars</td>
</tr>
<tr>
<td>Chemistry</td>
<td>C &amp; H contents at any rank are intermediate between exinite &amp; inertinite</td>
<td>has the highest H content but lowest C content</td>
</tr>
<tr>
<td>Toughness</td>
<td>polishing can give a negative relief</td>
<td>polishing can give a positive relief</td>
</tr>
<tr>
<td>Reflectance</td>
<td>value falls between exinite and inertinite</td>
<td>shows the lowest reflectance</td>
</tr>
<tr>
<td>Fluorescence</td>
<td>some vitrinite show a weak, brownish fluorescence under uv light</td>
<td>all exinite fluoresce when excited by uv light</td>
</tr>
</tbody>
</table>
### Table 1.3 Seyler's Classification of Coal

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Anthracite</th>
<th>Carbonaceous</th>
<th>Bituminous</th>
<th>Lignitic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anthracite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon over</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>93.3 per cent</td>
<td>93.3—91.2</td>
<td>91.2—89.0</td>
<td>89.0—87.0</td>
<td>87.0—84.0</td>
</tr>
<tr>
<td>Per-bituminous</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>genus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen over</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.8 per cent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Per-bituminous</td>
<td>Per-bituminous</td>
<td>Per-bituminous</td>
<td>Per-Lignitous</td>
</tr>
<tr>
<td></td>
<td>(Per-meta-bituminous)</td>
<td>(Per-ortho-bituminous)</td>
<td>(Per-para-bituminous)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bituminous genus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen 5.0—5.8</td>
<td>(Pseudo-bituminous species)</td>
<td>META-BITUMINOUS</td>
<td>ORTHO-BITUMINOUS</td>
<td>LIGHTITOUS</td>
</tr>
<tr>
<td>per cent</td>
<td></td>
<td></td>
<td></td>
<td>(Meta—)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semi-bituminous genus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen 4.5—5.8</td>
<td>(Ortho-semi-bituminous)</td>
<td>Sub-bituminous</td>
<td>Sub-bituminous</td>
<td>Sub-Lignitous</td>
</tr>
<tr>
<td>per cent</td>
<td></td>
<td>(Sub-meta-bituminous)</td>
<td>(Sub-ortho-bituminous)</td>
<td>(Meta—)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonaceous genus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen 4.0—4.5</td>
<td>(Ortho-carbonaceous)</td>
<td>Pseudo-carbonaceous</td>
<td>Pseudo-carbonaceous</td>
<td>Pseudo-carbonaceous</td>
</tr>
<tr>
<td>per cent</td>
<td></td>
<td>(Sub-meta-bituminous)</td>
<td>(Sub-ortho-bituminous)</td>
<td>(Sub-para-bituminous)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracite genus</td>
<td>ORTHO-ANTHRACITE</td>
<td>Pseudo-anthracite</td>
<td>Pseudo-anthracite</td>
<td>Pseudo-anthracite</td>
</tr>
<tr>
<td>Hydrogen under 4 per cent</td>
<td>True anthracite</td>
<td>(Sub-carbonaceous)</td>
<td>(Sub-meta-bituminous)</td>
<td>(Sub-ortho-bituminous)</td>
</tr>
</tbody>
</table>
Table 1.4 The British (NCB) Coal Classification System

<table>
<thead>
<tr>
<th>Group (S)</th>
<th>Class</th>
<th>Volatile Matter dry, mineral matter-free %</th>
<th>Gray-King Coke Type</th>
<th>General Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>101†</td>
<td>Under 9.1</td>
<td>A</td>
<td>Anthracites</td>
</tr>
<tr>
<td></td>
<td>102†</td>
<td>6.1-9.0</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>201</td>
<td>9.1-19.5</td>
<td>A-G8</td>
<td>Low-volatile steam coals</td>
</tr>
<tr>
<td></td>
<td>201a</td>
<td>9.1-13.5</td>
<td>A-G</td>
<td></td>
</tr>
<tr>
<td></td>
<td>201b</td>
<td>11.6-13.5</td>
<td>B-C</td>
<td>Dry steam coals</td>
</tr>
<tr>
<td></td>
<td>202</td>
<td>13.6-15.0</td>
<td>B-G</td>
<td>Coking steam coals</td>
</tr>
<tr>
<td></td>
<td>203</td>
<td>15.1-17.0</td>
<td>B-G4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>204</td>
<td>17.1-19.5</td>
<td>G1-G8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>301</td>
<td>19.6-32.0</td>
<td>A-G9 and over</td>
<td>Medium-volatile coals</td>
</tr>
<tr>
<td></td>
<td>301a</td>
<td>19.6-22.0</td>
<td>G4 and over</td>
<td></td>
</tr>
<tr>
<td></td>
<td>301b</td>
<td>27.6-32.0</td>
<td>G4 and over</td>
<td>Prime coking coals</td>
</tr>
<tr>
<td></td>
<td>305</td>
<td>19.6-32.0</td>
<td>G-G3</td>
<td>(Mainly) heat-altered medium-volatile coals</td>
</tr>
<tr>
<td></td>
<td>306</td>
<td>19.6-32.0</td>
<td>A-B</td>
<td></td>
</tr>
<tr>
<td>400-900</td>
<td>401</td>
<td>Over 32.0</td>
<td>A-G9 and over</td>
<td>High-volatile coals</td>
</tr>
<tr>
<td></td>
<td>402</td>
<td>Over 36.0</td>
<td>G9 and over</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>G9 and over</td>
<td>Very strong caking coals</td>
</tr>
<tr>
<td>500</td>
<td>501</td>
<td>Over 32.0</td>
<td>G5-G8</td>
<td>Strongly caking coals</td>
</tr>
<tr>
<td></td>
<td>502</td>
<td>Over 32.1</td>
<td>G5-G8</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>601</td>
<td>Over 32.0</td>
<td>G5-G4</td>
<td>Medium caking coals</td>
</tr>
<tr>
<td></td>
<td>602</td>
<td>Over 36.0</td>
<td>G1-G4</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>701</td>
<td>Over 32.0</td>
<td>B-G</td>
<td>Weakly caking coals</td>
</tr>
<tr>
<td></td>
<td>702</td>
<td>Over 36.0</td>
<td>B-G</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>801</td>
<td>Over 32.0</td>
<td>C-D</td>
<td>Very weak caking coals</td>
</tr>
<tr>
<td></td>
<td>802</td>
<td>Over 36.0</td>
<td>C-D</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>901</td>
<td>Over 32.0</td>
<td>A-B</td>
<td>Nonecaking coals</td>
</tr>
<tr>
<td></td>
<td>902</td>
<td>Over 36.0</td>
<td>A-B</td>
<td></td>
</tr>
</tbody>
</table>

* Coals of groups 100 and 200 are classified by using the parameter of volatile matter alone. The Gray-King coke types quoted for these coals indicate the ranges found in practice and are not criteria for classification.

† To divide anthracites into two classes, it is sometimes convenient to use a hydrogen content of 3.35% (d.m.m.f.) instead of a volatile matter of 6.0% as the limiting criterion. In the original Coal Survey rank coding system the anthracites were divided into four classes then designated 101, 102, 103, and 104. Although the present division into two classes satisfies most requirements, it may sometimes be necessary to recognize four or five classes.
Table 1.5 Arrangement of Coals from the United States in the Order of ASTM Rank

<table>
<thead>
<tr>
<th>No.</th>
<th>Class</th>
<th>Group</th>
<th>State</th>
<th>County</th>
<th>Coal analysis bed moisture basis</th>
<th>Rank FC</th>
<th>Rank Btu</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>VM</td>
<td>CC</td>
</tr>
<tr>
<td>1</td>
<td>I</td>
<td>1</td>
<td>Pa.</td>
<td>Schuykill</td>
<td>4.5</td>
<td>1.7</td>
<td>84.1</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>2</td>
<td>Pa.</td>
<td>Lackawanna</td>
<td>2.5</td>
<td>6.2</td>
<td>79.4</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>3</td>
<td>Va.</td>
<td>Montgomery</td>
<td>2.0</td>
<td>10.6</td>
<td>67.2</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>1</td>
<td>W. Va.</td>
<td>McDowell</td>
<td>1.0</td>
<td>16.6</td>
<td>77.3</td>
</tr>
<tr>
<td>5</td>
<td>II</td>
<td>1</td>
<td>Pa.</td>
<td>Cambria</td>
<td>1.3</td>
<td>17.5</td>
<td>70.9</td>
</tr>
<tr>
<td>6</td>
<td>II</td>
<td>2</td>
<td>Pa.</td>
<td>Somerset</td>
<td>1.5</td>
<td>20.8</td>
<td>67.5</td>
</tr>
<tr>
<td>7</td>
<td>II</td>
<td>2</td>
<td>Pa.</td>
<td>Indiana</td>
<td>1.5</td>
<td>23.4</td>
<td>64.9</td>
</tr>
<tr>
<td>8</td>
<td>II</td>
<td>3</td>
<td>Pa.</td>
<td>Westmoreland</td>
<td>1.5</td>
<td>30.7</td>
<td>56.6</td>
</tr>
<tr>
<td>9</td>
<td>II</td>
<td>3</td>
<td>Ky.</td>
<td>Pike</td>
<td>2.5</td>
<td>36.7</td>
<td>57.5</td>
</tr>
<tr>
<td>10</td>
<td>II</td>
<td>3</td>
<td>Ohio</td>
<td>Belmont</td>
<td>3.6</td>
<td>40.0</td>
<td>47.3</td>
</tr>
<tr>
<td>11</td>
<td>II</td>
<td>4</td>
<td>Ill.</td>
<td>Williamson</td>
<td>5.8</td>
<td>36.2</td>
<td>46.3</td>
</tr>
<tr>
<td>12</td>
<td>II</td>
<td>4</td>
<td>Utah</td>
<td>Emery</td>
<td>5.2</td>
<td>38.2</td>
<td>50.2</td>
</tr>
<tr>
<td>13</td>
<td>II</td>
<td>5</td>
<td>Ill.</td>
<td>Vermillion</td>
<td>12.2</td>
<td>38.9</td>
<td>40.0</td>
</tr>
<tr>
<td>14</td>
<td>III</td>
<td>1</td>
<td>Mont.</td>
<td>Musselshell</td>
<td>14.1</td>
<td>32.2</td>
<td>46.7</td>
</tr>
<tr>
<td>15</td>
<td>III</td>
<td>2</td>
<td>Wyo.</td>
<td>Sheridan</td>
<td>25.0</td>
<td>30.5</td>
<td>40.8</td>
</tr>
<tr>
<td>16</td>
<td>III</td>
<td>3</td>
<td>Wyo.</td>
<td>Campbell</td>
<td>31.0</td>
<td>31.4</td>
<td>32.8</td>
</tr>
<tr>
<td>17</td>
<td>IV</td>
<td>1</td>
<td>N. D.</td>
<td>Mercer</td>
<td>37.0</td>
<td>26.6</td>
<td>32.2</td>
</tr>
</tbody>
</table>

Data on coal (bed moisture basis):
M = equilibrium moisture, %; VM = volatile matter, %; FC = fixed carbon, %; A = ash, %; S = sulfur, %; Btu = high heating value, Btu per lb; rank Btu = moist mineral matter free Btu per lb; all calculations by Parr formulas
### Table 1.6 The International Coal Classification System

<table>
<thead>
<tr>
<th>GROUPS (determined by gross properties)</th>
<th>CODE NUMBERS</th>
<th>SUB-GROUPS (determined by volatile matter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group Number</td>
<td>Alternative group parameter</td>
<td>Lower Coarse rating 45-50</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>3</td>
<td>&gt; 4</td>
<td>&gt; 45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>21–45</td>
<td>21–25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1–2</td>
<td>1–5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0–1</td>
<td>0–3</td>
</tr>
</tbody>
</table>

**Class number**

- **Volatiles matter (wt%)**
  - 0–3: > 10
  - > 13: > 20
  - > 14: > 28
  - > 15: > 33

- **Gross calorific value (kJ/kg)**
  - > 2750: > 3200

**CLASS**

- **Non-inert (A)**
- **Inert (B)**
### Table 1.7 The European (ECE) Coal Classification System

<table>
<thead>
<tr>
<th>Vitrinite reflection (mean random)</th>
<th>Characteristics of reflectogram†</th>
<th>Maceral group composition (mmf)</th>
<th>Crucible swelling number</th>
</tr>
</thead>
<tbody>
<tr>
<td>code</td>
<td>$R_{\text{random}}$ %</td>
<td>code</td>
<td>standard deviation</td>
</tr>
<tr>
<td>02</td>
<td>0.2-0.29</td>
<td>0</td>
<td>≤0.1</td>
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<tr>
<td>03</td>
<td>0.3-0.39</td>
<td>1</td>
<td>&gt;0.1 ≤0.2</td>
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<tr>
<td>04</td>
<td>0.4-0.49</td>
<td>2</td>
<td>&gt;0.2</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3</td>
<td>1 gap</td>
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<tr>
<td>48</td>
<td>4.8-4.89</td>
<td>4</td>
<td>2 gaps</td>
</tr>
<tr>
<td>49</td>
<td>4.9-4.99</td>
<td>5</td>
<td>&gt;2 gaps</td>
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<tr>
<td>50</td>
<td>≥5.0</td>
<td>9</td>
<td>≥90</td>
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</table>

<table>
<thead>
<tr>
<th>volatile matter,§</th>
<th>ash, dry</th>
<th>total sulphur, dry</th>
<th>gross calorific value, daf</th>
</tr>
</thead>
<tbody>
<tr>
<td>daf mass% code</td>
<td>code</td>
<td>mass% code</td>
<td>mass% code</td>
</tr>
<tr>
<td>48</td>
<td>≥48</td>
<td>00</td>
<td>0-&lt;1</td>
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<td>02</td>
<td>2-&lt;3</td>
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<tr>
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<td>-</td>
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<td>12-&lt;14</td>
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<td>20-&lt;21</td>
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</tr>
<tr>
<td>01</td>
<td>1-&lt;2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* Higher rank coals are coals with: gross calorific value (maf) ≥24 MJ/kg and those with gross calorific value (maf) <24 MJ/kg, provided mean random vitrinite reflectance ≥0.6%.

† A reflectogram as characterised by code number 2 can also result from a high rank seam coal.

§ It should be stressed that some of the inertinite may be reactive.

§ Where the ash content of coal is more than 10%, it must be reduced, before analysis, to below 10% by dense medium separation. In these cases, the cutting density and resulting ash content should be stated.
Fig. 1.1 UK Energy Consumption (4)

1978
339.8 Mtce

1988
340.1 Mtce

(1 tce = 29225 MJ)
Fig. 1.2 Relationship between vitrinite reflectance and different chemical rank parameters
Fig. 1.3 Van Krevelen's H/C versus O/C diagram (7)
Fig. 1.4 Comparison on moist, wt.-basis of heat values and proximate analyses (12)
Fig. 1.5 Comparison of hydrogen and oxygen contents in coal macerals (7)
Continuous Variation in Composition of Coals from Lignites to Anthracites, C/O Co-ordinates.—Hickling.

Fig. 1.6 The change in carbon content with rank (8)
Fig. 1.7 X-ray diffraction curves of vitrinites and graphite
a) The coalification series  b) Graphite (100% C) (7)
Cross links

Layers

Pores

Amorphous material

80% C

Group of layers

20R

10R

8R

Single layers + amorphous material

89% C

Structural model of coal, according to Hirsch.

σ = "Open structure"; λ = "Liquid structure"; ε = "Anthracite structure". (7)

Fig. 1.8 Hirsch's Coal Model (7)
Fig. 1.9 The aromatic carbon content ($f_a$) of a coal and its macerals
Fig. 1.10 Variation of carbon aromaticity with rank (12)

Fig. 1.11 Variation of hydrogen aromaticity with rank (12)
Fig. 1.12 Given's Coal Model
Fig. 1.13 Model structures proposed by Pitt

* points where dimerisation could occur
Fig. 1.14 Model structure proposed by Wiser
Fig. 1.15 Aromatics distribution for interior province bituminous coal (34)
Fig. 1.16 Model structure proposed by Shinn (34)
Fig. 1.17 Tryptycene
Fig. 1.18 Seyler's Scientific Classification System
Fig. 1.19 Gray-King coke types
CHAPTER 2.0 COAL CARBONISATION AND CHARACTERISATION

Carbonisation is the process of destructive distillation of organic substances in the absence of air to give a high carbon content material along with liquid and gaseous products. Low-temperature carbonisation of coal is carried out at a temperature of 450 - 700 °C, medium-temperature carbonisation from 700 - 900 °C, and above that temperature the process is known as high-temperature carbonisation (Table 2.1) (32). In the slagging gasifier, coal undergoes low temperature carbonisation in the devolatilisation zone and because of the importance of this stage in the development of the coke structure, only low-temperature carbonisation will be discussed in detail.

2.1 Low-temperature Carbonisation

Four main products are produced by low-temperature carbonisation: - i) semi-coke, ii) tar, consisting largely of complex aromatic liquid hydrocarbons, iii) gases, and iv) aqueous liquor.

The solid product from low-temperature carbonisation is usually a soft, black, porous material which still contains considerable volatile matter. It has a resemblance to charcoal rather than high-temperature coke, and is often incorrectly called 'char'. 'Semi-Coke' is a better term when at least parts of the coal passes through a fluid state during carbonisation. There are several parameters which affect the product composition of coal carbonisation. These include: - i) heating rate, ii) temperature, iii) coal type, iv) pressure, and v) residence time.
2.1.1 Effect of Heating Rate

Coal carbonisation in industry is usually carried out at a relatively low average heating rate of about $3^\circ$C/min. This optimises char yields by the promotion of secondary reaction of the tar and results in a solid smokeless fuel for domestic use. The change in yield of products with increasing rate of heating is very evident (Table 2.2) (44). The yield of liquefied products becomes greater while the yield of gas, and low temperature coke is reduced with increasing heating rate.

Arendt and van Heek (45) pyrolysed several coals at different rates of heating. One series of experiments was carried out in a thermobalance (with 1.5g of coal) under an inert gas flow and in another 10mg of coal were pyrolysed using a wire-mesh screen under a closed system. The heating rates varied from $0.05 - 3$ °C/s for the thermobalance experiment and from $200 - 1200$ °C/s for the wire-mesh experiment. Their results showed that high heating rates increased tar formation. The tars produced at low heating rates are also lighter in molecular weight (46) as well as containing more low boiling point components than those produced under rapid low temperature carbonisation (Fig. 2.1) (44).

Howard (47) claims that heating rate has no effect on total volatile matter released and argues the different techniques used to produce the different heating rates influence the outcome. Factors such as particle size and reactor type (which influences residence times), and the final tempera-
ture reached in the experiment, not the heating rate, influence the production of volatiles. Howard explains the changes with heating rate of the time-temperature profile for maximum yield (Fig. 2.2) as follows. As the rate increases, so does the temperature where the maximum yield is found. In addition to this, as the rate increases, the range of temperature for devolatilisation increases and consequently, there is time for the occurrence of secondary reactions. Howard concludes that although the maximum rate of devolatilisation increases with increase in heating rate, it is temperature, rather than heating rate, that is important for high volatile yields.

O'Brien et al. (48) observed the effect of heating rate from 1 - 20 °C/s on a low rank bituminous coal and found that char yields increased with heating rate (Table 2.3) but not when the coal was mixed with sand. This led them to suggest that coal agglomerates to a greater extent at the higher heating rate. Gas yields were also higher with increase in heating rate and tars increased in aromaticity, containing fewer phenolic groups as a result of hydrocracking (Table 2.4).

Ikeda and Sakawa (49) studied the effect of heating rate on tar production and noted that tar formation began at a higher temperature as the heating rate was increased. This was caused by shorter integral time of reaction rate of higher rates of heating. The increase in tar yield with heating rate was explained by the fact that rapid heating made the residence time of tar in a coal particle shorter and reduced the chance of recombination and decomposition of unstable tar i.e. secondary reactions.
Effects of heating rate need to be considered in situations where secondary reactions are important (47). In addition to this, its effects on rate of devolatilisation has practical implications e.g. it may improve the contact between coal particles.

2.1.2 Effect of Temperature

Temperature is a very important variable in the study of coal carbonisation. At low temperatures (<600°C) tar and char production is favoured with water vapour being the dominant component of the gas. Intermediate temperatures (c. 700°C) maximize tar production, reduce char production and increase gas evolution (primarily CO). There is a significant increase in gas formation at higher temperatures (750-1100°C) as the result of secondary cracking of the tar (Fig. 2.3). Small quantities of light hydrocarbons and hydrogen are formed but carbon monoxide remains as the major gaseous product (44).

The decomposition of most coals begins at approximately 350°C and increasing the temperature gives a higher yield of volatiles. This reaches a plateau, where secondary reactions and the formation of coke occurs, and is strongly dependent on heating rate and residence time. The percentage of tar produced increases with temperature to about 650°C and levels off regardless of coal rank or the hold time.

Solomon (50) showed that the temperature dependence of the devolatilisation product distribution is the same for all the coals studied except for the evolution of CO₂ from a lignite. Water, tar, and light-hydrocarbon evolution increases with temperature before reaching a plateau.
Hydrogen and CO are evolved at higher temperatures and do not peak even at 1000 °C.

Using NMR, Collin et al. (51) showed that as the flash pyrolysis temperature increases, the chemical nature of the tar product changes. Above 600 °C, the tars have more fused aromatic rings and a decreased phenol content.

Temperature plays two roles in coal carbonisation. Its first effect is on the decomposition of the coal and this is followed by secondary reactions of the volatiles (47). In the absence of secondary reactions, the yield of a given volatile component increases monotonically with increasing temperature. The effects of temperature are coupled with those of time. The importance of time increases as heat and mass transfer limitations become more significant (47).

Although temperature is a very important variable in coal pyrolysis, other parameters e.g. heating rate, and pressure, interact with the devolatilisation process and the relationships need to be considered.

2.1.3 Effect of Coal Type

The yields, compositions and rates of evolution of pyrolysis products are strongly dependent on the type of starting material (Table 2.5) (47). Increasing rank is associated with a) decrease in oxygen content, and, b) a slight decrease in hydrogen content in the coal.

Upon carbonisation, coals of low rank produce higher yields of water and oxides of carbon. With high-rank coals, most of the hydrogen is released in the gaseous form. The decrease
in oxygen content with increasing rank is reflected in the pyrolysis products (as water, CO and CO₂).

Davies et al. (52) investigated the effect of rank using thermogravimetric analysis (TGA) and found that there is a correspondence between maximum point of weight loss in temperature and rank. It was also found that higher rank coals required a higher temperature to release volatiles at a rapid rate. Ko et al. (53) put forward a model which incorporated the idea that the number of labile bridges and the amount of abstractable hydrogen are directly proportional to the tar yields but the number of cross-linked bridges is inversely proportional.

The model of coal devolatilisation developed by Solomon et al. (54) combined the functional group (FG) model with the devolatilisation-vaporisation-crosslinking (DVC) model.

The FG model describes the formation of gas species. There are two competing mechanisms for the removal of a functional group from coal: - i) evolution as a part of a tar molecule, ii) evolution as a distinct gas species by decomposition of the functional group.

The DVC model describes the formation of tar. This involves a combination of polymerisation and transport processes. The weight of the coal molecular fragments are reduced via bond breaking and stabilisation of free radicals until the fragments are sufficiently small to be transported through the particle and away from the surface. This process continues until all donatable hydrogens are consumed. Crosslinking occurs simultaneously, and it is assumed that for each molecule of CO₂ or CH₄ that is evolved, one crosslink is formed in the coke.

26
Solomon et al. (54) highlighted that the major rank dependent phenomenon is the amount and rate of crosslinking which controls the yield of tar and molecular weight distribution in the tar and coke.

Since rank is associated with oxygen content, the effect of coal type can be discussed in terms of reactive species which contain oxygen. Hydroxyl and other reactive oxygen groups favour condensation reactions (to form semicoke) by consuming hydrogen that would otherwise promote tar evolution. Alternatively, these reactive oxygen species can increase coke formation directly through cross-bonding (47).

2.1.4 Effect of Pressure

The effects of inert gas pressure on carbonisation are usually explained in terms of secondary reactions of volatiles. Generally, an increase in pressure causes volatiles to stabilise in the fluid phase which can then be carbonised. This results in the production of more coke, methane and oxides of carbon but less tar. The largest effect of increasing pressure is increased yields of coke and light hydrocarbons at the expense of tar, particularly for bituminous coals.

Hammer and Treuling (55) carbonised a high volatile coal under pressure and found that under nitrogen, i.e. without any reaction of the carrier gas with primary pyrolysis products, the tar yield was optimal between 400-500°C. Aromaticity (percentage of H bound to aromatic C-atoms) of the fraction increased with temperature from 0.52 to 0.74 when the temperature was increased from 400 to 600 °C. But it decreased from 0.52 to 0.44 at 400 °C and 0.74 to 0.65 at
600 °C when the pressure was increased from 1.0 to 8.0 MPa. Their tar yield followed the same trend as that shown by Arendt and van Heek (45) i.e. tar yield decreases with increasing pressure of inert gas.

