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STRENGTH OF METALLURGICAL COKE IN RELATION TO FISSURE FORMATION

by

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Doctoral Thesis

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ABSTRACT

The size distribution and strength of metallurgical coke are factors vital for the steady and high-efficiency operation of a blast furnace, since these factors govern stack permeability. Coke strength influences the size of lump coke not only because of size degradation by impact and abrasion during transfer to and descent in the blast furnace, but also because of its influence on the fracture which takes place in the coke layer during carbonisation and the effect this has on the initial mean size and size distribution of the feed coke. Therefore, the elucidation of the relationship between coke strength and the fissure formation phenomena is significant.

In this study, therefore, the coke strength development during carbonisation has been examined in conjunction with various parameters, such as the degree of carbonisation of the coal, namely the extent or fraction of pyrolytic reaction, and the degree of graphitisation of the coke, as well as carbonisation temperature and heating regime. The porous structure of coke has also been examined with a view to establishing a relation between the porous structure and the coking properties of the coal carbonised. The quality of coke porous structure was evaluated by parameters introduced in this study, i.e., the pore size distribution and pore rugosity factors. A poor porous structure is shown to be associated with high proportion of small pores and pores with a rough surface. These features are considered to stem from poor coking properties and the consequent poor adhesion between coal particles.

An attempt has also been made to establish a mathematical model capable of predicting the degree of fissuring of coke during carbonisation by utilising the understandings obtained in this study of the coke strength development during carbonisation and the effect of coal properties on coke strength. Coke samples large enough to facilitate the observation of the degree of fissuring in relation to various coal properties and heating conditions, were made to evaluate the mathematical model and introduce the concept. The concept that fissuring takes place when developing thermal stress exceeds the developing coke strength is demonstrated to be capable to evaluate the effects of coal properties and heating conditions on the degree of fissuring observed.
ACKNOWLEDGEMENTS

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I am very grateful to Mr. Douglas Hays for his cooperation especially in relation to all experimental work in this study.

I would like to thank Nippon Steel Chemical Co., Ltd. for giving an opportunity and financial support to undertake this study as a research student with the Carbon Research Group, Loughborough University.

I also greatly appreciate encouragement given from my family and friends throughout the period from the beginning of the research work to the completion of the writing of this thesis.
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Metallurgical coke is a hard, porous form of carbon formed by the pyrolysis of coal. As its name implies, it is produced for use in the metal producing industries, most importantly for iron making in a blast furnace. The process has been used for making iron for more than 200 years since the technology of using coke for the blast furnace process became established. In the blast furnace, metallurgical coke has three major functions: 1) supplying the heat required for the process, 2) reducing the iron ore, and 3) maintaining the permeability of the furnace stack. The latter function as a packing is considered to be the most important one, especially since at the bottom of the stack coke is the only solid phase present.

Maintaining stack permeability, which allows easy passage for ascending gases and descending liquids, is important for efficient operation of the blast furnace. It requires a mean coke size near 50 mm at the bosh. Thus the particle size and size distribution of the feed coke, and its resistance to size degradation when exposed to the hostile environment in the blast furnace stack, must be balanced to achieve a suitable bosh mean size.

Coke is made by charging granular coal into hot, slot-type ovens, the coal then being heated by heat transfer from the walls. Only coals which soften, usually in the temperature range 350-500 °C, can be used for coke making. After charging, layers of plastic coal are formed parallel to the heated oven surfaces and these move progressively towards the oven centre as carbonisation proceeds. It is within these plastic layers that the processes which transform granular coal into massive coke take place. The evolution of hydrogen-containing gases from the pyrolysing coal into the plastic mass results ultimately in the porous structure of coke, but also contributes to the increase in the real density of the remaining solid. Thus shrinkage occurs on transforming coal to coke. Differential shrinkage of various layers after resolidification of the plastic coal to form semicoke, causes stresses to be set up which, if they exceed the breakage stress of the material, cause fissures to form. It is this network of fissures which controls the mean size of the coke lumps produced and influences their breakage in subsequent use.
highly-fissured coke is only suitable for combustion, large blocky coke is used in iron foundries while coke with a mean size of about 50 mm is required for blast furnace use. A sound knowledge of the complex phenomena of fissure formation would therefore be of considerable economic interest to cokemakers especially if it permitted the coke size and resistance to degradation to be predicted.

The overall objective of this study is to make a contribution to the understanding of the mechanism of fissure formation during the coking of coal. Since fissures are generated in coke during carbonisation when the thermal stress exceeds the strength of coke, a sound knowledge of fissuring requires an understanding of the development of the strength of coke as carbonisation proceeds and of the influence of coal properties on both the strength development and the stress generated.

Two experimental approaches were adopted. In the first, attention was given to the development of coke strength as carbonisation proceeded. Since coke is a porous material, this involved an evaluation of coke strength in terms of its porous structure. In the second, coals were carbonised under conditions which simulated those in a commercial coke oven so that the fissure pattern in the coke could be examined. Data from both approaches were used in an attempt to develop a mathematical model which quantitatively explained the observed fissuring.

In this thesis, following this introduction, the literature relating to coke strength and fissuring phenomena are reviewed in the second chapter. In the third chapter the evaluation of coke strength in terms of the porous nature of coke is described and effect of coal properties and heating conditions on the strength are discussed. In the fourth chapter, based on the obtained knowledge regarding the coke strength, fissuring phenomena are discussed on the basis of the measured degree of fissuring in cokes produced using the large scale furnace and the mathematical model of temperature, stress and strength development during carbonisation.
2 LITERATURE REVIEW

In this chapter, a brief introduction to metallurgical coke is given. Its production process, function in the blast furnace and the quality required to fulfil its roles in the blast furnace are first considered and fields of research, which directly relate to the present study, are reviewed in the following part of the chapter. Since the objective of this study is to elucidate the mechanism of fissure formation during carbonisation in relation to coke quality as described in this thesis, the following literature was reviewed to gain an understanding of the background of the study and define its scope.

a) Mechanical strength of metallurgical coke
b) Other properties of metallurgical coke
c) Fissure formation phenomena
d) Mathematical modelling of fissure formation phenomena
e) Prediction of coke quality

At the end of the chapter an outline of the present study is explained in relation to previous research in the field.
2.1 METALLURGICAL COKE

2.1.1 Production of metallurgical coke

Generally, metallurgical coke is produced in a chamber oven, which consists of two opposing vertical heating walls, with an accompanying adjacent flue for each wall, and a coal charge is carbonised from both walls (Figure 2.1 [1]). The coal charge is crushed to below 3 mm and charged from the top of the chamber. The carbonisation process is terminated when the centre of charge reaches a certain temperature. By then, the clearance between coke and wall has grown sufficiently wide to allow a stable discharge from the chamber. The output of product, which must meet the operational requirements of the blast furnace, is controlled by changing the flue temperature so that the carbonisation time allows the required output.