Ikeda and Sakawa (49) varied the gaseous atmosphere (\(H_2\) and \(N_2\)). They found the effect of nitrogen pressure gave trends similar to those reported by previous authors, but under hydrogen pressure, the tar yield increased. Analysis of the tar showed that the concentrations of benzene, toluene and xylene (BTX) also increased with pressure (Fig. 2.4). This was because the high pressure of \(H_2\) react with the tar which stabilise the fragments so preventing their recombination and decomposition (Table 2.6) (49).

Similar results were obtained by Takeuchi and Berkowitz (56) who in addition, found the tar yields increased appreciably when \(H_2O/CO\) was used instead of \(N_2\) or \(H_2\). The replacement of \(N_2\) by \(H_2\) greatly enhanced the generation of gases (\(CO\), \(CO_2\), \(CH_4\)) mainly at the expense of water, possibly via :-

\[
C + 2H_2 \rightarrow CH_4
\]

and some concurrent reduction of carbon oxides.

The effects of pressure are most evident for bituminous coals. It appears that secondary reactions which includes cracking and coke formation play a large role in product yields. This can be summarized in terms of increases in coke yield, less tar, more methane plus more \(CO\) and \(CO_2\).
2.1.5 Effect of Residence Time

Time plays an important role in coal carbonisation in terms of heat and mass transfer effects. Residence time of the coal in the heated zone depends on both the type of reactor and coal properties. This period of time includes time for transport of the products out of the coal, which in turn is directly related to the coal particle size and porosity.

Lowenthal et al. (57) correlated the swelling of the coal particle to tar formation under rapid pyrolysis conditions. The swelling properties of the coal directly related to the solids residence time and the time of transport of the products out of the coal particle. The swelling additionally influences the heat transfer from the gaseous phase to the particle.

Howard (47) has reported pyrolysis experiments at temperatures up to 1800 °C using various methods such as disperse laminar flow, free fall and crucible heating to cover coal residence times from 0.01s to 12 h (Fig. 2.5) (47). The overall trends show falls in elemental composition (C, H, O, N, S) with increase in residence times from 0.01 to 1s but level off with longer times.

The temperature-time histories of the three experimental techniques used to obtain a wide range of residence times are different. This is most significant between the laminar flow runs and the crucible runs (47). Therefore, the results of the crucible runs should not be interpreted as the extension of corresponding laminar flow runs at long residence times.
2.2 Coal Behaviour During Carbonisation

As coal is heated progressively to high temperatures in an inert atmosphere it decomposes with the evolution of water, tar and gas to give a solid residue of coke with varied composition and properties which are dependent on the experimental conditions, in particular, heat treatment and the rank of coal used. In the temperature 350-500 °C coking coals soften, undergo a plastic stage, coalesce and swell to form, in the normal carbonisation process, a solid porous structure (coke). This process can be divided into three stages (Fig. 2.6) (58).

2.2.1 The Pre-Plastic Stage

This first stage involves the evolution of volatile matter (water, carbon dioxide and some light hydrocarbons) from the removal of various surface groups from the condensed aromatic structures. At this stage there is no definite evidence of any substantial change in the coal but small changes, including some loss of surface groups and a limited amount of depolymerisation do occur.

2.2.2 The Plastic Stage

The plastic stage is the most important stage in the coking process. It is sometimes termed 'active' thermal decomposition (59) and begins at 350-400 °C and ends around 550 °C. This is the carbonisation temperature range which covers the softening of the coal and its resolidification to form the semi-coke. This is also the temperature range where optical texture changes. Within this range of temperature, there is
extensive molecular disruption and considerable evolution of volatile matter including both aromatic and aliphatic components.

In prime coking coals (which have a volatile content of 20-32 wt% d.m.m.f.) the main volatile matter evolution follows the onset of plasticity and these coals are so named because they yield strong coke with good abrasion resistance (33). Viscosity and rate of devolatilisation of the plastic mass are such that intragranular swelling is high and neighbouring coal particles are able to adhere strongly. This produces a coke with fairly uniform pores of small diameter surrounded by relatively thick walls and consequently has a high resistance to abrasive forces.

Coal with higher volatile matter i.e. low rank, begin decomposition before the plastic temperature zone. Intragranular swelling often occurs and the whole mass may foam and result in a coke with thin walled pores of large diameter i.e. high porosity, and with a relatively low resistance to abrasion.

The initial phase of the thermal decomposition of coking coal can be considered as a depolymerisation, giving rise to smaller molecules which have sufficient mobility to produce the plasticity that is observed (58). Although decomposition products may be closely related to the parent coal, secondary reactions also need to be considered (60).

Generally, the plastic stage of the coking process involves the breakage of cross-linkages (ether, sulphur, methylene)
between neighbouring aromatic groups giving rise to products of various molecular masses. Those of low molecular weight lead to the gaseous volatile matter being composed largely of methane and other hydrocarbons while heavier molecules form the highly complex coal tar mixture. Those of even higher molecular weight remain to form the semi-coke on solidification.

2.2.3 The Post-Plastic Stage

After the plastic mass has solidified, an increase in temperature causes the solid to contract but at a non-uniform rate and is dependent on the rate of devolatilisation and reorientation of aromatic lamellae which vary from coal to coal. This stage also involves the progressive elimination of hydrogen and the growth of graphite-like layers which are formed in the resolidification to form semicoke at the end of the plastic stage (Fig. 2.7) (58).

2.3 Thermoplastic Properties of Coal

Depending on the severity of heat treatment, temperature can affect the behaviour of coal in three ways. At temperatures of between 350 - 500 °C the coal softens and become plastic with the particles caking to form a foaming mass which swells then solidifies to form a solid with a porous structure, i.e. coke (61). Coke is made up of structural units which consist of 8-10 aromatic rings of carbon.

Increase in heat-treatment temperatures up to 1000 °C result in the loss of heteroatoms. In the temperature range 1000-1500 °C, very few heteroatoms are left. The structural units
align themselves into stacks which are irregular because of the size and shape heterogeneity of the constituents.

Between 1500-3000 °C coke undergoes a gradual transformation into graphite i.e. graphitisation, where three-dimensional order is attained.

2.3.1 Softening

Coal softens in the temperature range of 325-450 °C depending on the rank of coal and experimental conditions. Initially, individual coal particles become mobile and fill spaces in the coal bed. Larger particles have a lesser degree of softening than smaller ones and fuse with the smaller particles. At certain temperatures and depending on the particle size and nature of the coal, 'fusion' pores begin to form from the interparticle spaces. The coal material becomes more homogeneous with increasing softening and pores caused by fusion become indistinguishable from those formed by gaseous devolatilisation. Increase in the softening also decreases the viscosity of the plastic mass, and leads to the disappearance of particle boundaries and an increase in gas evolution (62). It is recognised that a fusible material is formed during softening of the coal on heating, but there are different theories concerning the origin, nature and function of these materials (63).

In Audibert's melting theory (64), coal undergoes paste-like melting throughout the entire mass but decomposes at the same time giving rise to gases and infusible solid products. Resolidification corresponds to the completion of the transformation into infusible products. The plastic behaviour of a coal depends on the difference between the
softening point and the decomposition point. Non-caking coals have decomposition points that are lower than their softening points (61). However, this theory does not account for the reduction of fusibility and caking power by carbonisation under vacuum and the fact that not all macerals are affected during softening.

According to the partial melt theory, only a fraction of the coal fuses which then solvates the remaining coal to provide a certain degree of plasticity (61). The fusible fraction or 'coking principle' has been identified with, although is not necessarily the same as, the fraction of coal soluble in organic solvents e.g. benzene and chloroform and termed 'bitumen'. Although the extracts are very fusible and the residue have almost no plastic properties, the mixture of the two does not give the exact properties of the initial coal. Additionally, a mixture of extract from a coking coal with the residue of a noncaking coal does not give a fusible product.

The metaplast or thermo-bitumen theory regards softening as a consequence of pyrolysis. Pyrolysis transforms coal into a fluid product either completely or partially and these products are called 'thermo-bitumens' which mean that they are produced by pyrolysis and do not pre-exist in coal. This theory begins with the assumption that coke formation can be described by three consecutive reactions (65).

1) Coking coal (P) $\xrightarrow{k_1}$ metaplast (M)

2) Metaplast (M) $\xrightarrow{k_2}$ semicoke (R) + primary gas (G₁)

3) Semicoke (R) $\xrightarrow{k_3}$ coke (S) + secondary gas (G₂)
Reaction 1 is a depolymerisation reaction in which an unstable intermediate phase, the metaplast, is formed. This phase is responsible for the plastic behaviour. Reaction 2 is a cracking process in which the tar evaporates and the non-aromatic groups are split off. This reaction is accompanied by recondensation processes and ends with the formation of semicoke. The primary gases formed during this process cause the swelling of the coal. Reaction 3 is the secondary degassing reaction where the evolution of methane (and at higher temperatures, hydrogen,) increases the density of the semicoke into coke. There is a reduction in volume during this reaction. Assuming first-order reactions, this system can be described mathematically:

\[
\begin{align*}
\frac{dP}{dt} &= k_1 [P] \\
\frac{dM}{dt} &= k_1 [P] - k_2 [M] \\
\frac{dG_1}{dt} &= k_2 [M]
\end{align*}
\]

\(k_1 \) and \(k_2\) being the rate constants of the first two reactions.

The physical and physio-chemical theory proposed by Brown and Waters (66) incorporates some important features of both the physical melt and metaplast theories. Coking coals are considered to consist of molecules and highly polymerised macromolecules (humins) joined by hydrogen bonding and van der Waals forces to form a rigid gel structure with the molecules of oily and solid hydrogen rich bitumen trapped in the pores of the matrix. Molecules in low rank coals are more rigidly bonded by an extensive network of crosslinks (ether, sulphur and methylene), but with coking bituminous coals the crosslink density is less extensive and therefore when a bituminous coal is heated, a greater degree of molecular mobility is possible.
2.3.2 Swelling

Swelling has been considered as a consequence of the softening of coal as well as the liberation of gas. The formation of an impermeable plastic mass is a required precondition for swelling to occur. There are two types of swelling: - i) the swelling of an individual coal particle (intragranular) and ii) the swelling of an assembly of coal particles (intergranular) (61).

Swelling in a single particle is the result of the formation of a plastic mass which eliminates the fissures and micropores through which the evolved gas would otherwise flow. The gas bubbles are formed with high internal pressure and deform the plastic mass of coal (63).

Intergranular swelling is similarly caused by the closing of passages between the particles which soften and fuse together resulting in a plastic mass of low permeability and hindering the escape of gases. This explains why swelling increases with heating rate because the yield of gas evolved increases with heating rate.

The relative importance of the two types of swelling depends on both the particle size and the nature of the coal itself. Intergranular swelling is a necessity to produce a strong coke as this aids particle fusion. Intragranular swelling causes interstices to be filled and is only considered to be important for very weakly caking coals. For highly plastic coals it may be impossible to distinguish the two types of swelling.
In the mechanism proposed by Berkowitz (67), swelling is viewed as a process that is independent of softening, but instead attributed to the pressure of the gas forcing a path through the micropores of the coal. This mechanism offers an explanation of intragranular swelling but not intergranular swelling which depends on the release or escape of volatiles through or from a fused plastic mass formed by decomposition of coal particles.

2.3.3 Resolidification

Resolidification is generally considered to be caused by a series of cracking reactions which are followed by condensation and polymerisation reactions. The medium-sized molecules forming the plastic phase cleave and the smaller fragments form the gas and tars. The heavier fragments remain and bond together to form the large graphitic-like sheets, composed of 8-10 rings of carbon atoms, of which the semicoke is composed.

2.3.4 Factors Affecting the Thermoplastic Properties of Coal

Coal undergoing carbonisation may be affected by oxidation or hydrogenation in addition to the presence of sulphur and other mineral matter in the coal (33). Higher heating rates affect the rate of release of volatiles and increase fluidity and swelling as well as the temperature range over which the coal is plastic. Some coals only soften and swell when heated at a high rate. Coals which soften and swell to form coke under atmospheric conditions do not necessarily give a coherent coke when heated under reduced pressure.
Conversely, if a coal is heated under pressure, the softening point decreases and swelling may decrease to produce a stronger than expected coke or alternatively, increase in pressure results in high fluidity which closes 'transport pores' and enhances swelling (68). The plastic properties of coals are affected strongly by even mild oxidation, which results in narrowing of the plastic temperature range along with decreases in fluidity and swelling. This effect is attributed to increases in crosslinking by the oxygen.

The effect of sulphur is similar to that of oxygen. Mild hydrogenation of coal increases the swelling and the fluidity. It also widens the plastic range (33).

2.4 Measurement of Coal Thermoplastic Properties

A large number of techniques have been used for studying the plastic behaviour of coal during heating. Tests have been devised which allow this behaviour to be characterised by empirical indices. These indices are important for classifying coals and predicting their behaviour during combustion, gasification, and carbonisation. It should be remembered however, that the different techniques measure different aspects of thermoplastic phenomena and there is no single 'best' technique to characterise the plastic properties of coals (63) (Table 2.7).

2.4.1 Free Swelling Index Test (9)

In the free swelling test, finely powdered coal is heated in a crucible or tube to 800 °C at a fixed heating rate. After resolidification and cooling, the degree of swelling can be
assessed from the ratio between the volume of the coke obtained and the initial volume of coal. Alternatively, it can be compared with a series of reference profiles which enables a 'swelling index' to be established.

These tests are also known as agglomerating tests since they indicate the tendency of the particles to fuse together and allow caking and non-caking coals to be distinguished, although this is only valid for the particular rate of heating used for the tests. These are empirical tests and the numerical indices have no value without well defined operational conditions (e.g. BS1016, ASTM, ISO etc.). They do, however, give reproducible results and provide a useful guide to caking properties.

2.4.2 Hot-stage Microscopy

In hot-stage microscopy a sample of coal heated under a current of inert atmosphere to prevent oxidation and to remove gases evolved is observed continuously. The changes which occur can be followed visually or photographically. An alternative method is to carbonise a sample of coal in a furnace at a controlled heating rate to a specific temperature and cooled rapidly before examining it by ordinary microscopic methods using a polished surface or thin section. The changes can be observed by repeating the experiment at different temperature intervals (between 0 - 1000°C).

Microscopic examination allows softening and resolidification points to be determined but it only gives a qualitative assessment of the plastic properties.
2.4.3 Dilatometry

Dilatometers measure the change in the length or volume of a coal sample when heated. They have been developed in many countries to study coal swelling under various conditions.

The Audibert-Arnu Dilatometer

This apparatus (Fig. 2.8) (61) can be used in two ways:--

a) The furnace is heated to a preset temperature and maintained constant before the sample is introduced and the displacement of the piston is followed as a function of time (Fig. 2.9a). This method in its original form, is rarely used for coal characterisation because of the time consuming nature of the test to cover a range of temperatures.

b) This method involves heating the furnace to below the softening temperature of the coal to be tested before introducing the sample. The temperature of the furnace is raised at a constant rate and the movement of the piston is followed as a function of temperature (Fig. 2.9b). The graph shows the softening point ($T_1$), maximum contraction temperature ($T_2$), final swelling temperature ($T_3$), contraction ($c$), dilatation ($d$), and swelling ($s = c + d$), where $c$, $d$ and $s$ are expressed as a percentage of the initial length of the sample.

These characteristics are strongly dependent on operational procedure and are only useful if carefully defined experimental conditions (in particular the heating rate) are used. The start of contraction corresponds to that of
softening, but the maximum value of the contraction does not characterise the plasticity of coal (61). It is more or less constant for coals over a fairly wide range of rank.

Chevenard-Joumier Dilatometer (61)

This is similar to the Audibert-Arnu dilatometer except that this can carry out tests up to 1000 °C and includes a very accurate recording device. It measures expansion directly as a function of temperature using a system of levers operated simultaneously by the stem of the piston. With this dilatometer, it is possible to analyse contraction of the semicoke after the resolidification stage (Fig. 2.10). From this curve, the contraction coefficient, 'a', can be calculated from the following equation:

\[ a = \frac{1}{L_0} \cdot \frac{dL}{dT} \]

where \( L_0 \) is the length of the sample at the point of resolidification, and \( L \) is its length at temperature \( T \).

Ruhr Dilatometer

The Ruhr dilatometer (Fig. 2.11) (62) is based on the Audibert-Arnu instrument. Curves obtained with this instrument are used to calculate the coking capacity, \( G \).

\[ G = \frac{(E + V)(K + D)}{2(VK + ED)} \]
K = contraction (%)  
D = dilatation (%)  
E = softening temperature (°C)  
V = resolidification temperature (°C)

Good coking coals have G values between 1.05 and 1.10. This equates to coals with swelling of about 100%.

**Sheffield Dilatometer**

The Sheffield dilatometer operates differently from the previous instruments in that the coal sample is not formed into a pencil but is compressed at the bottom of a tube. As a result, the contraction observed is less. The piston is suspended by a counterweight and is therefore easy to change the pressure exerted by the piston. Since the diameter of the piston is considerably less than that of the tube, the apparatus acts as a penetrometer (Fig. 2.12) (61).

**Hoffmann Dilatometer (61)**

This apparatus is very similar to the Sheffield dilatometer. Again the coal sample is only lightly compressed directly into the retort and the diameter of the piston is considerably smaller than that of the retort. Curves obtained by this apparatus differ from those given by the Audibert-Arnu dilatometer and coals are classified into four categories (Fig. 2.13).
Shock Dilatometer (62)

All the dilatometers mentioned so far have low heating rates, typically 3 °C/min. A new dilatometer is required to characterise coals to be used in processes with higher heating rates. The shock dilatometer (Fig. 2.14a) uses the principle of the Audibert-Arnu dilatometer and permits heating rates between 1 and 700 °C/min. It can be used isothermally or at a constant heating rate on either coals pencils or loose coal (Fig. 2.14b).

British Gas High-Pressure Dilatometer

This apparatus can be used to measure swelling at atmospheric pressure under the conditions set out by the British Standard Method (9). Additionally, it can be operated at heating rates of up to 60 °C/min and pressures up to 10 MPa (Fig. 2.15) (68).

The pressure housing is made of stainless steel (Type 321), and the top part, which is water-cooled, contains a linear transducer (Sangamo Type AC 150) which monitors the movement of the piston. The temperature of the coal pencil is measured with a chromel-alumel thermocouple positioned in a recess at the base of the retort. The dilatometer is heated by a three-zone furnace (3x1960W) controlled by Eurotherm Type 810 and programed by Eurotherm Type 812 units. A pressure relief valve, operated by a microswitch ensures the tube is kept at a constant pressure throughout a run.
High-Pressure Microdilatometer (HPMD)

The most important part of the microdilatometer (HPMD) (Fig. 2.16) is the moveable linear variable differential transformer (LVDT) core which is directly attached to the plunger which, itself, rests on the surface of the coal sample. An electrical signal is generated when the LVDT core is moved and is proportional to the displacement. The signal is transferred to a chart recorder. The HPMD can be used with small samples (<100 mg) under various operating loads (up to 19.6 kPa) at high heating rates (65 °C/min) and pressures (7 MPa).

2.4.4 Plastometry

Coal plastometers measure the resistance to the rotation of a stirrer by a mass of powdered coal at a particular heating rate (and pressure). There are two types of plastometers:—
a) constant-torque plastometers,  b) variable-torque plastometers.

Constant-Torque Plastometers

In a constant-torque plastometer, the stirrer is subjected to a constant couple and the rate of rotation is measured.

The Gieseler plastometer (Fig. 2.17a) (61) has been used worldwide for investigating coal plasticity. The coal sample is usually heated rapidly to 300 °C and then at a constant rate of 2-3 °C/min. Figure 2.17b shows a typical Gieseler plastometer curve where the rate of rotation (deg/min) varies as a function of temperature.
Before the coal becomes plastic, the stirrer is blocked by compacted coal and only begins to rotate when the coal reaches a certain degree of plasticity. The rate of rotation increases with temperature, passes a maximum, then decreases to zero when the coal resolidifies. For higher rates of heating (up to 100 °C/min), the retort with the coal sample is immersed in the heating bath, preheated to a constant temperature, and the rate of rotation is measured as a function of time.

**Variable-Torque Plastometers**

Most coals when heated over the range 350-550 °C undergo complex physical and chemical changes. After initial loss of moisture, evolution of gases is accompanied by softening and the formation of a plastic mass. The solidification of this mass results in the formation of semicoke. During carbonisation, the stirrer in a variable-torque plastometer is rotated at a constant speed and the torque opposing its rotation is measured as a function of temperature.

**Davis Plastometer**

In the Davis plastometer, the coal is moved by the retort which itself moves the shaft. At a constant heating rate, the resistance only increases as the coal softens and adheres together (Fig. 2.18). As the plasticity of the coal increases, the torque decreases and passes through a minimum (often not much greater than the torque of cold coal). The reduction in plasticity preceding resolidification gives a large torque. This falls rapidly as the semicoke is broken up. The second peak in the curve corresponds to the
resolidification point and the magnitude of this peak gives an idea of the mechanical resistance of the semicoke (61).

**Brabender Plastometer**

Unlike the Davis plastometer, the retort is fixed but the shaft moves. The type of curve obtained by the Brabender plastometer is shown in Fig. 2.19 (62). The value of the first peak characterises the intensity of the beginning of softening and the height of the second maximum represents a measure of the strength of the semicoke (62). The Brabender plastometer is able to show all phases of coke formation and can be used for the preparation of feed coal blends e.g. for slot oven coking and hot briquetting.

**Cerchar Plastometer**

This instrument is specially designed to measure the resolidification temperature accurately (+/- 2 °C). The retort is fixed and a shaft is rotated in a similar way to the Brabender plastometer, but it has a much slower rotation (1 rev/h). It is only set in motion when the coal becomes plastic and the shape of curve obtained is illustrated by Fig. 2.20.

**British Gas High-Pressure Plastometer**

This apparatus is based on the Brabender plastometer but scaled down by 50%. It can be operated at pressures up to 10 MPa, heating rates up to 25 °C/min and rotational speeds in the range 2-30 rpm.
2.5 Physical Properties of Coke

2.5.1 Optical Anisotropy

Carbonaceous materials are generally either isotropic (usually non-graphitic) or anisotropic (usually graphitic) (70). Coke is a graphitisable carbon material i.e. it is a partially-graphitised carbon, which, on graphitisation heat treatment, is converted to graphitic carbon (71). Primary structures i.e. aromatic lamellae can be shown by X-ray diffraction and secondary structures by optical microscopy as optical anisotropy.

A common technique used to observe optical anisotropy is with a polarising light microscope in the reflectance mode with a half-wave retarder plate inserted between the surface of the sample and the analyser. The light beam is reflected from the polished carbon surface and undergoes a phase change due to the refractive index of the carbon. The reflected light undergoes a further phase change as it passes the half-wave retarder plate and finally through the analyser which is arranged in parallel to the polariser.

The generation of interference colours, usually blues, yellows and purples characterise the graphitic carbon in terms of size of isochromatic area and is known as ‘optical texture’. The blues and yellows indicate that prismatic edges are exposed in the polished surface, and blues change to yellows (and vice versa) on rotation of the specimen stage by 180° or by reversal of the half-wave plate.

The purples are indicative of basal planes i.e. the surfaces of the lamellae lying parallel to the polished surface. The
purple colour does not change upon rotation of the specimen stage and represents an isotropic surface (72).

In the formation of coke, the coal passes through a plastic phase and it has been suggested that towards the end of the plastic stage the decomposing coal undergoes a transition state that is similar to a lamellar nematic liquid crystal or mesophase (33). Brooks and Taylor (73) identified in pitch, the first and most common structure adopted by mesophase spheres (Fig. 2.21). The discotic (lamellar) molecules are arranged perpendicular to the poles and approximately parallel to each other.

During carbonisation, cross-linking reactions between lamellae result in the formation of semi-coke. The mesophase microstructure developed in the fluid phase of pyrolysis is thought to form the basis of the structure in coke although Patrick et al. (74-76) found no evidence of any formation, growth and coalescence of spherical mesophase during the carbonisation of a range of coals. This can be explained by the presence of non-carbon material e.g. O, S, which inhibit spherical mesophase development and by the heterogeneous nature of the coal constituents.

Cokes can be characterised according to their optical texture. This texture may be related to other physical properties such as reactivity (77) and mechanical strength (78). It is necessary to define precisely the different types of microtexture that may be identified in coke using polarised light microscopy in order to assess its optical texture. There are numerous texture classification systems and nomenclature used to distinguish between isotropic and anisotropic cokes and they all separate the anisotropic ones according to the size and shape of their texture (Fig. 2.22).
One of the most commonly used nomenclatures is shown in Table 2.8 and ranges from fine mosaics (0.5 μm) to large flow textures (>20 μm).