![Figure 2.1 Chamber oven](image)

During carbonisation, the initial packed bed of coal is converted into massive porous coke by passing through a plastic stage where adjacent coal particles melt and bond to each other. Only with coals having thermoplastic properties, is it possible to produce coke from this process and therefore good caking capacity is an indispensable property of coal in the coal charge. After passing through the plastic stage and resolidifying, the semicoke generated shrinks as carbonisation proceeds. Because carbonisation progresses from wall
side to oven centre, so that the temperatures differ considerably from the wall side to the oven centre, thermal stresses are raised in the coke and fissures are generated from the wall side when the stress exceeds the fracture strength of coke. Because of this fissuring, coke pushed from the coke oven has an approximately suitable size for the blast furnace process. The degree of fissuring governs not only the initial size of coke but also its resistance to the impacts occurring during handling and in the blast furnace. Therefore, the fissure formation phenomena in the coke oven chamber is one of the major factors which determine the coke size at a lower part of the blast furnace.

2.1.2 Function in the blast furnace

In the blast furnace, coke has to fulfil the following important functions [2]:

1) a thermal role, supplying the major part of the heat required for the process.
2) a chemical role, as a source of the carbon required for:
   a- the production of CO (reducing gas) by combustion at the tuyeres;
   b- for the partial regeneration of CO by the solution loss reaction in the high temperature zone;
   c- as reductant for the "direct" reduction of FeO in the liquid slag (solid/liquid reaction) and for the reduction of alloying elements like Si and Mn;
   d- as alloying element for the carburisation of the hot metal.
3) a physical role, when coke is the only solid material below the smelting zone of the iron bearing materials (Figure 2.2). On one hand, it forms a strong grid which supports part of the weight of the overlying burden and, on the other hand, it constitutes a highly permeable "trickling column" which allows an adequate percolation of the gases ascending from the "raceway" at the tuyeres.

Among these functions, the physical role is considered the most important role for coke in the blast furnace, since no other material has the mechanical properties to replace this function at acceptable cost.
2.1.3 Quality of metallurgical coke

In the blast furnace, as aforementioned, coke takes following three roles 1) fuel; supplying heat for reaction 2) reducing agent; reducing iron ore 3) spacer; keeping permeability in the blast furnace. To ensure these functions and to maintain stable and efficient operation of the blast furnace, the quality of coke is measured by both chemical and physical methods in industry.

2.1.3.1 Chemical properties of coke

Among chemical properties of coke, content of moisture, ash, volatile matter and sulphur are the major indices for blast furnace operation.
With regard to the moisture content, a practically dry coke with little variation in moisture content is required for stable blast furnace operation. The level of moisture content depends mainly on a method of quenching and generally, it is 1-4 % in wet quenching and 0.2-0.3 % in dry quenching [1].

The mineral matter content of coal is the most important chemical properties because it affects the total consumption of coke, the production of slag and hence general blast furnace performance figures [3]. Furthermore, the chemical composition of the ash is also important since it has an influence on the basic strength and viscosity of the slag [1]. The coke ash is determined by the mineral content of the coal charge and its usual level is between 8 % and 12 %.

The volatile matter of coke depends on the final carbonisation temperature, that is, the degree of carbonisation and basically it is below 1 % in general coke oven operation.

Because the sulphur content of coke directly affects the quality of pig iron and its cost, it is important to keep the sulphur content as low as possible. However, since, like other chemical components of coke, the sulphur content is controlled only by the sulphur content of the coal charge, it is not easy to lower the content in the commercial operation.

2.1.3.2 Physical properties of coke

Since coke plays a vital role in maintaining the permeability of the blast furnace, much importance has been attached to its strength and its size. In order to evaluate the strength of coke for the blast furnace use, coke is generally tested by means of the revolving drum tests. Several have been introduced in different countries using similar principles but to different standards (Table 2.1 [1]). As an example, the drum test apparatus for the micum test is shown in Figure 2.3. The micum indices are determined by revolving the drum 100 times at 25 rpm after charging a 50 kg of coke greater than 60 mm in size, and expressing the residue above 40 mm (M_{40} index) and the residue below 10 mm (M_{10} index) as percentages.

In the revolving drum tests, coke degradation takes place via two fracture mechanisms, namely breakage by impact and abrasion [3], which are considered to simulate the mechanical effects in the blast furnace. However, because the sizes of drum, lifter and coke specimen are different in each standard, the contribution of the two fracture modes
differs between standard tests and, therefore, it is difficult to compare directly the indices measured by the different standards.