Although there are similarities in the nomenclature used in the different classifications, tremendous variations in the grading of grain sizes exist e.g. a texture size of 1.3 μm that is regarded as coarse mosaic by one classification can be considered to be fine mosaic by another (79). However, this is a function of the chosen measurement area and equipment resolution. Most classifications, although different in detail, tend to give similar results as regards classification of cookes.

The degree of optical anisotropy is often reported as an arbitrary index (81, 82). The optical anisotropy index (OAI) is derived as percentages on an inerts-free basis using the equation:

\[
OAI = I + 2Mf + 3Mm + 4Mc + 5GF + 6F + 7B
\]

where \( I \) = isotropic; \( Mf \) = fine grain mosaic; \( Mm \) = medium grain mosaic; \( Mc \) = coarse grain mosaic; \( GF \) = granular flow; \( F \) = flow texture; and \( B \) = basic anisotropy.

Carbonisation of pitches has shown that optical anisotropy usually increases with decrease in viscosity of the mesophase (Fig. 2.23) (71). Cokes with high OAI values are thought to have undergone a highly fluid stage during carbonisation. Parameters which affect the viscosity of a carbonisation system include heating rate, heat-treatment temperature, soak time, pressure and coal rank (70, 75, 81-83).
2.5.2 Porosity and Structure

Coke is a highly porous material with pores of various shapes and dimensions. The formation of pores during carbonisation can be divided into four stages (84):

i) pore nucleation
ii) intraparticular pore growth
iii) post-fusion pore growth
iv) pore size reduction

Pores are formed by the release of gases from coal particles in the plastic phase. Pore growth causes individual coal particles to swell and completely fill the interparticulate voids. Fusion occurs when the volume of the pores exceeds the original void volume. After fusion, the pores grow and coalesce. Near the solidification temperature, the highly porous mass is converted into the denser semicoke and compaction results from further expulsion of volatile matter which causes the pores to partially deflate (Fig. 2.24)(84).

Some pores are closed but the majority of them are usually interconnected to form a network. Pore sizes range from micropores of less than 2 nm, and mesopores of 2-50 nm to macropores of >50 nm in diameter (24). There is no single analytical measurement technique which covers the entire range of porosity (85).

Porosity from Density Measurements

By measuring the true and apparent relative densities, the volume porosity can be calculated (9) using the equation:
Porosity \( \frac{100}{1 - \frac{\text{apparent density}}{\text{true density}}} \)

Loison et al. (86) measured the apparent density of cokes and found that at the apparent density of the coke is inversely related with the volatile matter of the coal charge and is practically proportional to the bulk density of the coal charge (Fig. 2.25).

**Mercury Porosimetry**

Mercury is forced under pressure into pores and porosity is calculated by measuring the volume of liquid penetrating the pores as a function of the applied pressure. The relationship between applied pressure and pore radius, assuming pores are cylindrically shaped is,

\[
 r = \frac{7500}{p}
\]

where \( p = \text{applied pressure (kg/cm}^2) \)

\( r = \text{pore radius (nm)} \)

This can give a pore size distribution of pore radii ranging from 20 nm to 0.25 mm (85). All porosity determinations which involve fluid penetration or displacement only measure open porosity.

Miura and Silveston (87) used mercury porosimetry to measure the porosity of coke carbonised to different temperatures. They found pore volumes and surface areas go through a maxima at temperatures between 600 and 800 °C and that some of the large devolatilisation pores have dimensions similar to the interparticular spaces.
Porosity from Gas Adsorption

Microporous structures can be studied using nitrogen or carbon dioxide adsorption. The volume of pores and surface area of the pore walls can be calculated using the B.E.T. equation (88).

Koba et al. (89) measured the specific surface areas of a number of cokes carbonised under pressure to 950 °C. Using CO₂ adsorption at -74 °C they found that specific surface areas of the pores decreased with increase in pressure. This decrease in pore volume restricts diffusion of reactant gases into the pores and therefore lowers the cokes’ reactivity to both steam and carbon dioxide (Fig. 2.26).

Nitrogen adsorption has been used for the determination of coke porosity in relation to combustion. Adams et al. (90) found the surface areas of cokes heat treated at 1000°C under a carbon dioxide atmosphere to be ten times that heated under a nitrogen atmosphere (80 m²/g and 8 m²/g respectively). This is attributed to oxidation by the Boudouard reaction,

\[ C + CO_2 \rightarrow 2 CO \]

De Koranyi (91) measured the total surface areas (TSA) of three cokes via CO₂ adsorption at -78 °C and CO₂ reactivity at 980 °C. A linear correlation existed between TSA and reactivity. This was explained by the direct relationship between active surface area and total available area.

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Porosity by Computerised Image Analysis

The characterisation of coke porosity can also be carried out electronically using a computerised image analysis system (92-95). The image created by a reflected light microscope is scanned by a closed-circuit television camera before being passed through a detector (containing an analogue-to digital converter) and analysed by a computer. In addition to total porosity, this apparatus can also measure pore size distribution, interpore spacing, number of pores, pore perimeter and ellipticity. It is necessary to examine a large number of images or 'fields', covering a representative sample to obtain reliable results.

Structure by X-Ray Analysis

The study of coke structure by X-ray diffraction gives a broad band, unlike the characteristic sharp <002> peak for graphite. This broadening, B, corresponds to the partial organisation of the carbon in a graphite lattice (85). From the width of the <002> and <100> lines, the diffraction broadening, B, can be determined and used to calculate the crystallite sizes; \( L_0 \) (crystallite height), and \( L_a \) (crystallite diameter), respectively, using the Debye-Scherrer equation,

\[
B = \frac{K \lambda}{L \cos \theta}
\]

where \( K \) is a constant of the order of unity, \( \lambda \) the wavelength of the radiation used, \( L \) the crystallite size perpendicular to the reflecting planes, and \( \theta \) the Bragg angle.
2.5.3 Coke Strength

Individual industries require specific coke properties to optimise their process. For the gasification industry, the coke should be sufficiently coherent to support the descending coal charge and should not disintegrate as it moves down the shaft. Otherwise this will widen the size range and lower the average size and importantly reduce the permeability to gas flow. The fuel bed will also be susceptible to choking with fines (96). Additionally, the high gas velocities used will lead to carry-over of this fine material.

Since coke is a brittle, porous and variable solid, its strength is difficult to assess. A large number of tests have been used to measure coke strength but most of these only give empirical results.

Shatter Test (9)

The standard shatter test involves subjecting a coke sample to impact breakage by allowing it to drop four times from a height of 1.83m (6 ft). A size analysis is carried out on the broken coke and the percentage by weight of the remaining material above a specified sieve size (2 in. for British Standard) gives the shatter index. This test does not take industrial conditions into account nor does it include the effect of abrasion between coke pieces.
**Abrasion Test**

The abrasion resistance of coke is measured with an abrasive disk (97), or more commonly, with a revolving drum (Fig. 2.27) (98). This technique has been used worldwide for assessing coke strength with each country adopting their own set of parameters (Table 2.9). Drum tests subject the coke to degradation in two ways. Size reduction initially results from impact breakage along the planes of large natural fissures and this is later followed by abrasion.

The rate of mechanical breakage is very rapid for the first 100-200 revolutions and is due to fissures and structural defects. The abrasion phase takes over after this, and the breakage slows down to a steady rate. Various drum tests have been shown to give contrasting results but correlations have been reported which enable data from one drum to be converted to those of another (99).

Since coke is principally used at high temperatures, several investigators have measured coke strengths at elevated temperatures (99). Their collective conclusions are:

i) coke strength is reduced at high temperatures i.e. in excess of the carbonisation temperature,

ii) coke strength measured at room temperature is not related to strength at high temperature,

iii) coke strength at high temperature is improved with long coking times where annealing relieves thermal stresses (quenching has opposite effects),
iv) good correlations exist at room temperature between the results from individual testing apparatus and the conventional drum tests.

Microstrength Test

The microstrength test devised by Blayden et al. (100) (Fig. 2.28) excludes the effects of macrofissures and macropores on coke strength i.e. it measures only the strength of the solid material. In this test, the coke is crushed (<1mm) to remove any macrofissures and macropores and is subjected to a large number of impacts. The separated fractions (by size) of the coke remaining after the test gives an empirical microstrength index which relates to the actual strength of the carbon (101-103). An advantage of this test is that it only requires a small sample weight and is therefore suitable for coke materials prepared on the laboratory scale.

It has been proposed (102, 104) that cokes with mosaic optical textures show the highest microstrength due to the interlocking of basal planes which bind the mosaic grains together. However, it has also been suggested (103) that boundaries between optical units have a similar effect on coke strength as porosity, i.e. they can act as either strengthening agents by dispersing strain energy so terminating cracks, or as weakening agents by being potential sites for stress to concentrate and facilitate crack initiation. This is dependent on the degree of pore elongation.
**Diametral-Compression Test**

Coke is a heterogeneous, porous, brittle material. Conventional techniques for determining tensile strength cannot be applied since it is difficult to prepare suitably shaped specimens and therefore, it has been necessary to use indirect methods e.g. the diametral-compression test (92-95, 105-109). This test is also known as the Brazilian or Carneiro test and involves the application of a compressive stress across the diameter of a disk-shaped piece of coke (Fig. 2.29).

Fracture occurs along the line of the applied load due to tensile forces developed perpendicular to the load. The tensile strength can be calculated from the equation,

\[
S = \frac{2W}{\pi DT}
\]

where,  
- \( S \) = tensile strength (Nm\(^{-2}\))  
- \( W \) = applied load (N)  
- \( D \) = diameter of the coke disk (m)  
- \( T \) = thickness of the coke disk (m).

Theoretically, the equation applies to an isotropic elastic material which is compressed diametrically by knife edges at opposite ends. Since these requirements are not completely fulfilled, the results can only be considered comparative. A good correlation was established between the average tensile strength of a number of foundry cokes and their Micum 10-mm...
indices. However, for blast furnace cokes, there was no correlation between the two different strength tests (99).

Although the diametral-compression test is a good method for measuring tensile strengths of brittle materials, it has some disadvantages largely associated with establishing a true tensile failure (106). Nevertheless the test has achieved increasing acceptance in fundamental studies of coke strength.

The tensile strength of coke, like other brittle materials, decreases with increasing porosity and rarely approaches the theoretical values calculated from chemical bonding (94). Griffith (110) proposed the hypothesis that brittle materials contain inherent microscopic flaws or defects which act as stress concentration centres so reducing the theoretical strength. Griffith extended the theory to consider crack propagation and derived the equation,

\[ S = \left( \frac{2EY}{\pi c} \right)^{1/2} \]

where
- \( S \) = the tensile stress required for failure (Nm\(^{-2}\))
- \( E \) = Young’s modulus (Nm\(^{-2}\))
- \( Y \) = free surface energy per unit area (Jm\(^{-2}\))
- \( c \) = half total crack length (m).

This theory indicates that if a crack is smaller than a critical length, it consumes more energy than it releases as relaxed strain energy so disfavouring crack propagation. If, however, a crack is longer than this critical length, it
will produce more energy than it consumes and propagation will result. This length is known as the 'critical Griffith crack length' and its value is dependent on the material.

Imperfections such as grain boundaries and pores provide the source of Griffith flaws responsible for breakage under applied load. The effect of porosity on coke strength has been studied extensively by Patrick, Stacey and Walker (92-95, 107-109, 111). They have formulated relationships between several parameters using statistical data. One of these can be expressed mathematically by the following equation:

\[ SN = k \left( \frac{w}{p^2} \right) - c \]

where,  
- \( S \) = tensile strength \((Nm^{-2})\)  
- \( N \) = number of pores  
- \( w \) = mean pore wall size  
- \( p \) = mean pore size  
- \( k \) & \( c \) = constants

This equation is based on the concept that strength is directly proportional to the amount of solid material but inversely proportional to porosity. It can be criticised on the basis of the inclusion of porosity related terms on both sides of the equation, but it has been found to be acceptable to quite a wide variety of cokes and carbons.

To improve the strength-structure relation, Patrick and Stacey (92-94) applied a more fundamental approach and used an equation derived from the Knudsen equation which had been used for graphites. The maximum Feret diameter \( (F_{\max}) \) and
minimum Feret diameter \((F_{\text{min}})\) are appropriate measures of pore dimensions and the ratio of the two gives a pore shape factor. The incorporation of Feret diameters gives the equation,

\[
S = k \ (F_{\text{max}})^{-0.5} \ \exp \left( -2 \left[ \frac{F_{\text{max}}}{F_{\text{min}}} \right]^{0.5} \ p \right)
\]

where \(S\) = tensile strength \((\text{Nm}^{-2})\)
\(F_{\text{max}}\) = maximum Feret diameter \((\mu\text{m})\)
\(F_{\text{min}}\) = minimum Feret diameter \((\mu\text{m})\)
\(p\) = fractional porosity

This equation combines the factors which affect the strength of a material by measuring the dimensions of the critical flaws, their shape, and the volume porosity. It can predict the tensile strength from structural information and shows good correlation with measured tensile strength.

2.6 Summary

There is an array of instrumentation available for studying coal thermoplasticity. Although the broad outlines are established, the precise mechanisms are still unexplained.

Softening may be a purely physical phenomenon and high plasticity is only observed when decomposition reactions have been initiated. It is probable that only a fraction of the decomposition products attains a true fluidity. It is clear that a multiphase system must exist and this is a complication which is extremely difficult to model.
Swelling is caused by the resistance to gas evolution in both the intra- and inter-particulate situation and is therefore a consequence of the plasticity (61).

Resolidification results from the disappearance of fluid products either by evaporation or decomposition with the formation of larger aromatic molecules by crosslinking.

There are many factors which influence the strength characteristics of cokes. The significance of optical texture and microstructure of coke have to be considered when optimising industrial processes e.g. carbonisation, and gasification.

The shape and size of pores are often more important in affecting tensile strength than percentage porosity alone. Spherical pores are better at distributing stress evenly and minimise the production of microfissures. Pore walls which are composed of the mosaic-type optical texture have the largest energy-absorptive capacity i.e. they are more resistant to fissuring.

Being a heterogeneous material, the study of coke properties may be best approached statistically. The conventional methods of coke analysis have changed little over the years. This indicates the value of the data obtained from these tests, and despite their empirical nature, they serve a good comparative purpose.
Table 2.1  Simple classification of carbonisation processes according to temperatures to which coal is heated

<table>
<thead>
<tr>
<th>Carbonization process</th>
<th>Final temp. range °C</th>
<th>Aim and benefits</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low temperature</td>
<td>450-700</td>
<td>Reactive coke and high tar yield</td>
<td>“Rexco” (700°C) made in cylindrical vertical retorts. “Coalite” (650°C) made in vertical tubes.</td>
</tr>
<tr>
<td>Medium temperature</td>
<td>750-900</td>
<td>Reactive coke with high gas yield, or domestic briquettes.</td>
<td>Town gas and gas coke (obsolete) “Phurnacite”, low volatile steam coal, pitch-bound briquettes carbonized at 800°C.</td>
</tr>
<tr>
<td>High temperature</td>
<td>900-1050</td>
<td>Hard, unreactive coke for metallurgical use.</td>
<td>Foundry coke (900°C) Blast furnace coke (950-1050°C).</td>
</tr>
</tbody>
</table>
### Table 2.2 Comparison of yields (g/kg) of pure coal at rapid and slow degasification rates

<table>
<thead>
<tr>
<th>Product</th>
<th>Degasification Ratio of Rapid to Slow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rapid</td>
</tr>
<tr>
<td>Gas</td>
<td>70.0</td>
</tr>
<tr>
<td>Coke-water</td>
<td>75.0</td>
</tr>
<tr>
<td>Light oil</td>
<td>18.7</td>
</tr>
<tr>
<td>Medium-heavy plus heavy oil</td>
<td>82.3</td>
</tr>
<tr>
<td>Pitch</td>
<td>86.0</td>
</tr>
<tr>
<td>Low temperature coke</td>
<td>668.0</td>
</tr>
</tbody>
</table>

### Table 2.3 Effect of heating rate on product distribution at 580 and 650 °C

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>580</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (°C s⁻¹)</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Methane</td>
<td>8.5</td>
<td>9.3</td>
</tr>
<tr>
<td>Total C₁-C₄ hydrocarbons</td>
<td>17</td>
<td>19</td>
</tr>
<tr>
<td>Char</td>
<td>44</td>
<td>38</td>
</tr>
<tr>
<td>Total liquids</td>
<td>35</td>
<td>38</td>
</tr>
</tbody>
</table>

### Table 2.4 Analytical data for 650 °C hydropyrolysis tars

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>25</th>
<th>50</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating rate (°C s⁻¹)</td>
<td>1</td>
<td>20</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>83.0</td>
<td>83.5</td>
<td>82.0</td>
<td>84.4</td>
</tr>
<tr>
<td>H</td>
<td>7.1</td>
<td>5.4</td>
<td>6.7</td>
<td>5.5</td>
</tr>
<tr>
<td>N</td>
<td>1.7</td>
<td>2.2</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>S</td>
<td>2.0</td>
<td>3.6</td>
<td>4.0</td>
<td>3.4</td>
</tr>
<tr>
<td>O</td>
<td>5.8</td>
<td>4.2</td>
<td>4.9</td>
<td>4.3</td>
</tr>
<tr>
<td>% acidic O</td>
<td>4.2</td>
<td>4.0</td>
<td>5.3</td>
<td>4.1</td>
</tr>
<tr>
<td>H/C</td>
<td>1.02</td>
<td>0.77</td>
<td>0.96</td>
<td>0.78</td>
</tr>
<tr>
<td>% aromatic H of total H</td>
<td>32</td>
<td>63</td>
<td>38</td>
<td>65</td>
</tr>
<tr>
<td>Number average molecular weight</td>
<td>280</td>
<td>260</td>
<td>240</td>
<td>250</td>
</tr>
</tbody>
</table>
Table 2.5 Effect of coal type on yields of gaseous pyrolysis products

<table>
<thead>
<tr>
<th>Analyses (wt %) of coal</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Number (see key in source note)</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>C (maf)</td>
<td>71.2</td>
<td>73.5</td>
<td>77.7</td>
<td>83.6</td>
<td>87.5</td>
<td>89.3</td>
</tr>
<tr>
<td>H (maf)</td>
<td>4.6</td>
<td>5.8</td>
<td>5.5</td>
<td>5.1</td>
<td>4.6</td>
<td>4.3</td>
</tr>
<tr>
<td>N (maf)</td>
<td>1.1</td>
<td>1.2</td>
<td>1.5</td>
<td>1.6</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>S (maf)</td>
<td>1.3</td>
<td>0.81</td>
<td>6.1</td>
<td>0.95</td>
<td>0.67</td>
<td>1.2</td>
</tr>
<tr>
<td>O (diff.) (maf)</td>
<td>21.8</td>
<td>18.7</td>
<td>9.2</td>
<td>7.6</td>
<td>5.3</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂O (as-received)</td>
<td>6.8</td>
<td>34.7</td>
<td>1.4</td>
<td>2.3</td>
<td>0.73</td>
<td>0.6</td>
</tr>
<tr>
<td>Ash (mf)</td>
<td>10.6</td>
<td>9.1</td>
<td>11.5</td>
<td>4.0</td>
<td>7.4</td>
<td>6.5</td>
</tr>
<tr>
<td>VM (maf)</td>
<td>44.3</td>
<td>—</td>
<td>46.6</td>
<td>39.5</td>
<td>28.9</td>
<td>19.1</td>
</tr>
<tr>
<td>Swelling index</td>
<td>0</td>
<td>—</td>
<td>3.5</td>
<td>7.5</td>
<td>9</td>
<td>0</td>
</tr>
</tbody>
</table>

Products (wt % of coal, maf)

| CO | 8.5 | 5.8 | 2.8 | 3.2 | 1.9 | 1.7 | 1.6 |
| CO₂ | 10.1 | 11.3 | 1.4 | 0.81 | 0.75 | 0.71 | 0.63 |
| H₂O | 11.6 | — | 7.4 | 2.4 | 1.3 | 1.1 | 0.72 |
| H₂ | 0.60 | 1.1 | 1.2 | 3.1 | 3.4 | 3.5 | 3.8 |
| N₂ | — | — | — | 0.95 | 0.66 | 0.42 | 0.35 |
| CH₄ | 1.6 | 4.8 | 2.9 | 4.2 | — | — | — |
| C₂H₆ | 0.67 | 0.24 | 0.95 | — | — | — | — |
| C₂H₄ | 0.24 | 0.89 | 0.58 | — | — | — | — |
| C₃H₆ | 0.17 | 0.47 | 1.5 | 0.29 | 0.26 | 0.12 | 0.01 |
| Total | 33.5 | 24.6 | 18.7 | 15.0 | 8.3 | 7.6 | 7.1 |

*Includes C₃H₆.

Source: Coal 1, Montana lignite, Savage Mine — Coal 2, Roland Seam subbituminous, Wyodak Mine — Coal 3, Pittsburgh Seam bituminous, Ireland Mine — Coal 4, Fürst Leopold — Coal 5, Gustav — Coal 6, Dickebank — Coal 7, Heinrich —

Table 2.6 Chemical mechanism of coal pyrolysis

<table>
<thead>
<tr>
<th>I (300-450°C)</th>
<th>II (450-600°C)</th>
<th>III (600-900°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>decomposition of bridges and side chains</td>
<td>decomposition of bridges and side chains</td>
<td>condensation-polymerization (carbonization)</td>
</tr>
<tr>
<td>stabilization of tarry fragments by inner hydrogen</td>
<td>recombination of many tarry fragments</td>
<td></td>
</tr>
<tr>
<td>in N₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>independence of atmospheric H₂</td>
<td>stabilization of tarry fragments by atmospheric H₂</td>
<td>hydrogasification of residual char</td>
</tr>
<tr>
<td>in H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Includes C₃H₆.
Table 2.7 Summary of various techniques to characterise the plastic properties of coals

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free-Swelling Index</td>
<td>visual comparison of cokes carbonized under well defined conditions, with standard conditions</td>
<td>inexpensive, rapid, reproducible</td>
<td>lack of flexibility; transition phenomena from coals to coke is not known</td>
</tr>
<tr>
<td>Hot-Stage Microscopy</td>
<td>morphological changes are observed by optical microscopy</td>
<td>appropriate to supply the changes in macerals when heated</td>
<td>provides qualitative information “subjective”</td>
</tr>
<tr>
<td>Foxwell/Gas Flow Method</td>
<td>measures the resistance of the gas flow through a bed of coal during continuous heating</td>
<td>indirectly measures the fluidity of the plastic mass by the pressure differences between the inlet and outlet ports</td>
<td>requires highly purified (oxygen free) gas to avoid oxidation</td>
</tr>
<tr>
<td>Plastometer</td>
<td>a. records the angular velocity of a rotating shaft through a bed of coal as a function of temperature</td>
<td>measures the changes in fluidity as a function of temperature, quite sensitive for determining extent of oxidation or weathering</td>
<td>does not provide data on swelling properties, limited heating rates (&lt;1°C/min)</td>
</tr>
<tr>
<td></td>
<td>b. records the changes in torque required to rotate a cylindrical retort (when coal is carbonized) at constant speed as a function of temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cilatometer</td>
<td>expansion, contraction, and volume change on resolidification are measured as a function of temperature when heated</td>
<td>provides data on dilation parameters and transition temperatures; wide range of heating rates (&lt;100°C/min)</td>
<td>does not provide quantitative information on changes in fluidity of coal</td>
</tr>
</tbody>
</table>
### Table 2.8 Classification of textural components

<table>
<thead>
<tr>
<th>Component type</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic</td>
<td>An optically-featureless material, often porous</td>
</tr>
<tr>
<td>Mosaic</td>
<td>Composed of small rounded isochromatic areas:</td>
</tr>
<tr>
<td>fine</td>
<td>Mean size 0.5 ( \mu )m</td>
</tr>
<tr>
<td>medium</td>
<td>Mean size 0.7 ( \mu )m</td>
</tr>
<tr>
<td>coarse</td>
<td>Mean size 1.3 ( \mu )m</td>
</tr>
<tr>
<td>Granular/coarse flow</td>
<td>An intermediate type between the coarse mosaic and flow types comprising rounded but elongated isochromatic areas, approximately &gt; 2 ( \times ) 1 ( \mu )m</td>
</tr>
<tr>
<td>Flow</td>
<td>Composed of elongated isochromatic areas often curved around pores. Can be subdivided into broad and striated types according to size</td>
</tr>
<tr>
<td>Basic</td>
<td>A non-porous relatively featureless anisotropic material which does not show evidence of fusing to form softening components</td>
</tr>
<tr>
<td>Inerts</td>
<td>An isotropic material identifiable by its wood-like structure or, if small, by unfused sharp edges</td>
</tr>
</tbody>
</table>

### Table 2.9 Comparison of standard drum test methods

<table>
<thead>
<tr>
<th></th>
<th>ASTM</th>
<th>Micum*</th>
<th>Irsid</th>
<th>Latest</th>
<th>ISO</th>
<th>JIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drum Diameter</td>
<td>910 (36 in.)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>(mm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length (mm)</td>
<td>455 (18 in.)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>Thickness (mm)</td>
<td>6 (\times 1 in.)</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flights</td>
<td>2</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Rotation (rpm)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Revolutions</td>
<td>1400</td>
<td>100</td>
<td>500</td>
<td>100/500</td>
<td>30/150</td>
<td></td>
</tr>
<tr>
<td>Sample Weight (kg)</td>
<td>10</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Size (mm)</td>
<td>75 \times 50 (3 x 2 in.)(^{a})</td>
<td>+60(^{a})</td>
<td>+20(^{a})</td>
<td>+20(^{a})</td>
<td>+50(^{a})</td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>&lt;1(^{b})</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td>&lt;3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indices (mm)</td>
<td>1</td>
<td>+2.5 ( \pm ) 1 in.(^{c})</td>
<td>+40</td>
<td>+20</td>
<td>+40</td>
<td>+15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>+6.3 ( \pm ) 1.( \frac{1}{2}) in.</td>
<td>+10</td>
<td>+10</td>
<td>+30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>+20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td>-10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The half-Micum test is also used: one-half-length drum. 25-kg sample of +50-mm size yields nearly identical results.

* Round-hole sieves—no upper limit—in ISO test, sample proportioned according to size analysis of gross sample.

* Separate tests for 30 and 150 revolutions.

* Square-mesh sieves: sample can also be 50% of 2\( \frac{1}{4} \) x 2 in. + 50% of 2 \( \times \) 1\( \frac{1}{4} \) in.

* After 100 revolutions sample is sieved to obtain Micum indices; fractions recombined, tumbled additional 400 revolutions, and sieved again for Irsid indices.
Fig. 2.1 Boiling point curves of rapidly carbonised tars

Fig. 2.2 Effect of heating rate on weight loss at different temperatures
Fig. 2.3  Effect of temperature on yields when rapidly degassing Leopold open-burning coal (44)

Fig. 2.4  Effect of $H_2$ pressure on yields of tar and BTX from coal pyrolysis (10 °C/min to 900 °C)
Fig. 2.5 Effect of residence time and maximum temperature attained on composition of char
Fig. 2.6 Thermoplastic Stages of Coal Carbonisation
Fig. 2.7 Hypothetical condensation process leading to layer growth
Fig. 2.8 Audibert-Arnu dilatometer
a) Audibert-Arnu Dilatometer. Swelling of Lens coal when heated at different constant temperatures.

b) Audibert-Arnu dilatometer. Heating rate 2°C/min dilatometric curve.

Fig. 2.9 Curves from Audibert-Arnu dilatometer
Fig. 2.10 Chevenard-Joumier dilatometry curve (2 °C/min heating rate)
The Ruhr dilatometer: 

- $a =$ electrically heated brass block
- $b =$ hole for dilatometer tube
- $c =$ screw for closing the dilatometer tube
- $d =$ coal briquet
- $e =$ steel loading plunger
- $f =$ steel dilatometer tube
- $g =$ nickel/nickel-chromium thermocouple
- $h =$ insulation material
- $i =$ recording pen
- $k =$ guides for the recording pen
- $l =$ recording drum with recording sheet

**Fig. 2.11 Ruhr dilatometer**
Fig. 2.12 Sheffield dilatometry curve (1 °C/min heating rate)

Fig. 2.13 Coal classification system based on the dilatometer curve.
a) High-temperature shock dilatometer.

b) Measuring equipment in the high-temperature dilatometer oven.

Fig. 2.14 Shock Dilatometer
Fig. 2.15 British Gas High-Pressure Dilatometer
Fig. 2.16 Microdilatometer
Gieseler plastometer.

b) Plasticity curve obtained with the Gieseler plastometer. Heating rate: 2°C/min.

Fig. 2.17 Gieseler plastometer and plasticity curve
Fig. 2.18 Davis plastometry curve

Fig. 2.19 Brabender plastometry curves

Torque curves of typical coals of different rank from the Ruhr district measured in the Brabender plastograph, compared with the course of dilatation and the swelling index: (1) plastic behavior, (2) course of dilatation, (3) coke-forming ability.
Fig. 2.20 Cerchar plastometry curve (61)
Fig. 2.21 Structure of anisotropic nematic liquid crystals, as spheres of mesophase within pyrolysing isotropic pitch (71)
Fig. 2.22 Comparison of coke mosaic grain size classifications (79)
Fig. 2.23 Variation between viscosity of a pyrolysing system and pyrolysis temperature leading to formation of mesophase (71)

Curve A - carbon having small mosaics of optical texture; Curve B - carbon having large mosaics of optical texture; Curve C - 'needle-coke' carbon having large sizes of optical texture.
Fig. 2.24 Relationship between coking characteristics and pore structure development
Fig. 2.25 Apparent density of coke as a function of charge density
Fig. 2.26 Relationship between reactivity and BET specific surface area (89)
Fig. 2.27 Drum for Micum and Irsid tests

Fig. 2.28 Microstrength test apparatus
Fig. 2.29 Stress distribution across loaded diameter for a cylinder compressed between two line loads.
CHAPTER 3.0 COAL GASIFICATION

One of the major objectives in coal gasification is the large scale production of 'substitute natural gas' (SNG) via catalytic methanation. SNG consists mostly of methane and is compatible with natural gas in that it may be mixed with, or substituted for natural gas and has a similar high calorific value (37 MJ/m³).

Medium B.t.u. gas (MBG) or 'synthesis gas' consist mainly of CO and H₂ and is a suitable fuel for industrial use. Its calorific value is comparable to coke oven gas or 'town gas' (18 MJ/m³). Low B.t.u. gas (LBG) has low calorific value (6 MJ/m³) and is produced by air-blown gasification. It contains around 50% nitrogen with smaller quantities of H₂ and CO (17, 43).

The high calorific value of SNG is attributed to its gasification process which uses steam and oxygen as opposed to steam and air.

3.1 Basic Principles

The chemical reactions which occur during gasification are simple. However, these reactions are reversible and complex interactions occur. Their equilibria positions are sensitive to changes in temperature and pressure (Fig. 3.1). The gasification of coal requires the addition of hydrogen or rejection of carbon (or a combination of both) to increase the H/C ratio. This can be achieved either by direct hydrogenation or by reaction with steam to produce synthesis gas, the latter being the primary process used in fixed bed gasifiers (112).
The gasification of coal can be described by the following chemical reactions:

a) Gasification with steam (water gas reaction)
\[
C + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad \Delta H_{1000K} = +136 \text{ kJ/mol} \\
\Delta G_{1000K} = -7.61 \text{ kJ/mol}
\]

b) Combustion with oxygen
\[
C + \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H_{1000K} = -394 \text{ kJ/mol} \\
\Delta G_{1000K} = -396 \text{ kJ/mol}
\]

c) Gasification with oxygen or air (partial combustion)
\[
C + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} \quad \Delta H_{1000K} = -112 \text{ kJ/mol} \\
\Delta G_{1000K} = -200 \text{ kJ/mol}
\]

d) Gasification with carbon dioxide (Boudouard reaction)
\[
C + \text{CO}_2 \rightarrow 2\text{CO} \quad \Delta H_{1000K} = +171 \text{ kJ/mol} \\
\Delta G_{1000K} = +5.34 \text{ kJ/mol}
\]

e) Gasification with hydrogen (hydrogasification reaction)
\[
C + 2\text{H}_2 \rightarrow \text{CH}_4 \quad \Delta H_{1000K} = -89.9 \text{ kJ/mol} \\
\Delta G_{1000K} = +19.3 \text{ kJ/mol}
\]

Other reactions may occur and are important for making gas mixtures with a specific CO/H\(_2\) ratio for use in subsequent syntheses (113). These include:

f) Water-gas shift reaction
\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \quad \Delta H_{1000K} = -34.6 \text{ kJ/mol} \\
\Delta G_{1000K} = -3 \text{ kJ/mol}
\]

g) Methanation (Sabatier reaction)
\[
\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{1000K} = -225.8 \text{ kJ/mol} \\
\Delta G_{1000K} = +27 \text{ kJ/mol}
\]
The equations a) to g) only give the stoichiometry and energy change of the reactions which occur in gasification. They do not provide any information on the complex mechanisms of the processes (113). Key factors which affect the position of the overall equilibrium have already been mentioned. Other parameters which need to be considered are particle size, temperature, and the relative velocities of gas and solid.

3.2 Processes in Coal Gasification

The complexity of the gasification process depends largely on the type of coal used and the required composition of the output gas. Some coals have caking characteristics when heated and these are difficult to manage in some gasifiers. This agglomerating characteristic can be reduced by a mild oxidation pretreatment process which consists of heating the coal in the presence of air or oxygen (Fig. 3.2).

The primary gasification step involves the thermal decomposition of coal. Air or oxygen facilitates combustion to provide the necessary heat. This produces a gas of low calorific value, which mainly consists of oxides of carbon, hydrogen, plus a solid residue of semicoke.

Secondary gasification involves the gasification of the semicoke with steam to produce carbon monoxide and hydrogen. Methane is produced from the catalysed reaction between carbon monoxide and hydrogen (idealised if present in the mole ratio of 1:3). This desired molar ratio may be achieved by making use of the water-gas shift reaction which increases the amount of hydrogen at the expense of carbon monoxide. Some gasifiers do not depend on the catalytic
methanation process to produce methane, but instead use hydrogasification i.e. direct addition of hydrogen to coal under pressure. The hydrogen-rich gas required for hydrogasification is produced by the water-gas reaction.

3.3 Types of Gasifiers

Four types of gasifiers can be identified: - i) fixed bed e.g. Lurgi, ii) fluidised bed e.g. Winkler, iii) entrained flow e.g. Texaco, Shell/Koppers, iv) molten bath e.g. Rummel-Otto (Fig. 3.3) (114). These can operate at atmospheric or elevated pressure, depending on the composition of product gas required (Tables 3.1 - 3.3). The basic difference between the gasifiers is their mode of contact between the coal particles and the gas since this largely dictates the operating temperature and rate of heating (17, 115) (Table 3.4).

Fixed Bed Gasifiers

In a fixed bed gasifier the bed level remains static but the individual coal particles (of size 6-50 mm) move downwards under gravity counter-current to the product and gasifying agents. The temperature reaches a maximum in the region where oxygen is consumed (Fig. 3.3). Depending on the operating temperature, ash can be removed either as a solid via a grate, or run off as a slag. Clinkering is avoided because it cannot be removed easily from the gasifier and the build up of large agglomerations result in blockages.
**Fluidised Bed Gasifiers**

Powdered coal (3 mm) is used in fluidised bed gasifiers and is kept in suspension by the gasifying agents. Fast mixing and heat transfer gives uniformity of both composition and temperature throughout the bed (Fig. 3.3). The ash remains in the coke residue which is discharged at full reaction temperature.

**Entrained Flow Gasifiers**

Entrained flow gasifiers use pulverised coal (0.1 mm) which reacts cocurrently with the gasifying agent (steam and oxygen) in a high-temperature flame. The ash is removed as a liquid slag and leaves the gasifier close to the reaction temperature (Fig. 3.3). Some ash may be carried over by the product gas but this is later separated.

**Molten Bath Gasifiers**

In the molten bath gasifier, coal and gasifying agent are supplied cocurrently over a pool of slag, salt or metal. Again, product gas and ash leave the gasifier at reaction temperature without any heat exchange with the entering fuel or gasifying agent (Fig. 3.3).

The British Gas slagging gasifier is of the fixed bed type, and the remainder of this chapter will concentrate on this class of gasifiers.
3.4 Fixed Bed Gasifiers

This type of gasifier operates with the fuel moving counter-currently to the gasifying agent, as already mentioned. Heat exchanges occur between the coal and the ascending gases at various zones (Fig. 3.4). The coal is effectively carbonised before it reaches the combustion zone where it is gasified. The ash residue is discharged via a grate, or if the operating temperating temperature is sufficiently high to melt the ash, via a slag tap.

Coal is carbonised in the devolatilisation zone. The physical changes which it undergoes have been described in Chapter 2. Coals are required to descend the gasifier evenly and ensure good permeability for the ascending gases. Additionally, coals that cake and swell must either be pretreated or subjected to mechanical breakage in the gasifier to prevent bridging and blockages. It is desirable to have a uniform flow of fuel particles which are in the range of 6-50 mm in the reduction zone. High gas velocities in the slagging gasifier makes it prone to dust carry-over.

In the non-slagging mode of operation, steam and oxygen (or air) enter the gasifier through the ash zone where it is preheated by heat exchange before entering the combustion zone. Oxygen reacts completely with carbon in the combustion zone, generating carbon dioxide and heat. This heat is used to drive the water gas and Boudouard forward reactions. The maximum temperature is maintained below the fusion point of ash by supplying excess steam (or excess air for medium BTU type applications). Mixtures of unreacted steam and gasification products pass into the reduction zone where further endothermic water gas and Boudouard reactions occur. As a consequence there is a fall in temperature to a level
where these reactions cease. The mildly exothermic water gas shift reaction also occurs in the reduction zone and is limited by the quantity of steam present.

Operating under slagging conditions increases the output while reducing the amount of steam required. Using oxygen instead of air fuses any ash into a liquid slag and produces a synthesis gas that is nitrogen-free, typically, 5% CH₄, 65% CO and 30% H₂ (114). These changes result in an improved overall thermal efficiency. This margin of improvement, however, is reduced if a coal with high-reactivity and high fusion point is gasified, especially if the mineral content is over 30 wt %, although this does not necessarily preclude their use (114, 116, 117).

In addition to these reactions, some hydrogasification also occurs when gasification is carried out under pressure. This strongly exothermic reaction is promoted by pressure and its heat not only gasifies carbon but also helps to support the endothermic water gas reaction (114). Gasification under atmospheric pressure produces some elemental hydrogen but at pressures above 0.5 MPa it is evolved primarily as methane. At high pressure, hydrogen produced by the water gas reaction in the reduction zone can react via hydrogasification to produce methane.

3.4.1 The Lurgi Gasifier

The high-pressure Lurgi gasifier dominates the oxygen-blown fixed bed class of gasifiers (Fig. 3.5). First built in 1936 by Lurgi Kohle und Mineralöltechnik GmbH, Frankfurt, West Germany, it has since been modified and improved.
Operating at high pressures (3 MPa), graded coal is fed into the gasifier via a lock hopper to a distributor which spreads it evenly across the surface of the fuel bed. A stirrer attached to the distributor can break up any agglomerated mass formed by caking coals (Fig. 3.6a). The fuel bed is supported on a rotating grate through which gasifying agents are introduced and ash removed (Fig. 3.6b). Gases ascending the fuel bed undergo counter-current heat and mass transfer before leaving the gasifier at a temperature range of 300-500 °C.

The Lurgi gasifier can gasify a wide range of feedstocks from peat to anthracite (Table 3.5) with a preference for those graded between 6-50mm. Particles which are below 1mm or above 50mm are not recommended. Ash properties largely determine the ratio of gasification steam to oxygen. This ratio is usually between 6-10:1 v/v to avoid heavy clinker (Fig. 3.7) (118). Mineral matter contents of up to 30% by weight are acceptable but its ratio to fixed carbon should not exceed 0.7 (114).

3.4.2 The British Gas Lurgi Slagging Gasifier

The British Gas Lurgi slagging gasifier (Fig. 3.8a) consists of a vertical cylindrical reactor to which coal is fed through a pressurising lock hopper to a rotating distributor. The fuel slowly disintegrates as it descends the gasifier while gases pass up through the bed (Table 3.6) (116). The fuel bed rests on a conical refractory hearth surrounded by four tuyeres fitted with nozzles, through which steam and oxygen are injected at velocities of between 53-79 m/s (Fig.3.8b) (116,117).
The ratio of steam to oxygen within this zone is controlled at a low value, usually between 1-2 v/v (Fig. 3.7) (118). This produces a high temperature which avoids heavy clinker and effectively melts the mineral matter content in the fuel, forming a slag which drains into the hearth. The slag is discharged through a centrally positioned slag tap (up to 13600 kg/h) and is quenched in water to form a glassy frit (114,117). Operating under these conditions also gives a higher percentage of carbon monoxide in the product gases (Fig. 3.9) (118) which is important for the production of SNG (via catalytic methanation). The high thermal efficiency of the slagging gasifier can be attributed to the reduction in volume of steam used.

The predominant reaction at the tuyere level is the combustion of carbon to give a mixture of very hot gases, principally oxides of carbon (2000 °C). As these hot gases ascend the gasifier, more carbon is gasified by reaction with steam and carbon dioxide via the water-gas and Boudouard reactions, respectively. These strongly endothermic reactions cause the gas temperatures to fall (Fig. 3.3) so limiting the high temperature combustion zone to a small volume (Fig. 3.4). The carbon gasification reactions proceed up the reduction zone, causing progressively lower temperatures and lower gasification rates until it reaches a stage where the temperature falls to a level at which reactions effectively cease and all oxygen consumed (c. 600 °C).

In the drying and devolatilisation zone, the temperature falls as the result of heat transfer to the fuel bed or through small heat losses. As the ascending gases reach the top of the bed it comes into contact with fresh coal. Heat transfer dries the coal and initiates devolatilisation reactions so cooling the ascending gases. These reactions
produce tars, oils, some methane, carbon oxides, and sulphur compounds which are all carried out of the gasifier with the product gases at temperatures of between 300-500 °C.

The by-product tar and oils can be separated from the product gases and recycled via injection through the tuyeres (Fig. 3.10) (119). Sulphur compounds are removed by the Stretford process which converts hydrogen sulphide into saleable sulphur with a 99% efficiency (Fig. 3.11) (119). The alternative Claus process is a dry oxidation process which is best suited for the removal of organic sulphur and has an efficiency of between 90 - 95% (12).

For the manufacture of SNG, British Gas have developed the 'High Carbon Monoxide', HICOM methanation process, which is particularly suitable for use with purified gas from the slagging gasifier (Fig. 3.12) (117). In this route, the purified gas is saturated with water vapour before entering a 3-stage methanation system where the methanation catalyst is of the CRG-type. This will not be discussed in detail.

In addition to the production of SNG, the British Gas Lurgi slagging gasifier is important for the production of a clean fuel gas / synthesis gas for use in combined cycle power generation (Fig. 3.13) (119) or as a feedstock for the chemical industry. Since there is a current abundance of natural gas, the use of gases from the gasifier for power generation is economically more viable. This method of coal utilisation may also serve as a means to reduce the 'acid rain' problem (117).

The slagging gasifier, with a throughput of over 300t of coal per day is particularly suitable for high volatile bituminous coals (117,120). Coals with a wide range of
properties have been successfully gasified (Tables 3.7, 3.8) and although feedstock with a low mineral matter content is preferred, the gasifier has operated satisfactorily when the ash content (including flux) amounted to 33% (117).

3.5 Summary

Fixed bed gasifiers are the traditional methods of gasification. Although both fluidised bed (e.g. Winkler) and entrained modes (e.g. Koppers-Totzek) have been shown to be successful on a large industrial scale, the Lurgi gasifier is the only one which is commercially available for operating at high pressure (2-3 MPa).

The principles used in fixed bed gasification are simple and by having the feedstock flowing countercurrent to the products, they have high thermal efficiencies because of good heat exchange from the sensible heat of the product gases.

The size of coal particles that can be used fall between 6-50 mm. Fines (<3mm) are usually avoided because they reduce fuel bed permeability which may result in 'choking' (96). This could be a disadvantage because modern mining produces coal with a high content of fines. Coals with 10% (coal rank 702-802) and 30% (coal rank 502) fines have been successfully gasified either by feeding the fines directly at the top of the gasifier, or injection via tuyeres. Alternatively, the fines can gasified as briquettes.
In contrast to other systems, the product gas and vapours leave the gasifier at relatively low temperatures (300 - 500 °C). By operating under slagging conditions, the British Gas Lurgi gasifier has many desirable features. These include low oxygen and steam consumption, high output per cross sectional area of the gasifier, and the ability to gasify a wide range of coals. In addition to this, it can provide a convenient synthesis gas stage of a combined-cycle electric generating system.
Table 3.1  Classification of gasification processes (names in boxes are commercially available)  (17)

<table>
<thead>
<tr>
<th>Pressure</th>
<th>Gasifying agent</th>
<th>Type of process</th>
<th>Process name</th>
<th>Typical product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near atmos pressure</td>
<td>Oxygen</td>
<td>Fluidised bed - Non agglomerating</td>
<td>Winkler</td>
<td>Synthesis gas and feed to SNG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entrained</td>
<td>Koppers - Torzok</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molten bath</td>
<td>Algas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Otto-Rummel</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>Fixed bed - Non slagging</td>
<td>Kellogg</td>
<td>Producer gas</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entrained</td>
<td>RJhgas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molten bath</td>
<td>Combustion Eng</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>VEW</td>
<td></td>
</tr>
<tr>
<td>Elevated pressure</td>
<td>Air</td>
<td>Fixed bed - Non slagging</td>
<td>Lurgi (Lunen)</td>
<td>Gas for power generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Agglomerating</td>
<td>Westinghouse</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>U-gas (IGT)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Battelle</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluidised bed</td>
<td>Trigas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NCB</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sunshine</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molten slag</td>
<td>Cogas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Exxon</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CO2 acceptor</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entrained</td>
<td>Foster Wheeler</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kellogg, Rock gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>Fixed bed - Stagging</td>
<td>Lurgi</td>
<td>Synthesis gas and feed to SNG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fluidised bed</td>
<td>BGC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Synthane</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Entrained</td>
<td>Bigas</td>
<td>Gas for power generation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shell/Koppers</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Texaco</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Saarberg-Otto</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molten salt</td>
<td>Hygas</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Hydrane</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2 Survey of major gasification processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Lurgi</th>
<th>Winkler</th>
<th>Cogas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of reactor</td>
<td>counter-current</td>
<td>fluidised bed</td>
<td>fluidised bed</td>
</tr>
<tr>
<td></td>
<td>fixed-bed</td>
<td></td>
<td>solid heat carrier</td>
</tr>
<tr>
<td>Development status</td>
<td>successful on a large industrial scale</td>
<td>successful on a large industrial scale</td>
<td>experimental plant</td>
</tr>
<tr>
<td>Coal type</td>
<td>weakly caking</td>
<td>lignites</td>
<td>lignites</td>
</tr>
<tr>
<td>Coal size (mm)</td>
<td>6 – 40</td>
<td>&lt; 8</td>
<td>---</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>2 – 3</td>
<td>atmospheric</td>
<td>0.2 – 0.3</td>
</tr>
<tr>
<td>Carbon conversion efficiency</td>
<td>99 %</td>
<td>90 %</td>
<td>96 %</td>
</tr>
<tr>
<td>Gasification efficiency</td>
<td>75 – 85 %</td>
<td>&lt; 75 %</td>
<td>68 %</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>75 %</td>
<td>80 %</td>
<td>86 %</td>
</tr>
</tbody>
</table>
Table 3.3 Survey of major gasification processes, (113)

<table>
<thead>
<tr>
<th>Process</th>
<th>Koppers-Totzek</th>
<th>Texaco</th>
<th>Rummel-Otto</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of reactor</td>
<td>co-current, entrained-flow</td>
<td>co-current, entrained-flow</td>
<td>co-current, liquid heat carrier</td>
</tr>
<tr>
<td>Development status</td>
<td>successful on a large industrial</td>
<td>tested on a large industrial</td>
<td>tested on a large industrial</td>
</tr>
<tr>
<td></td>
<td>scale</td>
<td>scale</td>
<td>scale</td>
</tr>
<tr>
<td>Coal type</td>
<td>any</td>
<td>any</td>
<td>any</td>
</tr>
<tr>
<td>Coal size (mm)</td>
<td>&lt; 0.1</td>
<td>&lt; 0.75</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Pressure (MPa)</td>
<td>atmospheric</td>
<td>1.5 - 8.5</td>
<td>atmospheric</td>
</tr>
<tr>
<td>Carbon conversion</td>
<td>90 - 96 %</td>
<td>90 - 98 %</td>
<td>99 %</td>
</tr>
<tr>
<td>efficiency</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasification efficiency</td>
<td>70 - 77 %</td>
<td>75 - 80 %</td>
<td>&gt; 80 %</td>
</tr>
<tr>
<td>Thermal efficiency</td>
<td>75 - 85 %</td>
<td>&lt; 85 %</td>
<td>83 %</td>
</tr>
</tbody>
</table>
### Table 3.4 Coal Characteristics For Different Gasifiers (115)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fixed bed</th>
<th>Fluidised bed</th>
<th>Entrained flow</th>
<th>Molten bath</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rank</strong></td>
<td>contribution of volatiles to products, char reactivity</td>
<td>char reactivity</td>
<td>contribution of volatiles to carbon conversion</td>
<td>any coal</td>
</tr>
<tr>
<td><strong>Mineral content</strong></td>
<td>fusion characteristics (ash / slag), catalytic influence, efficiency</td>
<td>high melting point, catalytic influence, intergrowth</td>
<td>low melting point, corrosion, efficiency</td>
<td>efficiency, melting point has no influence</td>
</tr>
<tr>
<td><strong>Particle size</strong></td>
<td>5-80 mm preferred, no fines</td>
<td>&lt;5 mm preferred, narrow size distribution</td>
<td>fines &lt; 0.1 mm</td>
<td>prefer &lt;3mm</td>
</tr>
<tr>
<td><strong>Grind-ability</strong></td>
<td>fines during mining and transportation</td>
<td>production of narrow size distribution</td>
<td>energy consumption</td>
<td></td>
</tr>
<tr>
<td><strong>Caking</strong></td>
<td>strong caking coals lead to operating problems</td>
<td>pretreatment or special feeding system required</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.5 Typical operation results for oxygen-blown Lurgi gasifiers using various coals