Figure 2.3 Micum drum test apparatus

Table 2.1 Revolution tests for coke strength indices

<table>
<thead>
<tr>
<th>Name of test</th>
<th>Standard</th>
<th>Diameter (mm)</th>
<th>Length (mm)</th>
<th>Number of lifters</th>
<th>Size (mm)</th>
<th>Amount (kg)</th>
<th>Speed (rpm)</th>
<th>Number (rev)</th>
<th>Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drum test</td>
<td>JIS K 2151-1977</td>
<td>1500</td>
<td>1500</td>
<td>6</td>
<td>&gt;50</td>
<td>10</td>
<td>15</td>
<td>30</td>
<td>$D_k^{15}, D_k^{20}, D_k^{40}$</td>
</tr>
<tr>
<td>Tumbler test</td>
<td>JIS K2151-1977</td>
<td>914</td>
<td>457</td>
<td>2</td>
<td>50-75</td>
<td>10</td>
<td>24</td>
<td>1400</td>
<td>$TI_6^<em>, TI_{25}^</em>$</td>
</tr>
<tr>
<td>Micum test</td>
<td>ASTM D 3402-81</td>
<td>36 in</td>
<td>18 in</td>
<td>2</td>
<td>2-3 in</td>
<td>22 lb</td>
<td>24</td>
<td>1400</td>
<td>&gt;1 in stability factor</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&gt;1/4 in hardness factor</td>
</tr>
<tr>
<td></td>
<td>ISO 556-1980</td>
<td>1000</td>
<td>1000</td>
<td>4</td>
<td>&gt;60</td>
<td>50</td>
<td>25</td>
<td>100</td>
<td>$M_{40}, M_{20}, M_{10}$</td>
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<tr>
<td></td>
<td>DIN 51717-1967</td>
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<td></td>
<td>NF M 03-020-1959</td>
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<td></td>
<td>GOST 8929-75</td>
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</tr>
<tr>
<td>Half micum test</td>
<td>BS 1016, Pt13:1980</td>
<td>1000</td>
<td>500</td>
<td>4</td>
<td>&gt;60</td>
<td>25</td>
<td>25</td>
<td>100</td>
<td>$M_{40}, M_{20}, M_{10}$</td>
</tr>
<tr>
<td></td>
<td>ISO 556-1980</td>
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<tr>
<td>IRSID test</td>
<td>NF M 03-023-1962</td>
<td>1000</td>
<td>1000</td>
<td>4</td>
<td>&gt;20</td>
<td>50</td>
<td>25</td>
<td>500</td>
<td>$I_{40}, I_{20}, I_{10}$</td>
</tr>
<tr>
<td></td>
<td>ISO 556-1980</td>
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Apart from the drum test, the shatter test, which assesses the resistance of coke to impact, has been used to assess the quality of coke from the early stages of the coke industry. In this method, the quality is assessed by dropping large coke pieces from 6 ft high on to a steel plate four times and measuring that remaining on 2 in, 1.5 in and 0.5 in sieves as percentages (Figure 2.4 [4]). Because of the simplicity and the fracture mechanism involved in the method, it is widely used for coke assessment in the foundry industry [5].

![Figure 2.4 Shatter index apparatus](image)

To take into account the effect of the reaction with CO₂ which takes place in the lower part of blast furnace, several formats for measuring the coke strength of high temperature have been proposed [1]. In Japan, the CSR index (coke strength after reaction) has been widely applied in the industry. This is obtained by measuring the size degradation, in an I type drum test, of 20 mm coke after reacting it in carbon dioxide at 1100 °C for 2 h [6].

With regards to coke size, it has been widely accepted that a relatively large coke, which remains large during handling before charging and during descent of the blast furnace shaft, is ideal for smooth blast furnace operation. On the other hand, at present, the tendency is to use a coke that is smaller but of narrow size range [3]. The desirable size range is generally considered the range with a lower limit around 20-30 mm and an upper limit around 80-100 mm.
2.2 MECHANICAL STRENGTH OF METALLURGICAL COKE

In industry, the strength of coke has been evaluated by the strength indices such as, the micum index, since such indices have been considered to be measured under conditions which simulate those in the blast furnace. They have proved to be convenient as an index for a quality control to maintain stable blast furnace operation. However, because of the complex mechanical behaviour, which takes place in the measurement, it is difficult to evaluate such indices as a mechanical parameter which represents the strength of the material. Therefore, studies which attempt to evaluate the fundamental strength of coke as a porous material have been made to improve the understanding of coke strength and its role in the blast furnace.

As aforementioned, the degree of fissure formation in coke affects its quality. The mechanical strength of coke is one of the most important factors which govern the degree of fissure formation in coke, since fracture occurs when a stress generated in the coke, exceeds the coke strength. Elucidation of the mechanical strength development of coke during carbonisation is, therefore, vital not only to evaluate the quality of the coke matrix itself, but also to elucidate the fissure generation phenomena and to estimate the quality of coke, taking account of the degree of fissuring present in coke.

Since coke is a typical brittle material, fracture occurs by a tensional stress rather than compressive stress. Therefore, in this section the tensile strength of coke is discussed as a representative mechanical strength of coke.

2.2.1 Mechanical test

2.2.1.1 Diametrical compression method

Because of the fragile nature of coke, an indirect tensile test, namely, the diametral compression method has been widely applied for the mechanical strength evaluation of coke [7-13]. An early attempt to measure the mechanical strength of coke was carried out by the British Coke Research Association [7]. They measured the tensile strength of an electrode graphite and a carbonised coal briquette using the disk and annulus breakage testing methods and compared the validity of the two methods. A schematic diagram of specimens for both methods and the maximum tensile stress developed in the specimen
are shown in Figure 2.5. It was reported that a breakage strength measured by the annulus method was evidently about three times larger than that given by the disk method. This difference was assumed to be caused by a difference in volume of the specimen used in the two methods. A greater volume has a greater probability of containing a major flaw which could cause a stress concentration in the coke specimen and result in a brittle fracture at low load.

![Diagram of disk and annulus test specimens](image)

**Figure 2.5** Maximum tensile stress developed in disk and annulus tests

Although the annulus method is less affected by the flaw in the specimen and the effect of shear near the loading plane, it was concluded that the disk method would be adopted for the exploratory studies because of the difficulty of making a reliable specimen for the annulus test. The tensile strength $P$ measured by the disk method is given by following equation:

$$P = \frac{2W}{\pi Dt}$$

(2.1)

where $W$ is the compressive line load and $D$ and $t$ are the diameter and the thickness of the disk.

Using the disk method, they discussed the effect of carbonisation temperature, rate of heating, briquetting pressure, test temperature and apparent density. It was reported that the greater the carbonisation temperature, briquetting pressure or apparent density, the greater was the breakage strength. However, no reasonable relation between the rate of heating and the breakage strength was found. A possible reason was that the porosity and
porous structure of coke specimen were easily affected by the rate of heating, since the swelling behaviour of the coal briquette depended on the rate of heating. Although the tensile strength measured at the final carbonisation temperature was considerably smaller than that at room temperature when the final carbonisation temperature was 500 °C, the differences were small when the final carbonisation temperatures were 600, 700 and 800 °C. Therefore, it was concluded that it is possible to assess stress development in coke by the measured tensile strength at room temperature when the final carbonisation temperature is higher than 600 °C.