<table>
<thead>
<tr>
<th>Origin</th>
<th>Peat</th>
<th>Lignite</th>
<th>Subbituminous</th>
<th>Bituminous</th>
<th>Anthracite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size (in.):</td>
<td>0.6-1.0</td>
<td>0.04-0.4</td>
<td>0.16-1.20</td>
<td>0.2-1.2</td>
<td>0.2-1.2</td>
</tr>
<tr>
<td></td>
<td>0.2-1.2</td>
<td>0.2-1.2</td>
<td>0.2-1.2</td>
<td>0.2-1.2</td>
<td>0.2-1.2</td>
</tr>
<tr>
<td>Proximate analysis (wt %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter</td>
<td>57.3</td>
<td>36.8</td>
<td>29.1</td>
<td>30.5</td>
<td>19.7</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>25.2</td>
<td>32.6</td>
<td>34.4</td>
<td>38.7</td>
<td>31.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>15.5</td>
<td>24.5</td>
<td>16.5</td>
<td>18.5</td>
<td>15.7</td>
</tr>
<tr>
<td>Ash</td>
<td>2.0</td>
<td>4.1</td>
<td>6.2</td>
<td>14.3</td>
<td>12.4</td>
</tr>
<tr>
<td>HHV (Btu/lb, mad)</td>
<td>9,330</td>
<td>11,250</td>
<td>12,010</td>
<td>13,400</td>
<td>12,840</td>
</tr>
<tr>
<td>Fixed carbon (wt %, mad)</td>
<td>12.0</td>
<td>11.6</td>
<td>8.3</td>
<td>14.3</td>
<td>4.1</td>
</tr>
<tr>
<td>Sulfur (wt %)</td>
<td>0.1</td>
<td>0.6</td>
<td>1.1</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Ash fusion point (°F)</td>
<td>—</td>
<td>2,300</td>
<td>2,280</td>
<td>2,600</td>
<td>2,590</td>
</tr>
<tr>
<td>Operating conditions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>295</td>
<td>365</td>
<td>440</td>
<td>640</td>
<td>415</td>
</tr>
<tr>
<td>Steam oxygen (molar ratio)</td>
<td>8.7</td>
<td>8.7</td>
<td>9.3</td>
<td>6.7</td>
<td>6.8</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude gas composition (vol %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>17.0</td>
<td>19.1</td>
<td>11.9</td>
<td>20.2</td>
<td>21.4</td>
</tr>
<tr>
<td>H2</td>
<td>34.1</td>
<td>37.2</td>
<td>39.2</td>
<td>38.9</td>
<td>39.4</td>
</tr>
<tr>
<td>CH4</td>
<td>13.6</td>
<td>11.8</td>
<td>10.8</td>
<td>11.7</td>
<td>9.6</td>
</tr>
<tr>
<td>C2H6</td>
<td>0.6</td>
<td>0.4</td>
<td>1.2</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>H2S</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>CO2</td>
<td>3.38</td>
<td>30.7</td>
<td>32.2</td>
<td>28.1</td>
<td>28.9</td>
</tr>
<tr>
<td>N2</td>
<td>0.8</td>
<td>0.5</td>
<td>0.8</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>HHV (Btu/acf)</td>
<td>311.7</td>
<td>307.2</td>
<td>306.2</td>
<td>315.3</td>
<td>297.8</td>
</tr>
<tr>
<td>Specific data</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Consumption</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>scf/lb of coal (mad)</td>
<td>2.31</td>
<td>2.91</td>
<td>4.05</td>
<td>4.45</td>
</tr>
<tr>
<td>scf/10^6 Btu gas</td>
<td>322</td>
<td>326</td>
<td>392</td>
<td>422</td>
<td>446</td>
</tr>
<tr>
<td>Steam</td>
<td>lb of coal (mad)</td>
<td>0.96</td>
<td>1.20</td>
<td>1.79</td>
<td>1.42</td>
</tr>
<tr>
<td>lb/10^6 Btu gas</td>
<td>134</td>
<td>134</td>
<td>173</td>
<td>135</td>
<td>143</td>
</tr>
<tr>
<td>Production</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crude gas</td>
<td>scf/lb of coal (mad)</td>
<td>23.05</td>
<td>29.08</td>
<td>33.73</td>
<td>32.44</td>
</tr>
<tr>
<td>10^6 Btu/lb coal (mad)</td>
<td>16.09</td>
<td>20.01</td>
<td>23.14</td>
<td>23.62</td>
<td>28.84</td>
</tr>
<tr>
<td>Tar and naphtha (wt %, mad)</td>
<td>36.72</td>
<td>38.30</td>
<td>39.01</td>
<td>28.07</td>
<td>28.34</td>
</tr>
</tbody>
</table>

- Table 3.5 Typical operation results for oxygen-blown Lurgi gasifiers using various coals.
Table 3.6 Particle Size Distribution in Fuel Bed (%) (116)

| Fuel Size (mm) | Test A | | | Test B | | | |
|---------------|--------|--------|----------------|--------|--------|----------------|--------|--------|----------------|--------|--------|----------------|--------|--------|
|               | As Charged | Below Stirrer | At Tuyere Level | As Charged | Below Stirrer | At Tuyere Level |
| 40-25         | 24.6     | --      | --             | --       | --      | --             | --       | --      | --             | --       | --      | --             | --       | --      |
| 25-20         | 40.0     | --      | --             | --       | 21.0    | --             | --       | --      | --             | --       | --      | --             | --       | --      |
| 20-13         | 21.0     | 59.1    | 10.9           | 15.6     | 21.4    | 9.2            | 53.0     | 57.0    | 29.2           | 30.1     | 30.6    | 29.2           | 30.1     | 30.6    |
| 13-6          | 9.7      | 29.9    | 49.3           | 53.0     | 57.0    | 29.2           | 30.1     | 30.6    | 29.2           | 30.1     | 30.6    | 29.2           | 30.1     | 30.6    |
| 6-3           | 1.4      | 3.1     | 8.1            | 2.2      | 8.6     | 30.1           | 8.2      | 14.0    | 30.6           | 8.2      | 14.0    | 30.6           | 8.2      | 14.0    |
| < 3           | 3.3      | 3.7     | 29.7           | 8.2      | 14.0    | 30.6           | 8.2      | 14.0    | 30.6           | 8.2      | 14.0    | 30.6           | 8.2      | 14.0    |
Table 3.7 Coals run through the Westfield gasifier

<table>
<thead>
<tr>
<th>Coal</th>
<th>Manton</th>
<th>Rossington</th>
<th>Gedling</th>
<th>Ohio 9</th>
<th>Ohio 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source size (mm)</td>
<td>England 6-38 (with up to 35% &lt;8 mm)</td>
<td>England 6-38 (with up to 35% &lt;8 mm)</td>
<td>England 6-25</td>
<td>USA 6-32 washed</td>
<td>USA 6-32 unwashed</td>
</tr>
<tr>
<td>Moisture (wt %)</td>
<td>6.9</td>
<td>10.2</td>
<td>1.4</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>Ash (wt %)</td>
<td>7.3</td>
<td>4.3</td>
<td>5.8</td>
<td>12.0</td>
<td>20.8</td>
</tr>
<tr>
<td>VM (wt %)</td>
<td>31.9</td>
<td>33.3</td>
<td>31.5</td>
<td>39.7</td>
<td>32.3</td>
</tr>
<tr>
<td>FC (wt %)</td>
<td>57.8</td>
<td>55.5</td>
<td>52.5</td>
<td>46.9</td>
<td>42.2</td>
</tr>
<tr>
<td>Swelling No.</td>
<td>6.5</td>
<td>1.5</td>
<td>1</td>
<td>6</td>
<td>3.5</td>
</tr>
<tr>
<td>Caking (Gray King)</td>
<td>G6</td>
<td>E</td>
<td>C</td>
<td>G4</td>
<td>G</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coal</th>
<th>Pittsburgh 8</th>
<th>Hucknall</th>
<th>Comrie</th>
<th>Killoch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source size (mm)</td>
<td>USA 6-32 (with up to 25% &lt;8 mm)</td>
<td>England 6-25</td>
<td>Scotland 6-25</td>
<td>Scotland 6-25</td>
</tr>
<tr>
<td>Moisture (wt %)</td>
<td>2.1</td>
<td>5.0</td>
<td>2.7</td>
<td>7.7</td>
</tr>
<tr>
<td>Ash (wt %)</td>
<td>11.5</td>
<td>5.1</td>
<td>6.3</td>
<td>4.5</td>
</tr>
<tr>
<td>VM (wt %)</td>
<td>36.1</td>
<td>35.4</td>
<td>32.1</td>
<td>33.87</td>
</tr>
<tr>
<td>FC (wt %)</td>
<td>50.3</td>
<td>54.5</td>
<td>58.9</td>
<td>54.0</td>
</tr>
<tr>
<td>Swelling No.</td>
<td>7</td>
<td>3.5</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Caking (Gray King)</td>
<td>G6</td>
<td>G</td>
<td>G</td>
<td>E</td>
</tr>
</tbody>
</table>
Table 3.8 Performance data for British Gas/Lurgi slagging and dry-ash gasifier at Westfield

<table>
<thead>
<tr>
<th>Gasifier type</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>Coal</td>
<td>Origin</td>
</tr>
<tr>
<td>Size (mm)</td>
<td>6-25</td>
<td>England</td>
</tr>
</tbody>
</table>

### Approximate analysis (% wt/wt)

<table>
<thead>
<tr>
<th>Component</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>8.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Ash</td>
<td>4.4</td>
<td>2.7</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>32.9</td>
<td>18.6</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>54.0</td>
<td>53.2</td>
</tr>
</tbody>
</table>

### Estimate analysis (% wt/wt)

<table>
<thead>
<tr>
<th>Component</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>82.0</td>
<td>82.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.9</td>
<td>5.3</td>
</tr>
<tr>
<td>Oxygen</td>
<td>7.4</td>
<td>9.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>5.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Chlorine</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>B.S. Swelling No.</td>
<td>1½</td>
<td>4%</td>
</tr>
<tr>
<td>Caking index</td>
<td>G</td>
<td>G6</td>
</tr>
</tbody>
</table>

### Operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasifier pressure (MPa)</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>Steam/Oxygen ratio (v/v)</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Outlet Gas temperature (°C)</td>
<td>480</td>
<td>410</td>
</tr>
</tbody>
</table>

### Crude Gas Composition, (% v/v)

<table>
<thead>
<tr>
<th>Component</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>28.6</td>
<td>28.9</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>57.5</td>
<td>54.9</td>
</tr>
<tr>
<td>C₄H₄</td>
<td>6.7</td>
<td>7.1</td>
</tr>
<tr>
<td>C₂H₂</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>N₂</td>
<td>4.2</td>
<td>4.4</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.3</td>
<td>3.4</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### Derived data

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Slagging</th>
<th>Dry Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal gasification rate (kg m⁻³ h⁻¹)</td>
<td>35.8</td>
<td>28.0</td>
</tr>
<tr>
<td>Steam consumption, (kg/kg coal)</td>
<td>0.405</td>
<td>0.407</td>
</tr>
<tr>
<td>Oxygen consumption, (kg/kg coal)</td>
<td>0.539</td>
<td>0.547</td>
</tr>
<tr>
<td>Liquor production, (kg/kg coal)</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>Gasifier thermal output, (MJ m⁻³ h⁻¹)</td>
<td>1040</td>
<td>1040</td>
</tr>
<tr>
<td>Gasifier thermal efficiency (%)</td>
<td>83.4</td>
<td>82.1</td>
</tr>
</tbody>
</table>

Coal expressed 'moisture and ash free' is defined as total product gas thermal output (based on HHV, including tar, oil, naphtha) divided by corresponding thermal input of coal feedstock and the fuel equivalent of the steam and oxygen used.
Fig. 3.1 Variation of gas composition and heating value with pressure

Fig. 3.2 Schematic representation of coal gasification (42)
Fig. 3.3 Classification and characteristics of principal gasification systems
Fig. 3.4 The four main reaction zones in a non-slagging fixed-bed gasifier (114)
**Fig. 3.5** The Lurgi gasifier (114)

- Coal
- Distributor drive
- Jacket steam
- Steam
- Oxygen
- Quench liquor
- Crude gas
- Ash
- Distributor
- Drying
- Devolatilization
- Reduction
- Combustion
- Ash
- Grate
- Grate drive
Fig. 3.6 Examples of components of the Lurgi gasifier
a) a coal feed system and b) a mechanical grate (114)
Fig. 3.7 Curves showing the influence of steam : oxygen ratio on (118) :-

Curve 1.—The consumption of process steam.
Curve 2.—The undecomposed steam.
Curve 3.—The final reaction temperature of the gases leaving the gasification zone.
Curve 4.—The consumption of oxygen.
Fig. 3.8 The British Gas - Lurgi slagging gasifier (114)
a) the pilot-scale slagging gasifier, b) hearth and slag tapping
Fig. 3.9 Curves showing the influence of steam : oxygen ratio on gas composition (118)
Fig. 3.10 Schematic diagram of the SNG process

Fig. 3.11 The Stretford Process
Fig. 3.12 The HICOM Process

Fig. 3.13 Power generation with combined cycle and slagging gasification
CHAPTER 4.0 PROJECT OBJECTIVES

At the present time, supplies of natural gas are plentiful and will probably be sufficient to meet the demand in the immediate future. However, in the long term, it will be necessary to supplement these supplies with other sources such as substitute natural gas (SNG) from coal feedstocks. Oil is likely to run out before gas.

British Gas has a research programme which involves the development and demonstration of converting coal to SNG economically. The British Gas Lurgi slagging gasifier (BGL), based at the Westfield Development Centre (WDC), Scotland, has been developed with the cooperation of Lurgi GmbH for the production of SNG (121). Although much experience has been gained in operating this gasifier, there is a shortage of information detailing the chemical and physical processes which occur at the different zones in the gasifier.

The flow of the coal charge as it descends the gasifier is one of the most important factors affecting its operating characteristics. The coal introduced to the upper part of the fuel bed is carbonised by gases ascending from the gasification zones. In the devolatilisation (or carbonisation) zone, the coal may cake and swell to form coke. Large agglomerations of coke which may interfere with the smooth flow of solids down the gasifier are broken up by a stirrer. A characterisation of the caking and swelling properties of the coal feedstock under the conditions found at the top of the gasifier is important for obtaining the smooth flow of solids in the bed and optimum efficiency of operation.
4.1 Overall Objectives

There is extensive knowledge of the carbonisation processes which produce coke for use in the metallurgical industries. Few of the available data, however, are directly relevant to the slagging gasifier where the coal is subjected to relatively high rates of heating (20-60 °C/min) and high pressure (2.5 MPa) (122). Hence, the overall objective is to obtain relevant new data and to develop a novel overall picture of carbonisation behaviour under high pressure conditions. The aim, initially, is to provide relevant structural description including strength properties, of a range of carbonaceous materials produced under conditions which are similar to those found in the slagging gasifier. Secondly, the influence of factors such as nature of the feed, feed size, gas pressure and heating rate on the structural parameters will also be investigated.

4.2 Specific Objectives

The programme of work involved use of the laboratory-scale high pressure facilities of the London Research Station of British Gas to provide 'high-pressure' cokes.

Thermoplasticity

The thermoplastic behaviour of coals during carbonisation under pressure will be studied by means of:

i) high pressure dilatometry and,
ii) high pressure plastometry.
Coke Structure And Properties

Cokes produced by the high pressure autoclave will be examined using,

i) polarised light microscopy, to determine quantitative details of both the carbon matrix and the porous structure,

ii) the structural data will then be related to its strength as measured by a) diametral compression, b) microstrength, and c) abrasion tests.

These studies will provide a characterisation of the structural features and strength of high-pressure cokes and the means of formulating relationships and links between the coal thermoplastic properties under high pressure conditions and the physical properties of the resultant cokes (Fig. 4.1). These direct links e.g. between optical anisotropy and tensile strength, should facilitate the development of a better fundamental understanding of the mechanisms of the processes involved in the various stages of a high pressure gasifier.
Fig. 4.1 Coal Characterisation and Correlation.
CHAPTER 5.0 EXPERIMENTAL PROCEDURES

Three coals of different rank, Manton (NCB 502), Manvers Barnburgh (NCB 702) and Gedling (NCB 802) have been studied. The results of the analyses of the coals are shown in Table 5.1 (123).

5.1 Autoclave Carbonisations

The autoclave test rig (Photo. 5.1) is a special installation conceived and operated by British Gas at the London Research Station (LRS). Its purpose is to produce cokes under conditions which simulate those found in the slagging gasifier. The autoclave is designed to operate at high temperatures (800 °C) and high pressures (10 MPa) using a mixture of different gases. Three autoclave heads enable internal heating (Photo. 5.2a), shock heating (Photo. 5.2b), and stirring experiments (Photo. 5.2c) to be performed. These allow the parameters in the gasifier to be studied individually. Several hundred grammes of coal can be carbonised at any one time. A flowing system of gases enable both tar collection via a catchpot and on-line gas analysis by gas chromatograph (g.c.) to be initiated (Fig. 5.1) (124).

5.1.1 Shock Heating

High heating-rate carbonisations were carried out using the shock heating technique. About 200g of coal of particle size 2-3 cm was suspended in a sample holder (Photo. 5.2d) and positioned at the top of the autoclave head, which is water-
cooled. The autoclave was then filled with an atmosphere of nitrogen to the desired pressure before the four electrically-powered heating mats were switched on. Each heating mat was controlled by a Eurotherm heating unit.

Nitrogen was used as the 'inert' atmosphere to simulate the gasifier, since the zone where the coal is carbonised contains mostly carbon monoxide and hydrogen but very little oxygen. When the furnace reached the pre-programmed temperature of 700 °C, a flowing system was obtained by operating the appropriate valves. The flow rate was approximately 0.5 l/min. The suspended coal sample was released into the furnace for a soak time, i.e. time required for complete pyrolysis, of one hour.

The shock heating technique was used to carbonise each of the coals under the following pressures :- 0.5, 1.0, 2.0, 4.0, 8.0 MPa.

5.1.2 Slow Heating

The slow heating mode can carbonise up to 1kg of coal. The sample was placed in the reaction site of the autoclave before pressurising the system. The autoclave was heated according to a preset temperature ramp of 5 °C/min to 700 °C. The carbonisation process was deemed to be complete when there was little or no gas evolution, as monitored by the g.c.

Manvers Barnburgh and Gedling coals were carbonised via the slow heating technique under pressures of 0.5, 1.0, 2.0, 4.0 and 8.0 MPa.
5.2 Characterisation Of Cokes Produced Under High Pressure

Coke is the product of a devolatilisation process. Depending on the type of coal used, this may involve the caking and swelling of a plastic mass. Information describing the structure of the coke is required to understand coal thermoplastic behaviour. The following tests involve both physical and microscopic examination and characterisation of the cokes produced under high pressure in the autoclave.

5.2.1 Optical Texture

Samples for microscopic examination were prepared by mixing approximately 0.5g of crushed coke (120-600 μm) with a few drops of freshly prepared epoxy resin (Araldite). The sample was pressed in a mould to produce a thin disc. This was cemented with more epoxy resin and cured to give a resin block with the coke exposed on one surface. The coke surface was ground using successively finer grades of silicon carbide before polishing with alumina paste.

The polished coke surfaces were examined using a Leitz Ortholux microscope fitted with cross polars, a full wave retarder and a x100 objective to give an overall magnification of x1000. With the aid of an electronic point counter, determinations based on 500 point counts were made of the different optical textures (Photos 5.3a - 5.3j) for each coke. An optical anisotropy index was obtained for each coke using the OAI equation as discussed in Chapter 2.5.1.
5.2.2 Computerised Image Analysis

Small coke samples (1-2 cm) were cut and cleaned in a sonic bath to remove any debris. These were then mounted in an epoxy resin with the coke exposed on one surface. The resulting blocks were polished in the same way as for optical texture examination.

The polished coke surfaces were examined using a 'Cooke, Troughton and Simms' reflected-light microscope fitted with a x4 objective. High magnifications were avoided since many of the large pores would extend beyond the measurement area or 'field of view'. The image formed was relayed to a computer via a camera system and analysed using Joyce-Loebl's "Magiscan Genias 25 Rev. 1.2" program. This IBM-PC compatible software package captures, digitises and manipulates the input image.

Size measurements using various graticules were made to calibrate the system. In order to obtain directly comparable results, a 'measurement task file' was written (Appendix 1). This adapts Magiscan to measure only those parameters which are required. These include total porosity, number of pores, pore dimensions and perimeters. A guard region of 200 μm was used to reduce edge effects. The smallest and largest pores which can be measured were determined to be about 9 μm² and 2 mm² respectively.

Since coke is a heterogeneous material, a large number of fields have to be measured to reduce the degree of error. It was found that, for these cokes, a minimum of 40 fields per sample (Fig. 5.2) was required. The results from these measurements were stored as files on the computer. A 'results task file' (Appendix 2) was written to process and
display the data.

5.2.3 Density

The volume porosity of the cokes produced by the autoclave were also determined via density measurements. This required measuring both the apparent and true densities and using the relationship described in Chapter 2.5.2.

Apparent Density

Small, regular-shaped blocks of coke were cut using a diamond-tipped rotary saw (10 for each shock heated sample). For the slow heated cokes, cores were drilled out and cut to give about 40 cylinders of approximately 10mm x 10mm. These were cleaned in a sonic bath and dried before being weighed. Their dimensions were accurately measured using a micrometer. The apparent density was calculated from the mass/volume ratio.

True Density

The true densities of the high pressure cokes were determined using the method described in BS:1016 (9). Measurements were carried out in duplicate for each coke. The samples were ground to <212 μm and dried at 110 °C to a constant mass. About 2g of coke were accurately weighed and transferred into a 50 ml density bottle which had already been calibrated with distilled water at 35 °C. This was filled with about 25 ml of distilled water and placed in a vacuum vessel to eliminate the air. After de-aeration, the
density bottle was completely filled with distilled water, stoppered and immersed (up to the neck) in a water bath at 35 °C. At the end of 1 h, the density bottle was removed and thoroughly dried before being accurately weighed again. The true densities were calculated using the following equation:

\[ A = \frac{m}{m + m_1 - m_2} \]

where, 
- \( A \) is the true density
- \( m \) is the mass of dry coke used (g)
- \( m_1 \) is the mass of the density bottle completely filled with water at \( t \) °C (g)
- \( m_2 \) is the mass of the density bottle plus dry coke filled with water at \( t \) °C (g)

5.2.4 Abrasion Test

The abrasion test was carried out in a metal drum with a diameter of 275 mm and a depth of 175 mm. There were 12 'lifters' evenly spaced in the inner perimeter of the drum. These comprised metal rods of diameter 6 mm and length 175 mm. The drum was tilted back from the horizontal by an angle of 15° and rotated at a constant rate of 10 revolutions per minute. This relatively slow rate of rotation was chosen to ensure that the sample rolled along the bottom of the drum causing abrasion rather than being lifted and dropped, where attrition could be due to impact.

For each coke sample, at least two pieces of near-equal size were chosen such that the total weight of coke was as near to 30g as possible. This was charged to the drum and
subjected to abrasion for a total of 100 minutes, i.e. 1000 revolutions. The drum was, however, stopped at intervals of 5, 10, 15, 20, 30, 40, 50, 60, 80, and 100 minutes where the coke was removed and sieved. Coke particles <2 mm were considered to result from abrasion and the amount was determined by difference between the weight of coke originally charged and the weight of coke >2 mm after testing. After sieving and weighing, the fraction >2 mm was returned to the drum for further testing.

5.2.5 Microstrength Test

The microstrength test was carried out using apparatus similar to that described by Blayden (100) (Fig. 2.28). It consists of two, 305 mm long stainless steel tubes of 25.4 mm internal diameter each of which contain 12 stainless steel balls of 7.9 mm diameter. The distance between the inside faces of the steel closure screw-caps when these are in position is 300 mm.