Since the method applied to the coke tensile strength measurement was based on the basic theory of elasticity, the applicability of the method to coke was discussed. To evaluate the applicability of the method for coke, the stress-strain relation was observed by means of a strain gauge fixed to the test specimen. The results indicated a satisfactorily linear relationship between the tensile stress and strain up to the limiting breakage stress, as shown in Figure 2.6. Therefore, it was considered reasonable to conclude that coke and semicoke are elastic materials and the theory of elasticity is applicable to coke.

![Figure 2.6 Typical stress-strain curve (South Wales coal carbonised to 900 °C)](image_url)
Following the above work, which examined laboratory coke, Patrick and Stacey [8] applied the method, the diametral-compression test, to industrial coke. The test specimens were obtained from half-oven-width lumps by drilling cores from a series of positions across the lumps. The validity of the application of the diametral-compression test to an industrial coke was examined by the photoelastic technique. The technique allowed the stress distribution in the disk specimen to be observed and to determine whether the stress distribution required by the theory of the diametral-compression test was obtained from the test pieces of the commercial coke when they were subjected to the applied load. The results are shown in Figure 2.7 where a stress distribution close to that required by the theory was obtained. However, compared to the laboratory coke, marked deviations might occur with the industrial coke samples because of surface cracks, any inhomogeneity of the sample and edge crushing.

![Industrial coke and Laboratory coke](image)

**Figure 2.7 The stress distribution in specimens under diametral compression**

It was reported that the tensile strength of the industrial coke varies widely both across the oven width and positions in the oven. In general, the lowest tensile strength was observed from the specimens which were taken from near the oven centre, where the apparent density was also lowest. Although there was a general relationship between the
tensile strength and the apparent density, it was shown that cokes having similar mean apparent density can have quite different mean tensile strength. This suggested that to estimate the tensile strength of coke, it is necessary to elucidate the effect of the porous structure and other factors on the strength.

To improve an understanding of the mechanical properties of coke and their significance in industrial practice, the relations between the tensile strength and the strength indices used in the industry were examined for both foundry coke [9] and blast-furnace coke [10]. The micum indices $M_{10}$ and $M_{40}$, which are primarily associated with resistance to abrasion and with impact breakage due to fissures, respectively, were taken as the coke properties used in the industry. It was found that there was strong evidence of a systematic relationship between the average tensile strength and the $M_{10}$ micum index for foundry coke. However, there was no clear relation between the tensile strength and the $M_{40}$ micum index for foundry coke. It was assumed that this difference in both relations stems from the different fracture mechanisms involved, namely, the $M_{10}$ micum index is affected by a fracture of matrix itself; on the other hand the $M_{40}$ micum index is strongly related to the fracture caused by extension of fissures present in the coke lump.

Unlike foundry coke, no useful relation between the micum indices and the tensile strength was found in case of the blast furnace coke. It was concluded that, for blast furnace coke, there were some factors, not significant in the case of foundry coke, playing an important role in the breakage process occurring either in the micum drum test or the diametrical compression test. The possible causes were assumed to be differences in distribution, size, shape or concentration of microcracks or flaws which are recognised as playing such an important role in the process of brittle fracture.

To evaluate the strength of formed coke and a binder for formed coke, Miyagawa and Fugishima used the indirect tensile test for measuring the tensile strength of coke [11]. From the correlation between the tensile strength and the micro strength, which was considered to represent the degree of fusion bonding between coal particles, they suggested that the tensile strength measured from the indirect method represents an overall evaluation of the particle bonding, that is the strength of coke matrix. However, because they omitted the effect of porosity and porous structure, the relation contained rather large scatter [12].
2.2.1.2 Tensile method

A direct tensile test has been widely applied for various materials. However, since coke is a brittle material and, therefore, preparation of samples for measurement is extremely difficult, only a limited number of direct measurements of tensile strength have been carried out [14, 15].

Fukai et al. [15] showed the possibility of applying the direct tensile test to coke. In their study, to avoid fracture during the shape manufacturing process, samples were carbonised in the shape for the tensile test on the basis of a thermal stress estimation during carbonisation. The measured tensile strength was evaluated by comparison with results from the four point bending method. It was reported that the tensile strength measured by the tensile method was approximately one fourth of the value measured by the four point bending method.

2.2.1.3 Compression method

Since fracture which takes place in coke is considered to be caused by tensile stress, study of the compressive strength of coke has been limited [13, 14, 16]. Jeulin et al. reported the compressive strength calculated by following equation [13]

\[ \sigma = \frac{F}{\pi R^2} \]  

(2.2)

where F is an applied force and R is a radius of a cylindrical specimen. The measured compressive strength was compared with the tensile strength measured by the diametral compression method and it was reported that the compressive strength was approximately four times larger than the tensile strength.

2.2.2 Relation between porous structure of coke and mechanical strength

As a porous material, whose strength is strongly governed by the porous structure, the relation between strength and porous structure of coke has been studied [17-24].

By means of a computerised image analysis system, a quantitative characterisation of the porous structure, such as the number, shape and size of the pores were determined, and its
relation to the strength of coke, measured by the diametrical-compression method, was examined [17]. It was reported that, for metallurgical coke in general, no single structural parameter gives a good correlation with the tensile strength. By using more complex relationships involving several of the structural parameters, better correlation of the tensile strength and structural parameters was shown.

Further studies showed that the strength of coke, $S$, can be expressed by the following equation [18-20] on the basis of the Griffith theory [21]

$$ S = 450(F_{\text{max}})^{0.5} \exp[-2\left(\frac{F_{\text{max}}}{F_{\text{min}}}\right)^{0.5} P] $$

(2.3)

where $F_{\text{max}}$ and $F_{\text{min}}$ are the maximum and the minimum of the Feret's diameter and $P$ is porosity. In the equation, the critical flaw size in the theory was assumed to be equal to the maximum Feret's diameter and a stress concentration factor, associated with pore shape, was represented by the ratio of the maximum and minimum Feret's diameters as a measure of the ellipticity of the pores.