In the test, 2g of crushed coke of particle size 600-1200 μm were placed in a tube and two of these were mounted at right angles in a frame and rotated at a constant speed of 25 revs m⁻¹ for 100, 200, 400 and 800 revolutions. The amount of breakage at each interval was determined by sieve analysis of the resulting material. The test was carried out in triplicate and the mean microstrength indices (M.I.) were calculated.

\[
\text{M.I.} = \frac{\text{mass of coke remaining on 600 μm sieve}}{\text{mass of coke remaining on 212 μm sieve}}
\]
5.2.6 Diametral Compression Test

The diametral compression test was used to measure the tensile strengths of slow heated cokes produced in the autoclave. The shock heated samples were, however, too small to be tested in this way. Since coke is a highly heterogeneous material, the tensile strengths were determined using many coke specimens to give a statistically-reliable mean result.

Up to fifty cylindrical test pieces were cored and cut from each slow heated coke. These were cleaned in a sonic water-bath and dried to constant mass. Prior to testing, the specimens were accurately weighed and their dimensions measured (for apparent density calculations).

An Instron universal testing machine, fitted with flat loading platens operating with a crosshead speed standardised at 0.5 mm min\(^{-1}\) was used to measure the tensile strengths. Values of the load at failure were recorded according to the deflection of the pen on a chart recorder. The tensile strengths were calculated using the equation described in Chapter 2.5.3 and a statistical analysis was obtained for each coke using a BASIC computer program.
5.3 High Pressure Dilatometry

**Preparation of Coal Pencil**

Samples of coal were dried and crushed to <212 μm. Approximately 10g of this was mixed thoroughly with 1 ml of water. A small quantity of the moistened coal sample was placed into the mould and compressed using a ram and mallet (Fig. 5.3). This was repeated until the barrel of the mould was completely filled. After the last portion of coal had been inserted, the pencil was compressed further, via a screw press, by applying a load to a maximum of 1.5 t. The pencil was expelled from the mould via a plunger, and trimmed at the narrow end to a length of 60mm with a sharp knife.

**Determination of Dilatation**

A coal pencil was placed in the dilatometer retort and a piston was inserted so that it rested on the coal pencil. The retort was then connected to the pressure housing and a thermocouple inserted into the base plug (Fig. 2.15). The apparatus (Photo. 5.4) was filled with nitrogen and vented several times to purge any air from the system before it was pressurised to the required level. Each experiment was carried out with a programmed linear heating rate up to 550 °C and the dilatometry curve plotted on a XY-plotter.
The resulting coke samples were mounted in epoxy resin and polished for optical anisotropy measurements as described in Chapter 5.2.1.

The effects of pressure (0-6 MPa) and heating rate (3-40 °C/min) were investigated for each of the coals studied.

The following parameters were obtained from the dilatometry curves:

i) softening temperature, \( T_1 \)
ii) temperature of maximum contraction, \( T_2 \)
iii) resolidification temperature, \( T_3 \)
iv) maximum contraction, \( c (\%) \)
v) maximum dilatation, \( d (\%) \)

5.4 High Pressure Plastometry

Sample Preparation

Coal samples were kept under deoxygenated distilled water for long term storage. Samples were obtained at random and dried at about 90 °C. These were ground and sieved to give samples with particle sizes of between 500 - 1000 μm. In order to reduce the effects of oxidation, the ground samples were stored in a refrigerator, and the time between milling and the plastometry measurements was kept to a minimum.
Plastometry Measurements

About 12.5g of coal were fed into the retort of the high pressure plastometer (Photo. 5.5) via a hopper. The plastometer was sealed and pressurised with nitrogen to the required level by operating the appropriate valves.

A thermocouple inserted into the wall of the retort was used to measure the temperature of the sample. The plastometer was heated by a four zone furnace with three zones situated around the retort and one in the centre. The heating zones were each controlled by a Eurotherm Type 810 unit with thermocouples positioned in the appropriate part of the retort. A Eurotherm Type 821 programmer was used to set the required temperature ramp.

For each experiment the stirrer was rotated at a constant angular velocity (10 revolutions per minute) and a linear heating rate up to 550 °C. The torque developed was relayed continuously to a chart recorder via a Phillips Type 9910 transducer to give plastometry curves (Fig. 5.4).

The following parameters have been obtained from the plastometer curves:—

i) softening temperature, $T_1$
ii) caking temperature, $T_2$
iii) temperature of maximum fluidity, $T_3$
iv) coking temperature, $T_4$
v) coke breakage temperature, $T_5$
vi) caking intensity, $I_2$
vii) maximum fluidity, $I_3$
viii) coking intensity, $I_4$
The effects of pressure from 0 - 6 MPa, and heating rate from 3 - 25 °C have been investigated for each coal.

Cokes produced from high pressure plastometer carbonisations were mounted in epoxy resin and polished for optical anisotropy measurements as described in Chapter 5.2.1.
<table>
<thead>
<tr>
<th>COAL</th>
<th>Manton</th>
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<th>Barnburgh</th>
<th>Gedling</th>
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<td>802</td>
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<td>--</td>
<td>1.76</td>
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Fig. 5.1 Autoclave Gas Flow System (124).
Fig. 5.2 Magiscan : Determination of minimum number of fields
Fig. 5.3 Dilatometry mould, press and accessories
Fig. 5.4 High Pressure Plastometry Parameters
Photo. 5.2  High pressure autoclave heads, a) internal heating, b) shock heating, c) stirring.

d) Sample holder for autoclave shock-heating carbonisations
Photo. 5.3a Optical texture: Isotropic (I)
Photo. 5.3b Optical texture: Fine mosaic (Mf)
Photo. 5.3c Optical texture: Medium mosaic (Mm)
Photo. 5.3d Optical texture: Coarse mosaic (Mc)
Photo. 5.3e  Optical texture : Granular flow (GF)
Photo. 5.3f  Optical texture: Striated flow (F)
Photo. 5.3h  Optical texture: Patterned Anthracitic (B)
Photo. 5.3i  Optical texture: Plain/Basic Anthracitic (B)
Photo. 5.3j  Optical texture: Inert
Photo. 5.4 High pressure dilatometer
Photo. 5.5 High pressure plastometer
CHAPTER 6.0 RESULTS AND DISCUSSION

6.1 Coke Yield

The coke yields from high pressure carbonisations carried out in the autoclave (at 0.5 - 8 MPa) via slow heating and shock heating techniques are shown in Figures 6.1 and 6.2.

Effect of Pressure

Applied pressure prevents the release of volatiles from coal in the plastic stage of carbonisation and consequently promotes re-polymerisation reactions. The mass balance can be equated with an increase in coke yield and a decrease in the quantity of volatiles (e.g. tar, methane, and oxides of carbon).

Figures 6.1 and 6.2 show coke yields increasing with increase in pressure up to 2 - 3 MPa when a limiting value was reached. Much of the effects of pressure are seen in the relatively low pressure region probably because there is a twenty-fold increase from atmospheric pressure to 2 MPa but only a four-fold increase from 2 MPa to 8 MPa.

Effect of Heating Rate

The results show that carbonisations carried out at low heating rates e.g. 5 °C/min favour coke formation, hence the coke yields are higher (Fig. 6.2). This is because the volatile matter stays within the carbonising coal mass longer and promotes polymerisation and condensation reactions.
**Effect of Coal Type**

The coke yield increases with increase in rank (Fig. 6.1). This is a reflection of the coal volatile matter content, which decreases with increase in rank (Table 5.1). The results show carbonisation at atmospheric pressure gives minimum coke yields. This is approximately equivalent to complete devolatilisation i.e. wt% coke yield = 100 - wt% volatile matter (on a dry basis).

**6.2 Characterisation of High Pressure Cokes**

**6.2.1 Optical Anisotropy**

Optical textures have been measured on the high pressure cokes produced by the autoclave, dilatometer and plastometer. Their degree of optical anisotropy has been calculated from the equation described in chapter 2.5.1 to give optical anisotropy indices (Tables 6.1 - 6.3).

**Autoclave Samples**

The effect of pressure and heating rate on the OAI of the autoclave samples are shown in Table 6.1. Cokes produced by the shock heating technique (Fig. 6.3) have OAI values which increase with increase in pressure. The slow heated cokes, however, do not appear to be affected very much by pressure (Fig. 6.4). In addition to this, the OAI of shock heated cokes also increase with increasing rank. In terms of heating rate, the shock heated cokes also have significantly higher OAI values than the corresponding slow heated coke.
Optical anisotropy development can be enhanced either by increases in fluidity or the retention of a greater quantity of appropriate molecular species both of which facilitate three-dimensional ordering. High pressure plastometry results (Chap. 6.4) show that increases in heating rate lengthens the plastic range and increases the fluidity, both of which accounts for the relatively high OAI values of the shock heated samples.

Dilatometer Samples

Indices of optical textures of cokes carbonised in the high pressure dilatometer are given in Table 6.2. At a low heating rate of 3 °C/min, pressure has a minimal effect on OAI (Fig. 6.5), except for Manton where there is an increase but this reaches a limiting value at 1 MPa. Pressure has a larger effect on OAI at the higher heating rate of 40 °C/min (Fig. 6.6). The OAI increases steadily with increase in pressure from 0 - 6 MPa.

Carbonisations carried out at constant pressure indicate that heating rate enhances the development of optical texture. This is reflected in the magnitude of the OAI measured (Fig. 6.7). The effects of heating rate at different pressures show that a combination of high heating rate and high pressure gives the maximum OAI (Fig. 6.8).

Another parameter which affects the degree of optical anisotropy is coal rank. The results show that OAI increases with increase in rank. This trend is present for carbonisations under applied pressures of 0 - 6 MPa (Fig. 6.6) and heating rates from 3 - 40 °C/min (Fig. 6.7).
Although both increases in pressure and heating rate results in increased fluidity, the latter also leads to an increased rate of decomposition. It has been proposed that the development of optical anisotropy in cokes requires two basic conditions (81). These are i) the presence of planar molecules of appropriate size and ii) the existence of conditions that will ensure sufficient mobility required for the ordering of the lamellae. Rapid release of volatile matter from high heating rates may increase the amount of appropriate molecules to coalesce and form the anisotropic textures observed.

**Plastometer Samples**

The OAI of coke carbonised in the high pressure plastometer are given in Table 6.3. These show that at a low heating rate of 3 °C/min, pressure has little effect on OAI (Fig. 6.9) except for Manton where an increase in pressure results in a large increase in OAI but this reaches a limiting value around 1.0 MPa. This is a similar trend to that observed with the dilatometer samples.

Pressure is more effective at higher heating rates (20 °C/min). An increase in pressure gives an increase in OAI through the pressure range 0 - 6 MPa for all three coals studied (Fig. 6.10).

Heating rate has a greater effect on OAI than pressure (Fig. 6.11). A moderate increase in heating rate results in a large increase in OAI.
OAI also increases with increase in coal rank. This can be attributed to the degree of fluidity which the coal undergoes during carbonisation and is measured by high pressure plastometry as the maximum fluidity. Of the three coals studied, Manton is the highest rank and has stronger caking ability than both Manvers Barnburgh and Gedling. This explains the relatively high OAI values shown by Manton cokes.

These plastometry OAI trends are consistent with OAI results measured on corresponding cokes carbonised in the high pressure dilatometer.

The OAI results indicate that optical texture development is directly related to the influence of pressure and heating rate i.e. it is dependent on the retention of plastic material (which increases fluidity) and the lengthening of the plastic range during carbonisation.

6.2.2 Computerised Image Analysis

Data collected from Magiscan image analysis has been processed and the mean values are displayed in Tables 6.4 - 6.6.

The porosity values are calculated from pore areas divided by field areas. The tensile strengths are calculated using pore dimensions which can be translated as Feret diameters and fitted into the Patrick-Stacey equation described in Chapter 2.5.3.
The porosity of the slow heated cokes increased with increase in pressure up to a limiting value at about 3 MPa (Fig. 6.12). The values for Manvers Barnburgh are higher than Gedling at all pressures. This increase in porosity can be related to thermoplastic properties, namely swelling.

Cokes produced by the shock heating technique generally show less porosity in terms of pore volume (Fig. 6.13). The number of pores per unit area, however, are significantly higher in the shock heated cokes i.e. there are a large number of small pores (Table 6.6). The effect of pressure also gives more complicated trends.

On application of the equation $S * N = k (w / p^2) - c$, the tensile strengths of the slow heated Manvers Barnburgh cokes ($S_m$), measured by diametral compression increase with increase in thickness of the pore walls ($w / p^2$) from Magiscan measurements (Fig. 6.14). The corresponding Gedling cokes show no relationship between their measured tensile strengths ($S_m$) and pore wall thickness ($w / p^2$).

The strength-porosity relationship improves when the revised Patrick-Stacey equation, which is based on Feret diameters, is applied. This also takes the shape of the pores into consideration. This allows tensile strengths to be predicted and these calculated tensile values ($S_c$) have been plotted against those measured by the diametral compression experiment (see Chapter 6.2.6) to give the good correlation (Fig. 6.15). Manvers Barnburgh slow heated coke shows a linear relationship between its measured strength, ($S_m$), and the predicted strength, ($S_c$).
Gedling slow heated coke, however, shows no relationship between $S_m$ and $S_c$. This is not surprising because all the applied strength equations are based on brittle fracture of well-bonded materials and the Gedling cokes often crumbled during the diametral compression test due to its poor bonding of the coke particles.

The Magiscan results highlight the complexity of the porosity/swelling and porosity/strength relationships. Although the slow-heated cokes generally follow a linear pattern, the shock-heated cokes illustrate that the simple inverse correlation is not universally applicable. This will be discussed further in Chapter 6.5.

6.2.3 Density

The true and apparent relative densities of the high pressure cokes carbonised in the autoclave are shown in Tables 6.7 - 6.9. From these density measurements, the percentage porosity have been calculated using the relationship described in Chapter 2.5.2.

The results show that pressure has minimal effect on true relative density but has a complicated effect on apparent relative density. The slow heated cokes have apparent densities which decrease with increase in pressure. This trend agrees with increases in their calculated porosities and is probably a reflection of the swelling which increases with increase in pressure.
The effect of pressure on apparent densities of the shock heated cokes shows a complex pattern. This also appears in the porosity calculations. There is, however, agreement with the porosities measured by Magiscan image analysis.

The apparent relative densities of the shock heated cokes are generally higher than those of the slow heated cokes. Thus the calculated porosities of the shock heated cokes are lower. This indicates an unexpected trend of porosity decreasing with heating rate since dilatometry results shows that dilatation increases with heating rate.

Porosity can generally be assumed to increase with increase in swelling. Bearing in mind that the dilatometry measurements have only been carried out at heating rates of up to 40 °C/min, the anomalously low porosities of the shock heated cokes (which have been carbonised at a much higher heating rate) could be due to the formation of a 'coke shell' which would restrict normal swelling behaviour.

The porosities of the cokes calculated from density measurements have been plotted against corresponding porosities measured by Magiscan image analysis (Fig. 6.16). This shows a linear relationship with a slight bias towards the results calculated from density measurements. It is interesting to note that porosity values determined from simple 'old-fashioned' density measurements are comparable to those obtained from sophisticated modern techniques i.e. Magiscan image analysis. But in addition to porosity, Magiscan can also provide pore shape values (Feret diameters) and pore size distribution.
6.2.4 Abrasion Test

Results of the abrasion test on the cokes carbonised in the high pressure autoclave are shown in Tables 6.10 - 6.12. The accumulated mass of coke abraded after 1000 revolutions have been plotted against pressure applied during carbonisation (Figs. 6.17, 6.18).

The results show that the strength of the cokes in terms of abrasion resistance are influenced by pressure applied during carbonisation. The abrasion of Manton and Gedling shock-heated cokes increases with increase in pressure and shows a maxima i.e. low strength at around 2 MPa. Manvers Barnburgh shock-heated coke, however, decreases with increase in pressure until it reaches a limiting value at about 5 MPa. In all cases, the mass of shock-heated coke abraded during the test falls into a relatively narrow band when compared to the corresponding slow-heated cokes.

Cokes produced by the slow-heating technique appear generally less resistant to abrasive forces. The abrasion of both Manvers Barnburgh and Gedling cokes increases with increase in pressure to a maximum at 2-3 MPa then decrease gradually with further increase in pressure. This follows a similar trend as dilatation which also passes a maximum at 2-3 MPa (Chapter 6.3). It can therefore be deduced that the low abrasion resistance of these cokes is attributed to their high swelling. In addition to this, Magiscan image analysis results show that the slow-heated cokes generally contain larger pores. This will aid attrition during the abrasion test (Chapter 6.2.2).
Heating rate has a large effect on coke abrasion resistance. Abrasion occurs to a lesser degree with the shock-heated cokes than the slow-heated ones. The relatively high density of the shock-heated cokes (Chapter 6.2.3) may provide an explanation for their unexpectedly high abrasion resistance.

6.2.5 Microstrength Test

The results of the microstrength test on the cokes produced by the high pressure autoclave are shown in Tables 6.13 - 6.15. Microstrength indices calculated from various coke fractions after 100 revolutions are shown in Figure 6.19 as a function of pressure.

It appears that apart from the Manvers Barnburgh slow heated coke, pressure has very little effect on microstrength. This is perhaps not unexpected since the test uses very small size particles and was devised to measure the strength of cokes 'free' of macro-defects e.g. pores. Small pores are still present in the samples tested and the small variations in microstrength are probably a combination of experimental error plus the effect of pores.

The effect of coal rank can be seen in the microstrength test. Coke microstrength indices increase with increase in rank from Gedling (NCB 802) to Manton (NCB 502). This may be due to the higher rank coal being more able to cake and fuse individual particles during the carbonisation process.
It has been reported that high microstrength is associated with the 'mosaic' type of optical texture (102, 104). This correlation has not been observed with any of the cokes produced by the high pressure autoclave.

One of the original intentions of the microstrength test was to provide data to supplement already existing techniques such as shatter and abrasion tests (100). Blayden et al. (100) observed microstrength correlations with electrical conductivity, porosity and oxidation rate. The results obtained, however, do not appear to correlate with any other test e.g. optical texture, abrasion resistance, density, tensile strength, most of which are dependent on macroporosity. The microstrength test requires small coke particles which are effectively free of macroporosity, and this may explain why no correlations have been observed.

6.2.6 Diametral Compression Test

The tensile strengths of the slow heated (5 °C/min) cokes carbonised in the high pressure autoclave have been measured using the diametral compression test and are shown in Table 6.16.

These results show that pressure has a significant effect on the tensile strength of the slow heated cokes. For Manvers-Barnburgh, an increase in pressure results in a decrease in strength with a minimum at around 3 MPa (Fig. 6.20). This trend agrees with the Magiscan results which shows that the porosity of slow heated Manvers Barnburgh coke increases with pressure up to a limiting value at about 3 MPa. The
dilatometry results (Chapter 6.3) show that at low heating rates (3 °C/min), the dilatation of Manvers Barnburgh increases with increase in pressure to a limiting value at about 3 MPa. Therefore, it can be deduced that the decreases in tensile strength (and consequently, increases in porosity) with increase in pressure are a reflection of the coal's swelling behaviour during carbonisation. Correlations reported by Walker (111) between tensile strength and optical anisotropy have not been observed.

At a heating rate of 3 °C/min, Gedling has a swelling behaviour similar to that of Manvers Barnburgh coal (Chapter 6.3). However, being a lower rank coal (NCB 802) than Manvers Barnburgh (NCB 702), it has less caking ability. This is reflected in the coke tensile strength which is much smaller than that of the Manvers Barnburgh coke. Additionally, the tensile strength of Gedling does not appear to be affected very much by pressure (Fig. 6.20). This may not be the 'complete picture' because during the diametral compression test some Gedling samples crumbled due to poor bonding leading to low strength (<1 MN/m²) and did not follow brittle fracture behaviour (which has been assumed in this test).

The diametral compression test gives a reliable means for measuring tensile strengths of brittle materials due to the large number of measurements required. But it should be emphasised that these figures are statistical mean values and that actual measured tensile strengths fall into quite a large range of results as indicated by the standard deviations (Table 6.16). This is normal for heterogeneous brittle materials.
6.3 High Pressure Dilatometry

The dilatometry results obtained in this study include heating rates ranging from 3 - 40 °C/min, and series of pressures from 0 - 6 MPa on coals of rank NCB 502 - 802. These are shown in Tables 6.17 - 6.19.

Effect of Pressure

The following trends were observed from dilatometry measurements at low heating rates (3 °C/min) with increase in pressure:–

1. The softening temperature ($T_1$) decreases considerably (Fig. 6.21).

2. There is a slight decrease in the temperature of maximum contraction ($T_2$).

3. The resolidification temperature ($T_3$) increases slightly for Manton, but is virtually unchanged for Manvers-Barnburgh and Gedling.

4. The contraction (C) does not change significantly.

5. The dilatation is dependent on the structure and rank of coal. The dilatation of Manton increases to a maximum at about 1 MPa then decreases to a limiting value. Manvers-Barnburgh and Gedling both show dilatations which increase to a limiting value at about 3 MPa (Fig. 6.22).
6. The decrease in softening temperature, coupled with the consistency of the resolidification temperature results in the lengthening of the plastic range \(T_3 - T_1\) with increase in pressure (Fig. 6.23).

At high heating rates \((40 \, ^\circ\text{C/min})\), the dilatometry measurements show the following trends with increase in pressure:

1. The softening temperature \(T_1\) decreases significantly (Fig. 6.24).

2. The temperature of maximum contraction \(T_2\) remains virtually unchanged.

3. The resolidification temperature \(T_3\) does not change significantly.

4. The contraction \((C)\) increases slightly for Manvers-Barnburgh, but there is no significant change for Manton and Gedling.

5. The dilatation of Manvers Barnburgh decreases. Manton and Gedling show dilatations which peak at about 1 MPa followed by a decrease to a limiting value (Fig. 6.25).

6. The lowering of softening temperature together with the consistency of the resolidification temperature, again, results in an increase in the plastic range \((T_3-T_1)\) with increase in pressure (Fig. 6.26).
Effect of Heating Rate

At constant pressure, the following trends of dilatometry parameters were observed with increase in heating rate:

1. The softening temperature \((T_1)\) increases steadily to a limiting value (Figs. 6.27, 6.28).

2. The temperature of maximum contraction \((T_2)\) increases slightly.

3. The resolidification temperature \((T_3)\) increases markedly.

4. The contraction \((C)\) decreases.

5. The dilatation increases markedly, particularly those measured at 0.5 MPa (Figs. 6.29, 6.30).

6. The large increase in resolidification temperature combined with only a small increase in softening temperature, results in an overall increase in the plastic range \((T_3 - T_1)\) (Figs. 6.31, 6.32).

Effect of Coal Type

Although one has to bear in mind the range of coals studied is quite limited, the effect of coal rank ranging from NCB 502 to 802 gives the following trends in dilatometry measurements:

1. Lower softening temperature \((T_1)\) with increase in rank (Figs. 6.21, 6.24, 6.27, 6.28). This contrasts previous results by Green et al. (68, 82).
2. No significant change in the temperature of maximum contraction ($T_2$).

3. The resolidification temperature ($T_3$) is slightly lower with increase in rank.

4. The contraction ($C$) increases with increase in rank but reaches a limiting value of about 30%. This is particularly evident at high pressures and high heating rates.

5. The dilatation increases with increase in rank at low heating rates (Fig. 6.22). However, it has been shown that this reaches a maximum with coals ranked NCB 400, after which, the dilatation decreases with further increase in rank (68, 82). The effect of rank on dilatation is more complicated with high heating rates (Fig. 6.25).

6. The lowering of $T_1$ along with relatively small changes in $T_3$ gives an overall increase in plastic range ($T_3-T_1$) with increase in rank (Figs. 6.23, 6.26). Previous work by Green et al. shows that this trend is only part of the picture and trend changes for higher rank coals (68, 82). One should be remember that high rank coals i.e. those above NCB 300, do not soften during carbonisation.

Again, it should be emphasised that these trends have been obtained from studying only a narrow range of coals (NCB 502 - 802) and some previous studies (68, 82) have indicated that a more complicated relationship exists between coal rank and its thermoplastic properties.
The high pressure dilatometry results show that the effects of pressure on swelling are dependent on heating rate. At high heating rates (40 °C/min), the dilatation-pressure curve decreases to a minimum above 3 MPa (Fig. 6.25), but at low heating rates (3 °C/min), dilatation increases gradually with increase in pressure to a maximum, again around 3 MPa (Fig. 6.22). These trends are in line with current literature (68, 82).