To characterise the porous structure of coke, especially under complex stress conditions, the fractal theory has been applied to the field [22]. The geometry of the porous network was analysed in terms of the fractal structure. It was suggested that there were two types of fracture, these are, the brittle fracture and the complex fracture. In the case of the brittle fracture, the strength was linked with the size of the largest pore, while, in the case of complex fracture, the strength was linked with the fractal dimension. Although the application of the method was limited, the possibility of explaining coke strength under complex stress was shown.

Because of the anisotropy of the porous structure in lump coke, the strength of coke also exhibits anisotropy. Especially in the commercial coke oven, where carbonisation progresses from a wall side to an oven centre, the shape of pore tends to be distorted by the effect of the coking pressure. The strength of coke can be assumed to differ from each direction in relation to the longer axis of elliptical pores of the porous structure. This phenomena was reported by Taits [23], who showed the different pore shapes in each directions in a lump coke. In longitudinal section, the shape of pores tends to be elliptical, while in the transverse section, they tend to be circular. By examining the compressive
strength of a coke which had an elliptical pore shape. It was showed that the compressive strength of coke, measured by compressing along the longer pore axis, was higher than that measured by compressing at right angle to the axis.

Not only the degree of pore distortion and the direction of it, but also the smoothness of the pore is also an important factor influencing the strength of coke, since pores in a material behave as major flaws. It was reported that because stress intensity in the vicinity of a flaw increases as the radius of curvature of the flaw decreases, coke which has relatively sharp pores should be weaker than coke which has round pores [24]. Since the dilatation of coal increases as the heating rate increases, it was suggested that coke of better quality could be made by making the radius of curvature of the pores larger. Thus it is important to maintain a certain heating rate during carbonisation.

2.2.3 Strength of coke matrix

To evaluate the strength of a porous material like coke, not only the porous structure, but also the strength of the matrix influences the strength of the material. Attempts to measure the strength of the coke matrix have been made using several methods [25, 26]. Although the fracture phenomena taking place in the test are rather complex and it is difficult to confirm what is being measured, the micro strength index [25] has been widely used and is considered to represent the strength of the matrix, at least to some extent [27, 28]. From a relation between the micro strength (M.S.I\textsubscript{65}), the composition balance index (C.B.I.) [29] and the mean reflectance of vitrinite in oil, Okuyama et al. suggested that M.S.I\textsubscript{65} possibly represents the state of bonding between coke particles, namely, the strength of the cell wall material in coke, in other words, the strength of matrix [27]. Nishioka and Yoshida [28] also reported that the measured micro strength across the oven width had no relation to porosity and increased as carbonisation temperature and degree of graphitisation increased. From this trend they concluded that the micro strength reflects the strength of the coke matrix.

However, the micro strength of coke only indicates a qualitative value of strength and does not represent a theoretically recognised value. To evaluate the actual value of the strength of the coke matrix, Pitt and Rumsey [30] estimated the strength on the basis of formulae (Table 2.2) which represent the relation between porosity and tensile strength.
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for several cokes. It was reported that the estimated pore-free matrix strength was usually quite similar for a particular coke, but differed from one coke to another. Values lay in the range 10-40 MPa which is approximately an order of magnitude greater than the strength of the coke.

Table 2.2 Tensile strength / porosity relationships

<table>
<thead>
<tr>
<th>Relationship</th>
<th>( \sigma/\sigma_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(1-P)</td>
</tr>
<tr>
<td>(2)</td>
<td>( 1-1.21P^{2/3} ) P \leq 0.52</td>
</tr>
<tr>
<td></td>
<td>( 1+\pi(a/r)^2-2[(a/r)^2-1/4]^{1/2}-4(a/r)^3\sin^{-1}r/2a )</td>
</tr>
<tr>
<td></td>
<td>(where ( P=\pi3[-8(a/r)^3+9(a/r)^2-3/4] ) P \geq 0.52)</td>
</tr>
<tr>
<td>(3)</td>
<td>( X/(1+0.437P+2.41P^{5/3}) ) (where ( X=\text{relationship}(2) ))</td>
</tr>
<tr>
<td>(4)</td>
<td>( (1-P)/(1+3P) )</td>
</tr>
<tr>
<td>(5)</td>
<td>( \exp(-bP) ) (where ( b ) is constant for a particular coke)</td>
</tr>
</tbody>
</table>

2.2.4 Development of coke strength

During carbonisation the strength of coke develops as the strength of the matrix develops and the porous structure changes. The development of the coke matrix strength stems from an internal structure change which takes place in relation to the pyrolysis reaction during carbonisation. This is accompanied by the development of the optical anisotropy observed by means of the polarising microscope [31, 32] and an improvement in the graphitisation of the carbon matrix [33]. As regards the porous structure, considerable change takes place during the plastic stage, when coal particles soften and bond to each other and the nature of the porous structure is practically determined at this stage, little further change occurring during later stages of carbonisation [34, 35]. Therefore, with regard to the strength development after resolidification, the role of the development of the coke carbon matrix is significant.

The properties of coke during carbonisation (500-1000°C) were investigated to clarify the influence of carbonisation temperature [36]. It was shown that the microstrength increased with the carbonisation temperature as well as the true density and crystallite
size of coke. This is considered to explain the reported trend of strength improvement during carbonisation [7, 14, 15, 37].

2.2.5 Fracture parameter of coke

A fracture parameter such as the fracture toughness is vital for evaluating fracture phenomena on the basis of the fracture mechanics. However, since there has been few attempts to evaluate quantitatively the fissuring phenomena based on the theory, few studies have been carried out to measure fracture parameters [16, 38].

The stress intensity factor $K_I$ was estimated based on the measured value of the thermal shock fracture toughness, which was determined by applying Joule heating to a disk specimen with an arranged crack [38]. It was reported that the fracture toughness was strongly dependent on the porosity and there was an optimum range of porosity for the highest fracture toughness.
2.3 OTHER PROPERTIES OF METALLURGICAL COKE

2.3.1 Young's modulus

Young's modulus is one of the most important mechanical properties and it is an indispensable parameter when estimating a stress generated in a material. However, in spite of its importance, few attempts to measure the Young's modulus of coke have been made. As with the measurement of coke strength, difficulties are met in sample preparation and in measurement. Therefore, it is important to establish the method which permits the measurement of Young's modulus not only accurately but also conveniently.

2.3.1.1 Method of measurement

Several methods have hitherto been proposed for Young's modulus measurement. Although the values measured by these methods were in relatively good agreement, the principle and conditions of the measurements were different in each method and none of them has yet been recognised as a standardised method.

It was reported by the British Coke Research Association [7] that Young's modulus could be determined from the average slope of the stress-strain relationship during the disk breakage test, an indirect tensile strength test, using a strain gauge. In this method the coke specimens were carbonised to final temperatures between 500 and 1000 °C and it was shown that the measured Young's modulus increased systematically as the carbonisation temperature increased. The Young's modulus measured by the static method, using a strain gauge, was compared with that measured by the dynamic method, or the resonance method [39]. It was reported that the two methods gave results of similar magnitude, but, nevertheless the results given by the dynamic method tended to be at least 30% greater than those given by the static method.

Gryaznov et al. [40] developed a special apparatus which allowed Young's modulus to be measured, either "hot" or "cold", under compression conditions. The modulus was determined by plotting loading-unloading diagrams. It was shown that "cold" samples had a much higher Young's modulus than the samples tested at the corresponding carbonisation temperature, namely, in the "hot" state. They concluded that this stems
from a difference in mobility of the molecular system and in the “hot” state the system was more mobile and could undergo greater internal stress relaxation. The difference between the compression test and the tensile test has been discussed by Jeulin [13] and Konyakhin [14]. Konyakhin reported that by examining the same sample by both the compression test and the tensile test in the “hot” state, the Young’s modulus obtained from the compression test was approximately two orders of magnitude higher than that obtained from the tensile test.

Aiming to measure Young’s modulus conveniently, Klose and Suginobe [41] developed a method to calculate the value from the widely used indirect tensile test on the basis of the Hertz contact problem of two cylinders. The effective Young’s modulus was calculated from the following equation

\[
\frac{2}{\pi F^2 H} = -F_{\text{eff}} d\left(\frac{v_o}{F}\right)
\]  

(2.4)

where \( F, H \) and \( v_o \) are the force applied to the sample, the sample height and the total deformation respectively. The Young’s modulus was determined using a force-deformation curve obtained during the indirect tensile test and the differential form of the equation. It was reported that the measured value correlated well with the value measured by static methods. The development of Young’s modulus was also followed using this method, but the relationship between Young’s modulus and the carbonisation temperature was rather ambiguous compared with another method [37].

The results obtained using these methods are shown in Table 2.3. Even if the variation of Young’s modulus amongst cokes is large, the difference between methods seems very high. This is considered to stem from the errors inevitably contained in each method and shows the necessity of developing an advanced method for the determination of the Young’s modulus of coke.

2.3.1.2 Relation between porous structure and Young’s modulus

The number of studies of the relation between Young’s modulus and porous structure is small.
It was reported that Young’s modulus tends to be smaller for more porous coke [7]. Jeulin [13] showed the following relation between Young’s modulus and apparent density:

\[ E = E_0 \exp(P \cdot d_a) \]  \hspace{1cm} (2.5)

where \( E \) and \( d_a \) are the effective Young’s modulus and the apparent relative density, \( E_0 \) and \( P \) are constants. This shows that, in common with the tensile strength, it is possible to express Young’s modulus as an exponential function of porosity.

On the other hand, Klose and Suginobe [41] applied a linear function for the relation between Young’s modulus and porosity, which was derived from an examination of a relation for other materials.

\[ E_{\text{eff}} = E_{\text{eff0}} (1 - A \varepsilon_z) \]  \hspace{1cm} (2.6)

where \( \varepsilon_z \) is total porosity, \( E_{\text{eff0}} \) is the Young’s modulus at zero porosity and \( A \) is constant.

### Table 2.3 Young’s modulus determined by several methods

<table>
<thead>
<tr>
<th>Testing method</th>
<th>Young’s modulus</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Diametrical compression (with strain gauge)</td>
<td>~20 GPa</td>
<td>B.C.R.A. [7]</td>
</tr>
<tr>
<td>2 Axial compression (“hot” and “cold”)</td>
<td>~1.5 GPa</td>
<td>Gryaznov et al. [40]</td>
</tr>
<tr>
<td>3 Dynamic (resonance) method</td>
<td>~4.5 GPa</td>
<td>Patrick et al. [39]</td>
</tr>
<tr>
<td>4 Axial compression</td>
<td>~1.3 GPa</td>
<td>Jeulin et al. [13]</td>
</tr>
<tr>
<td>5 Tensile test (“hot”)</td>
<td>~40 MPa</td>
<td>Konyakhin [14]</td>
</tr>
<tr>
<td>6 Diametrical compression</td>
<td>~0.7 GPa</td>
<td>Klose et al. [41]</td>
</tr>
</tbody>
</table>

#### 2.3.1.3 Relation between strength and Young’s modulus

The relation between strength and Young’s modulus of coke has been discussed by some researchers [7, 13]. However, no clear relation between two mechanical parameters has been found.
A fairly systematic relationship between the tensile strength, measured by means of the diametrical compression test, and the effective Young's modulus of various cokes was found by the British Coke Research Association [7]. On the other hand, Jeulin et al. [13] reported that although there was a close positive correlation between the compressive strength and the effective Young's modulus (Figure 2.8), no correlation could be observed between the tensile strength and the effective Young's modulus of coke.

![Figure 2.8 Relationship between elastic modulus and compressive fracture stress at room temperature (F: feed coke, T: tuyere coke)](image)

2.3.2 Contraction coefficient of semicoke

During carbonisation coal decomposes thermally. As a result of the reaction, coal turns into coke. In this transition, contraction of semicoke occurs due to a release of volatile matter during the reaction and it is this contraction which causes a thermal stress and a consequent breakage of the coke resulting in reasonably small coke lumps. Since this contraction of semicoke after resolidification is one of the major factors influencing fissuring, attempts have been made to understand and to measure the contraction of semicoke during carbonisation.
2.3.2.1 Method of measurement
Various methods have been used to measure the contraction of semicoke. In the early days, the contraction of semicoke was measured as the contraction of granular coke and monoliths cut from a piece of coke [42]. Another method attempted to measure the contraction of compressed coal disks during carbonisation up to a temperature of 650 °C using an optical-lever system (Figure 2.9) [43].