These observations can be explained by two competing processes which occur during carbonisation i.e. the volume of gas evolved, and the extent of secondary reactions (68, 122). Decreases in dilatation with increases in pressure result from a reduction of gas evolved whereas increases in secondary reactions (caused by increases in residence time of volatiles and subsequently fluidity) gives higher dilatation. Decreases in softening temperature along with the lengthening of plastic range with increase in pressure are probably the result of pressure-enhanced formation of tar.

Increases in heating rate will also promote gas and tar evolution as indicated by the improved coke yields from slow heated carbonisations (Figs. 6.1, 6.2). Figures 6.29 and 6.30 show that an increase in heating rate tends to increase dilatation. This follows the trend expected from the increases rate of gas evolution into the plastic phase.

The effect of pressure and heating rate on the coal thermoplastic properties as a function of rank is highly variable. This agrees with findings reported by Khan & Jenkins and Green & Thomas (63, 68, 69).
6.4 High Pressure Plastometry

The high pressure plastometer produced graphs which contain the parameters shown in Fig. 5.4. On heat treatment, coal particles soften at around 350 - 400 °C, \( T_1 \), and decompose with the evolution of tar which causes the particles to cake together. This agglomeration process generates resistance to the stirrer and leads to an increase in the torque required to maintain a constant angular velocity. This torque is measured and used to characterise and quantify the agglomeration process.

Decomposition proceeds with increase in temperature and the coal particles adhere more strongly. This results in an increase in torque until a maximum point known as the caking peak \( I_2 \). Both the temperature \( T_2 \) and magnitude \( I_2 \) of the caking peak are important agglomeration parameters.

Further heating increases the release of decomposition products and results in a decrease in resistance until it reaches a minimum value. This minimum torque or viscosity corresponds to the maximum fluidity \( I_3 \) and occurs at the temperature, \( T_3 \). Further heating to 450 - 500 °C causes resolidification of the plastic mass to form semicoke \( T_4 \), which is broken up by the stirrer \( T_5 \). The intensity of the coking stage is measured as \( I_4 \).

The maximum fluidity temperature \( T_3 \) occurs over a range and is difficult to determine precisely. Therefore they have not been included in the results.

The plastometer results are shown in Tables 6.20 - 6.22.
Effect of Pressure

At low heating rates (3 °C/min) the effect of pressure on the plastometer parameters gives the following trends:

1. The softening temperature ($T_1$) decreases with increase in pressure (Fig. 6.33). This agrees with the dilatometry results.

2. The caking temperature ($T_2$) decreases with increase in pressure.

3. The coking temperature ($T_4$) remains virtually unchanged.

4. There is no significant change in the complete coke breakage temperature ($T_5$).

5. There is no significant change in the magnitude of the caking peak ($I_2$) for each coal (Figs. 6.34 – 6.36). This consistency is probably because it is only the start of the decomposition process.

6. The maximum fluidity values ($I_3$) decrease slightly to a limiting value at around 2 MPa where it is most fluid (Figs. 6.34 – 6.36). This coincides with the dilatometry results where dilatation also increases to a limiting value around 2 MPa.

7. The intensity of the coking peak ($I_4$) decreases sharply with increase in pressure to a limiting value at around 2 MPa (Fig. 6.37). This can be compared to dilatometry swelling. It appears that the coking intensity decreases as swelling increases.
8. The plastic range \((T_5 - T_1)\) increases with increase in pressure to a limiting value at around 2 MPa (Fig. 6.38). This agrees with some recently published high pressure plastometry results (125).

At high heating rates \((20 \degree\text{C/min})\) the effect of pressure gives the following trends:

1. There is a gradual decrease in softening temperature \((T_1)\) with increase in pressure (Fig. 6.39).

2. The caking temperature \((T_2)\) again decreases with increase in pressure to a limiting value at 2 MPa.

3. No significant changes in the coking temperature \((T_4)\).

4. There is little or no change in the coke breakage temperature \((T_5)\).

5. The intensity of the caking peak \((I_2)\) is unaffected.

6. The maximum fluidity \((I_3)\) remains constant.

7. The coking intensity \((I_4)\) decreases rapidly with increase in pressure to a limiting value at 2 MPa (Fig. 6.40).

8. The plastic range \((T_5 - T_1)\) increases with increase in pressure to a limiting value at around 2 MPa (Fig. 6.41). These plastic ranges are all longer than those obtained from the lower heating rate of 3 \degree\text{C/min}. 

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Effect of Heating Rate

The effect of increasing the heating rate, ranging from 3 to 25 °C/min gives the following trends in plastometer parameters:

1. The softening temperature ($T_1$) increases steadily with increase in heating rate (Fig. 6.42).

2. There is a slight increase in the caking temperature ($T_2$) with increase in heating rate.

3. The coking temperature ($T_4$) increases with increase in heating rate.

4. The coke breakage temperature ($T_5$) increases rapidly with increase in heating rate.

5. The intensity of the caking peak ($I_2$) is virtually unchanged with increase in heating rate (Figs. 6.43 - 6.45).

6. The maximum fluidity values ($I_3$) falls slightly i.e. there is a small increase in fluidity with increase in heating rate (Figs. 6.43 - 6.45).

7. The coking intensity ($I_4$) decreases rapidly with increase in heating rate (Fig. 6.46). This supports the findings reported by Thomas and Chan (125).

8. The plastic range ($T_5-T_1$) increases with increase in heating rate and appears to have a limiting value at around 20 °C/min (Fig. 6.47). This point is not as clearly defined as the dilatometry result. The trend,
however, is consistent with the plastic range measured by high pressure dilatometry.

**Effect of Coal Type**

As mentioned in the dilatometry section, in studying the effect of rank on thermoplastic parameters it is necessary to include a wide range of coals. However, the following trends in plastometer parameters have been observed with the series of coals studied which range from NCB 502 - 802:-

1. The softening temperature \( T_1 \) decreases slightly with increase in rank (Figs. 6.33, 6.39, 6.42). This agrees with data published from plastometry experiments carried out under atmospheric pressures for the range of coal studied (126).

2. There is a small decrease in the caking temperature \( T_2 \) with increase in rank.

3. There are no significant changes in the coking temperature \( T_4 \).

4. The coke breakage temperature \( T_5 \) remains virtually unchanged.

5. The intensity of the caking peak \( I_2 \) increases with increase in rank (Figs. 6.34 - 6.36). This agrees with results obtained from atmospheric pressure plastometry (126).
6. There are no significant changes in the maximum fluidity ($I_3$).

7. There are no significant changes in coking intensity ($I_4$) (Figs. 6.37, 6.46).

8. The plastic range ($T_5-T_1$) increases with increase in rank (Figs. 6.38, 6.41, 6.47). This does not apply to high rank coals (above NCB 300) since they do not undergo any softening (126).

As with high pressure dilatometry, changes in plastometry parameters with pressure and heating rate can be rationalised in terms of devolatilisation processes. Swelling is an important phase in the coking process and also needs to be considered. Bearing this in mind, the lowering of $T_1$ and $T_2$ and subsequent lengthening of the plastic range with increase in pressure are the result of increased secondary reactions by decreasing the volatility of tar and increasing the residence time of the fluid phase.

Some decreases in viscosity ($I_3$) have also been observed with increases in pressure and heating rate. These conditions may encourage the development of optical texture and would account for the increase in OAI with both pressure and more importantly, heating rate.

Coking intensity ($I_4$) is a reflection of coke strength. This decreases to a limiting value around 2-3 MPa and mirrors the swelling pattern. This can also be related to the results obtained from the diametral compression test (Chapter 6.2.6) which show that the tensile strength of slow heated cokes decrease with increase in pressure.
By comparing Figures 6.29 and 6.30 with Figure 6.46, the inverse relationship between coking intensity ($I_4$) and dilatation can also be observed with increases in heating rate.

The effect of rank allow only tentative inferences to be made since only three coals have been studied. The magnitude of the caking peak ($I_2$) indicates coal’s ability to form a cohesive mass. This generally increases with increase in rank and it has been reported by Mulligan and Thomas (126) that under atmospheric conditions, coals of rank NCB 301, i.e. the so-called ‘prime coking coals’ show the maximum caking intensity. It is not recommended that this parameter be used as a measure of coke ‘strength’ because it is neither sensitive to changes in experimental conditions nor does it include the effects of swelling. It is not surprising that caking intensity does not correlate to coke strength measurements e.g. abrasion, tensile strength.

Both plastic range and (to a lesser extent) fluidity increase with increase in rank. The development of optical texture is related to the retention of plastic material and the plastic range. It therefore is possible to relate OAI with coal rank.

In addition to the relationships between swelling and plasticity, it is important to note that plastometry temperature parameters are consistent with dilatometry temperature parameters.
6.5 Coke Characterisation Relationships

The various physical tests used in the characterisation of cokes produced under simulated gasifier conditions have so far shown significant and often large effects of pressure, heating rate and coal type. It is interesting to also examine the relationships (if any) between these tests.

First of all, a comparison of the tests used to measure different aspects of 'coke strength' gives the following relationships:

i) Mass of coke abraded by abrasion test increases with increase in porosity (Fig. 6.48).

ii) Tensile strength of slow heated cokes measured by the diametral compression technique decreases linearly with increase in mass of coke abraded by abrasion test (Fig. 6.49), i.e. abrasion is linked to tensile strength.

iii) Microstrength does not correlate with any of the coke characterisation tests used. This is due to the use of small particle sizes in the test which removes most defects e.g. porosity.

iv) Coke porosity calculated from density measurements correlates closely with coke porosity measured directly (using Magiscan image analysis) (Fig. 6.16).
v) Tensile strength of slow heated cokes measured by the diametral compression test is directly related to its apparent density and hence also its porosity (Fig. 6.50).

vi) Tensile strengths measured by diametral compression are directly related to tensile strengths calculated from Magiscan porosity using Feret diameter measurements (Fig. 6.15).

Secondly, some coke properties evaluated from their physical characterisations e.g. optical anisotropy index and abrasion test, show definite trends with thermoplastic measurements from high pressure dilatometry and plastometry e.g. coking intensity and plastic range. This is accompanied by increase in fluidity (or lowering of viscosity).

Figure 6.51 shows that an increase in plastic range (measured by dilatometry) results in an increase in the optical anisotropy index (OAI). This is be attributed to reduced volatility, which leads to the retention of fluid material which otherwise might escape. This enhances OAI development because the type of optical texture observed can only develop if the coal undergoes a plastic phase during carbonisation and therefore an increase in plastic range allows more time for the aromatic molecules to re-arrange themselves in a more ordered way.

A comparison of the OAI results (Figures 6.3 - 6.11) shows that heating rate is critical for optical anisotropy development rather than pressure. There appears to be a
limiting effect of heating rate on OAI at about 20°C/min. This value coincides with the dilatometry plastic range which also reaches a limiting effect around 20 °C/min. This is also the limiting value of the plastometry plastic range although in this case it is less well defined.

Therefore, increase in OAI is associated with increases in the plastic range which is caused by increases in pressure and heating rate.

This can also be related to fluidity measurements i.e. OAI increases with increase in fluidity. Although the high pressure plastometry results shows only small increases in fluidity with increase in pressure and heating rate (Figures 6.43 - 6.45), it is important to consider the degree of fluidity the coal undergoes during carbonisation as well as its plastic range. Results obtained from high pressure plastometry show that the fluidity (I₃) of the coal undergoing carbonisation increases with increasing pressure and heating rate.

It is interesting to note that the plastic range of the coals measured by dilatometry are longer than the corresponding plastic ranges measured by plastometry (Fig. 6.52). This could be due to heat transfer effects. An alternative explanation for this phenomenon could be the high pressure plastometer's stirrer which mixes the coal during carbonisation and this action may accelerate the devolatilisation process by assisting the escape of volatiles (127, 128).
Figure 6.53 shows that abrasion is related to swelling (dilatation) but this is not a simple relationship since it varies with other experimental factors such as particle size and heating rate.

A small increase in swelling as measured by high pressure dilatometry, results in high abrasion for the slow heated cokes which is not matched by the shock heated cokes. This indicates that an increase in volume (porosity) alone does not necessarily weaken a coke in terms of abrasion resistance. Since it has been shown that there is a direct link between tensile strength and apparent density (which can be regarded as the inverse of porosity) (Fig. 6.50). One would expect the shock heated samples to be more susceptible to abrasion.

The inverse relationship between apparent density and dilatation is illustrated in Figure 6.54. There is a good correlation but only for the slow heated cokes. This is reflected in the (expected) inverse relationship between abrasion and apparent density (Fig. 6.55). However, this correlation is, again, only shown by the slow heated cokes.

Pictures of the slow and shock heated cokes may provide a reason for this anomaly. Slow and shock heated cokes are illustrated by Photographs 6.1 and 6.2 respectively. The slow heated cokes generally appear more homogeneous. The shock heated samples contain worm-like extrusions from cracks in the structure which have obviously been produced during the devolatilisation process. The smooth appearance of these extrusions indicate a fluid origin.
The cenosphere model (129, 130) involves severe swelling of small coal particles during carbonisation to form large hollow spheres i.e. cenospheres. An extension of this model can be used to explain the observations found in the cokes produced from the high pressure autoclave. High heating rates, e.g. shock heating, cause the coal in the plastic phase to become inflated with the outer shell solidifying as coke before the bulk of volatile matter has escaped. Rupture of this coke shell acts as an escape route for the volatiles which forms the worm-like extrusions observed.

The formation of the coke shell restricts swelling and this is reflected in the unexpected high apparent densities of the shock heated cokes compared with the slow heated ones (see Chapter 6.2.3). This is the reason why the porosity of the shock heated cokes does not correlate with the high heating dilatometry results (Fig. 6.5.7). This phenomenon also explains why only the slow heated cokes show a correlation between abrasion resistance and apparent density (Fig. 6.54).

The presence of this hard layer of coke is also a possible explanation for the unexpected high strength of the shock heated cokes in terms of abrasion resistance. Additionally, these cokes have undergone a highly fluid stage during carbonisation. This high fluidity consequently assists the elimination of particle boundaries and allow the coal pieces to merge into a more coherent 'homogeneous' plastic mass which upon cooling results in a relatively strong coke.
Fluidity results obtained from the high pressure plastometer (Figures 6.43 - 6.45) show that both increases in heating rate and pressure increase fluidity and provide evidence which agrees with this theory.

In addition to these relationships, others which involve different coal thermoplastic parameters have also been established i.e. between high pressure dilatometry and high pressure plastometry.

Figure 6.56 shows the correlation between dilatation and coking intensity at a constant heating rate of 3 °C/min for a range of pressures (from 0 - 6 MPa). The large gradient in Figure 6.56 indicates that the coking intensity is only reduced with relatively large increases in dilatation. Assuming that coking intensity is directly related to dynamic coke strength and indirectly related to coke strength measured by other methods then this would suggest that swelling alone does not control coke strength and may require taking into consideration the coals' caking intensity which decreases slightly with increase in heating rate (Figures 6.43 - 6.46) but does not change significantly with increase in pressure (Figures 6.34 - 6.36).

In this study, coal thermoplastic behaviour at elevated pressures and the physical properties of the resultant cokes have been investigated. These characterisations can be used to predict coal behaviour during gasification to some extent but it is almost impossible to simulate exactly those conditions found in the slagging gasifier on a laboratory scale.
Bearing in mind that these carbonisations (autoclave, dilatometry and plastometry) have been carried out under conditions which simulate those found in the gasifier, and the coke characterisations were only carried out at ambient temperatures, it is necessary to assume by extrapolation that the trends found during this study are also present in the gasifier.

Some of the techniques used for the characterisations can be criticised for only giving empirical figures. But as the results show, they do provide very useful information about the effect of experimental conditions on coal thermoplastic properties and coke structure. They also have the advantages of being simple and reliable. This is perhaps the reason why these tests have survived so long.
Table 6.1

Optical Anisotropy Index (OAI) Of Autoclave Samples

a) Shock heat

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b) Slow heat (5°C/min)

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Calculated error ± 6% (81)
**Table 6.2**

**Optical Anisotropy Index (OAI) Of Dilatometer Samples**

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<th>Gauge Pressure Rate (MPa)</th>
<th>Heating Rate (°C/min)</th>
<th>Optical Anisotropy Index Manton (NCB 502)</th>
<th>Manvers Barnburgh (NCB 702)</th>
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Calculated error ± 6 % (81)
Table 6.3

Optical Anisotropy Index (OAI) Of Plastometer Samples

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<th>Pressure Rate (MPa)</th>
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Calculated error ± 6 % (81)
### Table 6.4

Magiscan Mean Porosity Measurements Taken Over 40 Fields On Autoclave Slow And Shock Heated Cokes

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Estimated error ± 1 %

### Table 6.5

Calculated Tensile Strengths From Magiscan Image Analysis Measurements Taken Over 40 Fields On Manvers Barnburgh Slow Heated Cokes

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Estimated error ± 0.2 MN/m²
Table 6.6

MAGISCAN Porosity: Mean Number Of Pores Per Field Measured

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Estimated error ± 5 %
Table 6.7

**True And Apparent Relative Densities Of Cokes Produced By The High Pressure Autoclave**

Manton (NCB 502) shock heat

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<th>Gauge Pressure (MPa)</th>
<th>True Relative Density (kg/m³)</th>
<th>Apparent Relative Density (kg/m³)</th>
<th>Calculated Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1602</td>
<td>683</td>
<td>57.3</td>
</tr>
<tr>
<td>1.0</td>
<td>1626</td>
<td>645</td>
<td>60.3</td>
</tr>
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<td>2.0</td>
<td>1641</td>
<td>622</td>
<td>62.1</td>
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<td>4.0</td>
<td>1601</td>
<td>619</td>
<td>61.3</td>
</tr>
<tr>
<td>8.0</td>
<td>1588</td>
<td>659</td>
<td>58.5</td>
</tr>
</tbody>
</table>

True relative density calculated error 50 Kg/m³
Apparent relative density calculated error 50 Kg/m³
Porosity calculated error ± 1 %
### Table 6.8

**True And Apparent Relative Densities Of Cokes Produced By The High Pressure Autoclave**

**a) Manvers Barnburgh (NCB 702) shock heat**

<table>
<thead>
<tr>
<th>Gauge Pressure (MPa)</th>
<th>True Relative Density (kg/m³)</th>
<th>Apparent Relative Density (kg/m³)</th>
<th>Calculated Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1674</td>
<td>699</td>
<td>58.2</td>
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<tr>
<td>1.0</td>
<td>1666</td>
<td>726</td>
<td>56.4</td>
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<td>2.0</td>
<td>1675</td>
<td>784</td>
<td>53.2</td>
</tr>
<tr>
<td>4.0</td>
<td>1677</td>
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</tr>
<tr>
<td>8.0</td>
<td>1608</td>
<td>707</td>
<td>56.0</td>
</tr>
</tbody>
</table>

**b) Manvers Barnburgh (NCB 702) slow heat (5°C/min)**

<table>
<thead>
<tr>
<th>Gauge Pressure (MPa)</th>
<th>True Relative Density (kg/m³)</th>
<th>Apparent Relative Density (kg/m³)</th>
<th>Calculated Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1801</td>
<td>571</td>
<td>68.3</td>
</tr>
<tr>
<td>1.0</td>
<td>1633</td>
<td>520</td>
<td>68.1</td>
</tr>
<tr>
<td>2.0</td>
<td>1618</td>
<td>428</td>
<td>73.5</td>
</tr>
<tr>
<td>4.0</td>
<td>1685</td>
<td>424</td>
<td>74.8</td>
</tr>
<tr>
<td>8.0</td>
<td>1621</td>
<td>454</td>
<td>72.0</td>
</tr>
</tbody>
</table>

True relative density calculated error 50 Kg/m³
Apparent relative density calculated error 50 Kg/m³
Porosity calculated error ± 1 %
Table 6.9

**True And Apparent Relative Densities Of Cokes Produced By The High Pressure Autoclave**

a) Gedling (NCB 802) shock heat

<table>
<thead>
<tr>
<th>Gauge Pressure (MPa)</th>
<th>True Relative Density (kg/m³)</th>
<th>Apparent Relative Density (kg/m³)</th>
<th>Calculated Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1753</td>
<td>615</td>
<td>64.9</td>
</tr>
<tr>
<td>1.0</td>
<td>1732</td>
<td>586</td>
<td>66.2</td>
</tr>
<tr>
<td>2.0</td>
<td>1712</td>
<td>583</td>
<td>65.9</td>
</tr>
<tr>
<td>4.0</td>
<td>1574</td>
<td>574</td>
<td>63.5</td>
</tr>
<tr>
<td>8.0</td>
<td>1739</td>
<td>639</td>
<td>63.3</td>
</tr>
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</table>

b) Gedling (NCB 802) slow heat (5°C/min)

<table>
<thead>
<tr>
<th>Gauge Pressure (MPa)</th>
<th>True Relative Density (kg/m³)</th>
<th>Apparent Relative Density (kg/m³)</th>
<th>Calculated Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.0</td>
<td>1607</td>
<td>520</td>
<td>67.7</td>
</tr>
<tr>
<td>2.0</td>
<td>1682</td>
<td>545</td>
<td>67.6</td>
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<td>4.0</td>
<td>1533</td>
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</tr>
<tr>
<td>8.0</td>
<td>1612</td>
<td>506</td>
<td>68.6</td>
</tr>
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</table>

True relative density calculated error 50 Kg/m³
Apparent relative density calculated error 50 Kg/m³
Porosity calculated error ± 1 %
Table 6.10

Abrasion of Cokes Produced by the High Pressure Autoclave

Manton (NCB 502) Shock Heat

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass Of Coke Abraded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>4.1</td>
</tr>
<tr>
<td>20</td>
<td>6.2</td>
</tr>
<tr>
<td>30</td>
<td>7.8</td>
</tr>
<tr>
<td>60</td>
<td>12.8</td>
</tr>
<tr>
<td>100</td>
<td>16.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbonisation</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
<th>4.0</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gauge Pressure (MPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculated error ± 5 %
### Table 6.11

Abrasions of Cokes Produced By The High Pressure Autoclave

**a) Manvers Barnburgh (NCB 702) shock heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass Of Coke (g)</th>
<th>Abraded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>3.8</td>
<td>2.0</td>
</tr>
<tr>
<td>15</td>
<td>5.1</td>
<td>2.9</td>
</tr>
<tr>
<td>20</td>
<td>6.4</td>
<td>3.7</td>
</tr>
<tr>
<td>30</td>
<td>8.5</td>
<td>5.4</td>
</tr>
<tr>
<td>40</td>
<td>10.2</td>
<td>8.0</td>
</tr>
<tr>
<td>50</td>
<td>11.4</td>
<td>9.2</td>
</tr>
<tr>
<td>60</td>
<td>12.9</td>
<td>11.3</td>
</tr>
<tr>
<td>80</td>
<td>15.2</td>
<td>13.2</td>
</tr>
<tr>
<td>100</td>
<td>16.9</td>
<td>15.2</td>
</tr>
</tbody>
</table>

**b) Manvers Barnburgh (NCB 702) slow heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass Of Coke (g)</th>
<th>Abraded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.6</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>2.6</td>
<td>4.2</td>
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<tr>
<td>15</td>
<td>3.3</td>
<td>5.9</td>
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<tr>
<td>20</td>
<td>4.2</td>
<td>8.1</td>
</tr>
<tr>
<td>30</td>
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<td>11.0</td>
</tr>
<tr>
<td>40</td>
<td>6.9</td>
<td>13.5</td>
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<tr>
<td>50</td>
<td>8.4</td>
<td>15.7</td>
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<tr>
<td>60</td>
<td>9.6</td>
<td>17.8</td>
</tr>
<tr>
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<td>21.5</td>
</tr>
<tr>
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<td>13.6</td>
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</table>

Calculated error ± 5 %
Table 6.12
Abbreviation Of Cokes Produced By The High Pressure Autoclave

<table>
<thead>
<tr>
<th>a) Gedling (NCB 802) shock heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonisation Gauge Pressure (MPa)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass Of Coke</th>
<th>Abraded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.5</td>
<td>1.6</td>
</tr>
<tr>
<td>10</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>15</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>20</td>
<td>4.1</td>
<td>4.4</td>
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<tr>
<td>30</td>
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<td>5.8</td>
</tr>
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<td>11.5</td>
</tr>
<tr>
<td>100</td>
<td>11.8</td>
<td>13.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) Gedling (NCB 802) slow heat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonisation Gauge Pressure (MPa)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Mass Of Coke</th>
<th>Abraded (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.1</td>
<td>1.6</td>
</tr>
<tr>
<td>10</td>
<td>1.8</td>
<td>3.0</td>
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<td>8.6</td>
</tr>
<tr>
<td>50</td>
<td>6.7</td>
<td>10.1</td>
</tr>
<tr>
<td>60</td>
<td>7.7</td>
<td>12.1</td>
</tr>
<tr>
<td>80</td>
<td>9.8</td>
<td>14.4</td>
</tr>
<tr>
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<td>16.4</td>
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</table>