The standard method for the measurement of the contraction of semicoke uses a high temperature dilatometer. Using this method, it is possible to assess the contraction of semicoke from resolidification up to 1000 °C. The method is based on the Audibert-Arnu dilatometer. In this a pencil-shaped sample is heated in a furnace capable of heating to 1000 °C. The contraction is measured as the height displacement of the coke pencil and the contraction coefficient is calculated from the curve obtained. Figure 2.10 [44] shows a typical contraction curve after resolidification as a function of the carbonisation temperature. It is well known that the differential curve has two peaks, the first peak takes place immediately after resolidification and the second takes place at approximately 750 °C. It has been suggested that the first peak is mainly associated with the release of volatile matter content while the second peak takes place as result of hydrogen release, and consequent density increase due to a change in coke carbon structure [45].
2.3.2.2 Effect of coal rank on contraction coefficient

As shown in Figure 2.10, the first peak of the contraction coefficient strongly depends on the volatile matter content of the coal, whereas the second peak is almost identical for a wide range of coal rank. This feature of contraction of semicoke was also reported by Wandless [46], whose results emphasised this relation since it showed that coke breeze exhibited no first peak curve.

The temperature, where the contraction starts, also varies with coal rank. From examining 21 coals [44], it was reported that the temperature difference between the resolidification temperature and the temperature at which the contraction starts is approximately 5 °C.
2.4 FISSURE FORMATION PHENOMENA

In the slot type oven, carbonisation progresses from oven wall to oven centre as heat is conducted from the flues. Because semicoke progressively forms from the oven wall as carbonisation progresses and shrinks due to the thermal decomposition reaction, a thermal stress is generated within semicoke during carbonisation. When the thermal stress generated in the semicoke exceeds the strength of the semicoke, fissures are generated mainly perpendicular to the oven wall (longitudinal fissure) and less frequently parallel to the wall (transverse fissure).

Since fissure formation in semicoke has an influence on the quality of the product, especially on mean size and size distribution, some studies have been carried out to elucidate the mechanism of fissure formation during carbonisation. However, due to the complexity of the phenomena, relatively little progress has been made.

2.4.1 Observation of fissure formation

2.4.1.1 Fissure in coke
The study by Mott and Wheeler [47] is considered to be the first attempt to observe the degree of fissuring in lump coke. They showed the degree of fissure formation in lump coke using the method of Rose [48] who made a specimen for examination of the cell structure of coke by filling the coke pores and fissures with a plaster and polishing the coke surface. To explain the degree of fissure formation in cokes made from various coals and under different coking conditions, the available information on the factors affecting fissuring was discussed. They reported that the fissures propagated mainly perpendicular to the oven wall (longitudinal fissure) for most of the coals they studied. However, one coke made from Durham coal had transverse fractures in the lump cokes, but these were not as deep as the longitudinal fissures.

To make the fissuring phenomena visible, Peytavy and Lahouste [49] used a cineradiograph and observed fissure generation as carbonisation progressed. Results showed that initial fissures were generated from the heated oven wall after forming a sufficiently thick coke layer, and developed by following the boundary with the plastic layer.
In relation to the fissuring phenomena, Yamaguchi et al. [50] observed the warping of thin coke discs (Ø50 mm x 5 mm) during carbonisation by interrupting carbonisation after various time and fixing the disc in a plaster. It was found that the degree of curvature increased as the carbonisation proceeded. They also measured a pushing force generated by the bending deformation of the thin coke disc during carbonisation by means of a load cell. Since a change in the force during carbonisation corresponded to the degree of curvature of the disc, it was possible to detect evidence of fissure generation in the thin coke disc from the variation of the force during carbonisation. Based on the variation of the pushing force measured by this method, the temperature range in which an initial fissure is generated from an oven wall was estimated to be 500 to 600 °C.

To confirm their estimation, they later observed the fissuring phenomena during carbonisation [52] using the high temperature microscope technique devised in their earlier study [51]. In this technique, the phenomena was observed by microscopy measuring the intensity of light transmitted through the coke specimen during carbonisation. It was confirmed that the temperature of initial fissure generation was approximately the same as had been estimated previously.

Further work was carried out by Klose and Kunde [53] who used a carbonisation furnace with a 200 mm x 250 mm heating surface and a variable width of 200-450 mm. Several coals were carbonised until the temperature at the centre of the furnace attained the desired temperature. After cooling in nitrogen, the coke block was cast in white epoxy resin and the cast coke block was cut into 2 cm thick slices perpendicular to the direction of heat flow. It was reported that the fissure pattern was already formed during resolidification of softened coal and further rise in temperature merely resulted in growth of already existing fissures.

In connection with a coke pushing problem, Tucker et al. [54] investigated fissure patterns generated in coke and fragmentation of coke when it was subjected to a compressive stress imposed by a pushing ram. They showed that the greater part of fissures formed in coke were longitudinal fissures and the transverse fissures were formed by a compressive stress imposed by the pushing ram. The degree of transverse fissuring in the coke was strongly dependent on the applied ram pressure (Figures 2.11, 12). These results corresponded with the earlier research by Mott and Wheeler [47].
Figure 2.11 Classification system for coke breakage

Figure 2.12 Influence of applied ram pressure on the extent of lump breakage during compression
Sakawa et al. [55] directly observed fissure formation in coke during carbonisation by means of X-ray computerised tomography (CT), as commonly used in medical treatment. In their study, they set a small carbonisation box (50 mm width × 50 mm height × 150 mm length) in the CT and observed various phenomena during carbonisation such as, changes in the bulk density of the charge, the width and the movement of the plastic layer, expansion and shrinkage of the charge, and initiation and propagation of fissures in the coke. Figure 2.13 contains representative photographs of several stages of carbonisation in the oven under the steady wall heating rate of 20 °C/min as illustrated in the figure. It is possible to detect the progress of carbonisation in the carbonisation box clearly, since the density of the various layers (coal, plastic and coke) is different.

![Figure 2.13 Observation of the charge from coal to coke by the coke oven with CT scanner](image)

(Temperature is measured at the oven wall)
By using similar equipment, x-ray computerised tomography, Kawaguchi et al. [56] measured the degree of fissuring across the oven width. Lump cokes used as specimens were made in a 250 kg test oven. They defined the degree of fissuring in a lump coke by the following equation:

\[ D = \left( \frac{A}{L} \right)^4 \]  

(2.7)

where, A and L are area of coke and length of fissures in each tomogram, respectively.