Calculated error ± 5%
Table 6.13

Microstrength Of Cokes Produced By The High Pressure Autoclave

Manton (NCB 502) shock heat

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Carbonisation</th>
<th>Gauge Pressure (MPa)</th>
<th>Microstrength Index (M.I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Revs (x25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>71/23</td>
<td>69/19</td>
<td>74/20</td>
</tr>
<tr>
<td></td>
<td>(3.08)</td>
<td>(3.63)</td>
<td>(3.70)</td>
</tr>
<tr>
<td>8</td>
<td>49/32</td>
<td>45/35</td>
<td>53/34</td>
</tr>
<tr>
<td></td>
<td>(1.53)</td>
<td>(1.28)</td>
<td>(1.56)</td>
</tr>
<tr>
<td>16</td>
<td>18/44</td>
<td>16/36</td>
<td>29/40</td>
</tr>
<tr>
<td></td>
<td>(0.41)</td>
<td>(0.44)</td>
<td>(0.73)</td>
</tr>
<tr>
<td>32</td>
<td>3/33</td>
<td>2/20</td>
<td>3/33</td>
</tr>
<tr>
<td></td>
<td>(0.09)</td>
<td>(0.10)</td>
<td>(0.09)</td>
</tr>
</tbody>
</table>

Calculated error ± 1 %
**Table 6.14**

Microstrength Of Cokes Produced By The High Pressure Autoclave

**a) Manvers Barnburgh (NCB 702) shock heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Carbonisation</th>
<th>Gauge Pressure (MPa)</th>
<th>Microstrength Index (M.I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Revs (x25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>67/24</td>
<td>65/24</td>
<td>65/24</td>
</tr>
<tr>
<td></td>
<td>(2.79)</td>
<td>(2.71)</td>
<td>(2.71)</td>
</tr>
<tr>
<td>8</td>
<td>42/39</td>
<td>41/38</td>
<td>41/36</td>
</tr>
<tr>
<td></td>
<td>(1.08)</td>
<td>(1.08)</td>
<td>(1.14)</td>
</tr>
<tr>
<td>16</td>
<td>13/46</td>
<td>15/46</td>
<td>15/42</td>
</tr>
<tr>
<td></td>
<td>(0.28)</td>
<td>(0.33)</td>
<td>(0.36)</td>
</tr>
<tr>
<td>32</td>
<td>1/29</td>
<td>1/24</td>
<td>1/22</td>
</tr>
<tr>
<td></td>
<td>(0.03)</td>
<td>(0.04)</td>
<td>(0.05)</td>
</tr>
</tbody>
</table>

**b) Manvers Barnburgh (NCB 702) slow heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Carbonisation</th>
<th>Gauge Pressure (MPa)</th>
<th>Microstrength Index (M.I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Revs (x25)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>73/19</td>
<td>74/19</td>
<td>74/18</td>
</tr>
<tr>
<td></td>
<td>(3.84)</td>
<td>(3.89)</td>
<td>(4.11)</td>
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<tr>
<td>8</td>
<td>55/33</td>
<td>54/32</td>
<td>54/30</td>
</tr>
<tr>
<td></td>
<td>(1.67)</td>
<td>(1.69)</td>
<td>(1.80)</td>
</tr>
<tr>
<td>16</td>
<td>28/48</td>
<td>24/48</td>
<td>25/42</td>
</tr>
<tr>
<td></td>
<td>(0.58)</td>
<td>(0.50)</td>
<td>(0.60)</td>
</tr>
<tr>
<td></td>
<td>(0.10)</td>
<td>(0.07)</td>
<td>(0.09)</td>
</tr>
</tbody>
</table>

Calculated error ± 1 %
### Table 6.15

**Microstrength Of Cokes Produced By The High Pressure Autoclave**

**a) Gedling (NCB 802) shock heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Carbonisation (Rev/s)</th>
<th>Gauge Pressure (MPa)</th>
<th>Microstrength Index (M.I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>58/27</td>
<td>59/26</td>
<td>56/30</td>
</tr>
<tr>
<td></td>
<td>(2.15)</td>
<td>(2.27)</td>
<td>(1.87)</td>
</tr>
<tr>
<td>8</td>
<td>37/42</td>
<td>35/38</td>
<td>34/40</td>
</tr>
<tr>
<td></td>
<td>(0.88)</td>
<td>(0.92)</td>
<td>(0.85)</td>
</tr>
<tr>
<td>16</td>
<td>8/44</td>
<td>10/42</td>
<td>8/42</td>
</tr>
<tr>
<td></td>
<td>(0.18)</td>
<td>(0.24)</td>
<td>(0.19)</td>
</tr>
<tr>
<td>32</td>
<td>1/16</td>
<td>1/20</td>
<td>1/15</td>
</tr>
<tr>
<td></td>
<td>(0.06)</td>
<td>(0.05)</td>
<td>(0.07)</td>
</tr>
</tbody>
</table>

**b) Gedling (NCB 802) slow heat**

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Carbonisation (Rev/s)</th>
<th>Gauge Pressure (MPa)</th>
<th>Microstrength Index (M.I.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>62/26</td>
<td>57/28</td>
<td>50/33</td>
</tr>
<tr>
<td></td>
<td>(2.38)</td>
<td>(2.04)</td>
<td>(1.52)</td>
</tr>
<tr>
<td>8</td>
<td>38/37</td>
<td>33/40</td>
<td>24/45</td>
</tr>
<tr>
<td></td>
<td>(1.03)</td>
<td>(0.83)</td>
<td>(0.53)</td>
</tr>
<tr>
<td>16</td>
<td>14/42</td>
<td>10/39</td>
<td>5/42</td>
</tr>
<tr>
<td></td>
<td>(0.33)</td>
<td>(0.26)</td>
<td>(0.12)</td>
</tr>
<tr>
<td>32</td>
<td>3/24</td>
<td>1/19</td>
<td>1/17</td>
</tr>
<tr>
<td></td>
<td>(0.13)</td>
<td>(0.05)</td>
<td>(0.06)</td>
</tr>
</tbody>
</table>

Calculated error ± 1 %
Table 6.16

Tensile Strengths Of Slow Heated Cokes (5°C/m) Determined From Diametral Compression Measurements

a) Manvers Barnburgh (NCB 702)

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>No of samples</th>
<th>Mean Tensile Strength (MN/m²)</th>
<th>Standard Deviation</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>45</td>
<td>1.78</td>
<td>0.80</td>
<td>0.12</td>
</tr>
<tr>
<td>1.0</td>
<td>50</td>
<td>1.78</td>
<td>0.68</td>
<td>0.10</td>
</tr>
<tr>
<td>2.0</td>
<td>39</td>
<td>1.03</td>
<td>0.54</td>
<td>0.09</td>
</tr>
<tr>
<td>4.0</td>
<td>48</td>
<td>1.08</td>
<td>0.46</td>
<td>0.07</td>
</tr>
<tr>
<td>8.0</td>
<td>40</td>
<td>1.37</td>
<td>0.48</td>
<td>0.08</td>
</tr>
</tbody>
</table>

b) Gedling (NCB 802)

<table>
<thead>
<tr>
<th>Pressure (MPa)</th>
<th>No of samples</th>
<th>Mean Tensile Strength (MN/m²)</th>
<th>Standard Deviation</th>
<th>Standard Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>40</td>
<td>0.92</td>
<td>0.52</td>
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### Table 6.17

**Manton (NCB 502) High Pressure Dilatometry Results**

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Calculated dilatometry errors (95%):  
\(T_1 \pm 15\) °C  \(T_2 \pm 10\) °C  \(T_3 \pm 10\) °C  
\(C \pm 5\) %  \(D \pm 10\) %
### Table 6.18
Manvers Barnburgh (NCB 702) High Pressure Dilatometry Results

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Calculated dilatometry errors (9,68) :-

$T_1 \pm 15\, ^\circ\text{C}$  $T_2 \pm 10\, ^\circ\text{C}$  $T_3 \pm 10\, ^\circ\text{C}$

$C \pm 5\%$  $D \pm 10\%$
### Table 6.19

**Gedling (NCB 802) High Pressure Dilatometry Results**

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Calculated dilatometry errors (9,68) :-

- $T_1 \pm 15 \, ^\circ C$
- $T_2 \pm 10 \, ^\circ C$
- $T_3 \pm 10 \, ^\circ C$
- $C \pm 5 \%$
- $D \pm 10 \%$
### Table 6.20

**Manton (NCR 502) High Pressure Plastometry Results**

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**Calculated plastometry errors:**

- T<sub>1</sub> ± 10 °C  
- T<sub>2</sub> ± 10 °C  
- T<sub>4</sub> ± 15 °C  
- T<sub>5</sub> ± 10 °C  
- I<sub>2</sub> ± 5 Nm  
- I<sub>3</sub> ± 2 Nm  
- I<sub>4</sub> ± 5 Nm
### Table 6.21

**Manvers Barnburgh (NCB 702) High Pressure Plastometry Results**

<table>
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<tr>
<th>Pressure Heating (MPa)</th>
<th>Rate (°C/min)</th>
<th>( T_1 )</th>
<th>( T_2 )</th>
<th>( T_4 )</th>
<th>( T_5 )</th>
<th>( T_5 - T_1 )</th>
<th>Plastic Range (Nm)</th>
<th>( I_2 )</th>
<th>( I_3 )</th>
<th>( I_4 )</th>
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<td>423</td>
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<td>3</td>
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<tr>
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<td>423</td>
<td>50</td>
<td>23</td>
<td>4</td>
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0.0 20 430 436 486 504 74 13 1 15
0.5 20 415 427 497 518 103 14 1 9
1.0 20 409 425 496 518 109 11 2 9
2.0 20 409 421 482 505 96 10 1 7
4.0 20 398 413 478 492 94 10 1 7
6.0 20 396 414 486 487 91 11 2 8

2.0 10 398 410 472 483 85 17 2 14
2.0 15 412 424 474 500 88 9 2 8
2.0 25 418 435 492 510 92 10 2 7

**Calculated plastometry errors:**

\[
\begin{align*}
T_1 & \pm 10 \, ^{\circ}C \\
T_2 & \pm 10 \, ^{\circ}C \\
T_4 & \pm 15 \, ^{\circ}C \\
T_5 & \pm 10 \, ^{\circ}C \\
I_2 & \pm 5 \, Nm \\
I_3 & \pm 2 \, Nm \\
I_4 & \pm 5 \, Nm
\end{align*}
\]
Table 6.22
Gedling (NCB 802) High Pressure Plastometry Results

<table>
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<th>Pressure Heating (MPa)</th>
<th>Rate (°C/min)</th>
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<th>T2 (°C)</th>
<th>T4 (°C)</th>
<th>T5 (°C)</th>
<th>T5-T1 (°C)</th>
<th>I2 (Nm)</th>
<th>I3 (Nm)</th>
<th>I4 (Nm)</th>
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<td>505</td>
<td>93</td>
<td>8</td>
<td>1</td>
<td>5</td>
</tr>
</tbody>
</table>

Calculated plastometry errors:

- T1 ± 10 °C
- T4 ± 15 °C
- T3 ± 10 °C
- I2 ± 5 Nm
- T5 ± 10 °C
- I3 ± 2 Nm
- I4 ± 5 Nm
Fig. 6.1 Coke yields from shock-heated autoclave carbonisations
Fig. 6.2  Coke yields from slow-heated autoclave carbonisations
Fig. 6.3 Effect of pressure on optical anisotropy index (OAI) of shock-heated autoclave samples
Fig. 6.4 Effect of pressure on optical anisotropy index (OAI) of slow-heated autoclave samples
Fig. 6.5 Effect of pressure on optical anisotropy index (OAI) of 3 °C/min dilatometry samples
Fig. 6.6 Effect of pressure on optical anisotropy index (OAI) of 40 °C/min dilatometry samples
Fig. 6.7 Effect of heating rate on optical anisotropy index (OAI) of 2MPa dilatometry samples
Fig. 6.8 Effect of heating rate on optical anisotropy index (OAI) of dilatometry samples
Fig. 6.9 Effect of pressure on optical anisotropy index (OAI) of 3 °C/min plastometry samples
Fig. 6.10 Effect of pressure on optical anisotropy index (OAI) of 20 °C/min plastometry samples
Fig. 6.11 Effect of heating rate on optical anisotropy index (OAI) of 2MPa plastometry samples
Fig. 6.12 Effect of pressure on porosity of slow-heated cokes (measured by Magiscan image analysis)
Fig. 6.13 Effect of pressure on porosity of shock-heated cokes (measured by Magiscan image analysis)
Fig. 6.14 Effect of pore spacing (W/P²) on tensile strength of slow-heated cokes
Fig. 6.15 Comparison of measured and calculated tensile strength

\[ S = 23F_{\text{max}}^{-0.5} \exp[-2(F_{\text{max}}/F_{\text{min}})^{0.5} \times P] + 1 \]

**Manvers B. slow heat**
Fig. 6.16 Comparison of coke porosity measured by density and Magiscan image analysis
Fig. 6.17 Effect of pressure on abrasion of shock-heated cokes
Fig. 6.18 Effect of pressure on abrasion of slow-heated cokes
Fig. 6.19 Effect of pressure on coke microstrength
Fig. 6.20 Effect of pressure on coke tensile strength measured by the diametral compression test.
Fig. 6.21 Dilatometry: Effect of pressure on softening temperature ($T_1$)
Fig. 6.22 Dilatometry: Effect of pressure on dilatation (3 °C/min heating rate)
Fig. 6.23 Dilatometry: Effect of pressure on plastic range \((T_3 - T_1)\)
Fig. 6.24 Dilatometry: Effect of pressure on softening temperature ($T_1$)
Fig. 6.25 Dilatometry: Effect of pressure on dilatation
(40 °C/min heating rate)
Plastic Range ($^\circ$C) vs. Gauge Pressure (MPa)

+ Manvers B. 40°C/min  
□ Gedling 40°C/min  
Diamond Manton 40°C/min

Fig. 6.26 Dilatometry: Effect of pressure on plastic range ($T_3 - T_1$)
Fig. 6.27 Dilatometry: Effect of heating rate on softening temperature ($T_1$)
Fig. 6.28 Dilatometry: Effect of heating rate on softening temperature ($T_1$)
Fig. 6.29 Dilatometry: Effect of heating rate on dilatation (2 MPa pressure)
Fig. 6.30 Dilatometry: Effect of heating rate on dilatation
Fig. 6.31 Dilatometry: Effect of heating rate on plastic range $(T_3 - T_1)$
Fig. 6.32 Dilatometry: Effect of heating rate on plastic range $(T_3 - T_1)$
Fig. 6.33 Plastometry : Effect of pressure on softening temperature ($T_1$)
Fig. 6.34 Plastometry: Effect of pressure on Manton (NCB 502) at 3 °C/min heating rate
Fig. 6.35 Plastometry: Effect of pressure on Manvers Barnburgh (NCB 702) at 3 °C/min heating rate
Fig. 6.36 Plastometry: Effect of pressure on Gedling (NCB 802) at 3 °C/min heating rate
Fig. 6.37 Plastometry: Effect of pressure on coking intensity ($I_3$)
Fig. 6.38 Plastometry: Effect of pressure on plastic range
Fig. 6.39 Plastometry: Effect of pressure on softening temperature
Fig. 6.40 Plastometry: Effect of pressure on coking intensity ($I_3$)
Fig. 6.41 Plastometry: Effect of pressure on plastic range
Fig. 6.42 Plastometry: Effect of heating rate on softening temperature ($T_1$)
Fig. 6.43 Plastometry: Effect of heating rate on Manton (NCB 502) at 2 MPa pressure
Fig. 6.44 Plastometry: Effect of heating rate on Manvers Barnburgh (NCB 702) at 2 MPa pressure
Fig. 6.45 Plastometry: Effect of heating rate on Gedling (NCB 802) at 2 MPa pressure
Fig. 6.46 Plastometry: Effect of heating rate on coking intensity ($I_3$)
Fig. 6.47 Plastometry: Effect of heating rate on plastic range
Fig. 6.48 Correlation between abrasion and porosity (from density measurements)
Fig. 6.49 Relationship between abrasion and diametral compression test
Fig. 6.50 Effect of pressure on Manvers Barnburgh slow-heated coke
Fig. 6.51 Effect of plastic range on optical anisotropy index (OAI) of 40 °C/min dilatometry samples
Fig. 6.52 Comparison of plastic range measured by dilatometry and plastometry
Fig. 6.53 Relationship between dilatation and abrasion
Apparent Density ($\text{kg/m}^3$)

Dilatation ($\% \ C + D$)

- Manvers B
- Manvers B
- Gedling
- Gedling
- Manton

**Fig. 6.54 Relationship between apparent density and dilatation**
Fig. 6.55 Relationship between abrasion and apparent density
Fig. 6.56 Relationship between dilatation and coking intensity at 3 °C/min heating rate
Photo. 6.1  Shock heated coke
Photo. 6.2  Slow heated coke
CHAPTER 7.0 CONCLUSIONS AND FURTHER RESEARCH

7.1 Conclusions

These studies have shown the complex relationship which exist between coal thermoplastic properties and physical coke properties. These properties have been found to be highly dependent on experimental conditions applied during the carbonisation process e.g. pressure and heating rate.

The following conclusions have been derived from this characterisation study.

1) High pressure dilatometry (Chapter 6.3) and plastometry (Chapter 6.4) results show that increases in pressure lower the coal softening temperature and this leads to an increase in the plastic range. This is associated with retention of volatile matter which results in improved coke yields (Chapter 6.1).

2) Both increases in pressure and heating rate lengthen the apparent plastic ranges measured by dilatometry and plastometry. For pressure, this is effected by lowering the softening temperature. For heating rate, this is caused by raising the solidification temperature.

3) There is a linear relationship between dilatometry plastic range and corresponding plastometry plastic range, with the former being generally longer (Chapter 6.5).
4) The caking intensity measured by high pressure plastometry is not affected by pressure. It is slightly reduced with increase in heating rate. It is mostly dependent on coal type and increases with increase in rank.

5) Optical anisotropy development is enhanced by increases in fluidity and plastic range which are themselves increased respectively by increases in pressure and heating rate up to about 3 MPa and 20 °C/min.

6) Pressure affects dilatation in several ways but they all have limiting values around 2 - 3 MPa after which further increase in pressure has negligible effect (Chapter 6.3).

7) Upto 8 MPa, pressure effects the greatest changes in swelling in the range between 0-2 MPa. This is because there is a twenty-fold increase from atmospheric pressure to 2 MPa but only a four-fold increase from 2 MPa to 8 MPa.

8) At low heating rates (3 °C/min) dilatation increases with increase in pressure until a limiting value of about 3 MPa. However, with higher rates of heating (40 °C/min), increases in pressure gives more complicated swelling patterns (Chapter 6.3).
9) Dilatation increases with increase in heating rate. This effect reaches a limiting value around 20 °C/min. This value coincides with the effect of heating rate on dilatometry and plastometry plastic ranges.

10) Shock heated cokes do not swell as much as cokes heated rapidly (40 °C/min) in the dilatometer. This can be attributed to heat transfer limits imposed by the large coal particles used in shock heating which may form a ‘coke shell’ so restricting swelling (and the release of volatiles).

11) Depending on the coal and the rate of heating, increases in pressure can increase or decrease coke strength. Generally, this is based on the coal swelling behaviour.

12) For any individual coke, the largest abrasion attrition coincides with the maximum dilatation (Chapter 6.2.4).

13) The tensile strengths of slow heated cokes as measured by the diametral compression test is inversely related to dilatometry swelling (and pressure). In terms of fracture, this shows that the pores enhance crack initiation and propagation rather than act as crack terminators.
14) Coke apparent densities decrease with increase in swelling i.e. increase in porosity.

15) Porosity measurements from density determinations are consistent with porosity measurements from Magiscan image analyses and a linear relationship exists between the two techniques (Chapter 6.2.3).

16) Coke tensile strengths measured by the diametral compression test correlates well with the predicted tensile strengths calculated from Magiscan porosity and Feret diameter measurements (Chapter 6.2.2).

17) Coke strength as measured by the abrasion test correlates with plastometry coking intensity.

18) The mass of coke abraded during the abrasion test increases linearly with decrease in tensile strength measured by the diametral compression test.

19) Apparent densities of slow heated cokes decrease with increase in dilatation. This relationship is more complex for shock heated cokes. The reason for this is the caking on the outside of large lumps.
The microstrength test gave no correlations with either pressure or heating rate due to the removal of porosity effects in the test samples. A small increase in microstrength with increase in coal rank was detected. This may be due to increase in caking with increase in coal rank.

A qualitative model involving the release of volatiles, the generation of fluidity during pyrolysis and carbonisation with the development of porous structure has been established. The dilatometry results obtained from a pencil of small particles shows that swelling increases with increasing heating rate i.e. the rate of release of volatiles through the porous structure is altered leading to increased swelling. Similarly the plastometry results change with heating rate. In general the caking peak is unchanged but the fluidity increases (point of maximum fluidity decreasing) and the coking peak decreases with increasing heating rate but swelling increases as indicated by the dilatometry results. The effect of pressure on thermoplastic properties of small particles is more complicated with the same general relationships between swelling and coking intensity occurring. The caking intensity remains essentially unchanged with pressure. Similar conclusions have been published previously (125) and this work extends these ideas to include coke porosity and structure. Optical anisotropy data indicates that usually an increase in heating rate results in increased anisotropy and this is possibly related to the increased fluidity. The changes in OAI are usually much smaller with change in pressure.
Low heating rate carbonisations (3°C/min) give dilatations which increase with increase in pressure. Due to heat and mass transfer effects, cokes produced by shock heating (>40°C/min) form a 'coke shell' which restrict the release of volatiles and limit any dilatation. This results in a stronger than expected coke e.g. in terms of abrasion resistance. These changes are accompanied by changes in porous structure and density i.e. they are more dense than expected and contain a large number of small pores (compared to the slow heated cokes).

7.2 Recommendations For Further Work

The characterisation carried out in this study has shown several important relationships which exist between coal thermoplastic properties and physical properties of cokes produced under high pressure conditions.

Further work is needed to provide more data to give a better understanding of processes that occur during high pressure carbonisations, and in particular, their implications for the gasification industry.

This should include the following:

1) High pressure thermogravimetric analysis to measure rates of coal devolatilisation. Experimental parameters could include heating rate, and atmosphere type in addition to the effects of pressure.
2) Quantitative analysis and monitoring of gases evolved during high pressure carbonisations.

3) Variation of gas atmosphere used in autoclave carbonisations, dilatometry and plastometry measurements. This will simulate better, those conditions found in the slagging gasifier (which contains mostly carbon monoxide and hydrogen).

4) Measurement of coke strength at elevated temperatures e.g. hot abrasion testing.

5) Carbonisation and characterisation of a wider range of coals.

6) The effect of particle size. The escape of volatiles are hindered with large particles. This will affect swelling which in turn will affect coke properties.

7) The effect of pitch addition on thermoplastic behaviour at elevated pressures. Since it has been found that viscosity affects coke properties e.g. optical texture. Its use as a briquette binder for the gasifier warrants further investigation.
8) The effect of flux additions. Flux is added in the gasifier to produce a slag of sufficient fluidity for tapping.

9) Tensile strength determinations of shock heated cokes. This may be possible by preparing the coke specimens into cubes rather than cylinders and developing a suitable test procedure.

10) The action of stirring during high pressure autoclave carbonisations and its effect on coke properties.

This should facilitate a good understanding of fundamentals involved in the various stages of the high pressure gasifier and optimise its operation.
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Appendix 1 : Magiscan Task File For Data Capture

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Change
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Image
IMAGE SOURCE
Image
IMAGE TYPE
BINARY
IMAGE TYPE
Quit
IMAGE SOURCE
Quit
ENVIRONMENT
Quit
( End of insertion. )
MAIN MENU
Capture
CAPTURE
Quit
MAIN MENU
Binary
BINARY OPS
Image-based
IMAGE-BASED OPS
Erode
1 ( BINARY OPS: How many passes [1..50] ? )
IMAGE-BASED OPS
Dilate
1 ( BINARY OPS: How many passes [1..50] ? )
IMAGE-BASED OPS
Quit
BINARY OPS
Quit
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Measure
Objects
0 ( Nesting levels? [0 = no nesting] )
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MEASUREMENTS 1
Area
MEASUREMENTS 1
Breadth
MEASUREMENTS 1
Detected-area
MEASUREMENTS 1
Height
MEASUREMENTS 1
Length
MEASUREMENTS 1
Perimeter
MEASUREMENTS 1
Width
MEASUREMENTS 1
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Quit
Yes
END
Appendix 2 : Magiscan Task File For Data Analysis

( Original task file \chi\chiirsepsp.TSK )

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Quit
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STATISTICS / CALCULATOR
Get
STATISTICS
Run
STATISTICS
Print
STATISTICS
Change
Replace
ob
Accept
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STATISTICS
Run
STATISTICS
Print
STATISTICS
Change
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Replace
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Accept
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STATISTICS
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Change
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ow