Figures 2.14, 15 show heating patterns of the test oven and the consequent degree of fissure distribution in the lump coke respectively. They concluded that the distribution of fissures across the oven width was strongly influenced by the heating conditions.
2.4.1.2 Fracture surface

Although the examination of fracture surfaces seems likely to give useful information relevant to the understanding of the fissuring phenomena, little research has been carried out. French and Marsh [57, 58] studied the texture structure in the vicinity of fissures with regard to coke degradation phenomena caused by thermal shock and gasification in a blast furnace. It was reported that size, shape and orientation of fissures were dependent upon the character of the optical texture of the area in which they occurred. Since they focused on micro cracks and phenomena in a blast furnace, the phenomena they discussed is considered to be quite different from the phenomena examined in this study. Further study was made by Hays et al. [59] who examined fracture surfaces created by tensile fracture during diametrical compression by means of polarised light microscopy and scanning electron microscopy. Results indicated that the fracture features were dependent upon the textural composition of the fracture surface. Therefore it was suggested that the textural composition of coke should be taken into account when investigating the fissure formation phenomena in the coke oven.

2.4.2 Effect on coke quality

It is well known that the size distribution of coke after impact shows two peaks [60]. It is considered that the coarser component is produced by volume breakage while the finer component is mainly by abrasion [3]. Despite the fact that the volume breakage is strongly affected by fissures present in coke, the effect of fissuring on the quality of coke was mainly discussed with regard to an average diameter and diameter distribution of coke. Due to the difficulty of defining the degree of fissuring in coke, there have been few studies which compare the degree of fissuring and the quality of coke directly and quantitatively. Mott and Wheeler [47] reported that a shape of coke pieces was defined by major fractures. As regards hardness defined by the shatter drum, they showed that the greater the number of initial fissures in a piece of coke the weaker was the coke. In addition to this, they noted that the hardness of coke was affected not only by the number but also by the extent of penetration of fissures into the coke.
A similar concept was put forward by Nadziakiewicz [61], who suggested that the fissuring in coke was one of the possible causes of a low mechanical strength of coke as defined by the Micum drum or similar test. From the observation and measurements of the coke sections, it was concluded that a clear relationship exists between the mechanical strength of coke and the fissures. It was also noted that differences in the pore structure and the inherent strength of the coke substance have little influence on the mechanical strength such as the Micum index. Moreover, a relation between the average separation of fissures and the hardness of coke measured by a small drum test was observed [62]. The value of the average separation of fissure was estimated from an extended breakage test and the hardness of coke was defined as the percentage remaining on a 40 mm round-hole sieve after 100 revolution in the small drum. It was clearly shown in Figure 2.16 that there is a correlation between the average separation of fissures and the percentage of coke retained on a 40 mm round-hole sieve.

![Figure 2.16](image)

**Figure 2.16 Relationship between mean separation of fissures (Sf) and residue on 40 mm after 100 turns in small drum (m40)**

From detailed research with regard to the coke degradation phenomena in the drum test, Wallach and Sichel [60] suggested the mechanism could be divided into two independent processes, one of which is abrasion and the other is breakage by impact. Based on their definition, Loison et al. [3] suggested that the brittle fracture by impact, which breaks
lump coke into a very small number of pieces, is due to the extension of fissures already present in the coke.

Further research of Arima et al. [63] showed that the size distribution of lump coke after testing is not strongly influenced by abrasion, but is mostly determined by the initial coke size and the volumetric breakage which is determined by the degree of fissuring present. They also reported that the smaller the initial coke size, the lower the volume breakage rate and hence the larger the coke size after stabilisation.

With regard to a diameter distribution of lump coke, Kawaguchi et al. [56] reported that the greater the variation in the degree of fissuring across the oven width, the greater the diameter distribution of the coke. It was suggested that to make a larger size coke, it is necessary to control the fissure generation in the vicinity of the oven wall.

2.4.3 Parameters influencing fissure formation

During coking fissures in coke are generated when the thermal stress exceeds the strength of the coke. Thermal stress arises in the coke layer because of the variation of temperature in the layer when the shrinkage of the layer is restrained by the adjacent relatively low-temperature coke layer. The intensity of the thermal stress generated in the layer is dependent on the thermal strain and the Young’s modulus of the coke layer. The thermal strain depends on the difference in shrinkage between adjacent layers, in other words, a difference of temperature or the degree of thermal decomposition, and the coefficient of contraction. Studies have been carried out to evaluate the effect of these two parameters, especially the effect of the contraction coefficient because of its practical applicability.

2.4.3.1 Effect of contraction coefficient

An early study carried out by Mott and Wheeler [47] showed that it is possible to control the degree of fissure formation in lump coke by reducing the contraction of the coke by adding low-temperature coke breeze to the charge. Figure 2.17 shows sections of the coke made from Sarre coking coal alone and from a blend of the same coal with 17 per cent of a low-temperature coke breeze. It is clear that the coke made from the Sarre coal alone is much more fissured than the coke made from the blended charge.
The contraction coefficient of various coals and the average fissure separation in each coke was compared in BCRA, Coke Research Report No.10 [62]. The contraction coefficient of coke in relation to carbonisation temperature was derived by measuring the yields and density of the coke. The average separation of fissures in the coke was estimated from data obtained from extended breakage tests in a small drum and determinations of apparent specific gravity. Figure 2.18 shows that a large shrinkage coefficient is associated with small values of the average fissure separation, where, $S_1$ and $S_2$ are maximum values of the contraction coefficient at temperature near $550 \, ^\circ C$ and $750 \, ^\circ C$, respectively.

Meimarakis and Boyer [64] used low-temperature semicoke and high-temperature coke breeze to control the rate of contraction. They reported that these additives modify the contraction curve effectively and therefore affect fissuring. Low-temperature coke primarily affects fissuring in the cauliflower end, while high-temperature coke breeze is primarily effective near the charge centre. From the experimental results and theoretical considerations, it was suggested that the ideal inert from the point of view of fissuring would be a hard material without contraction at $500 \, ^\circ C$, contracting as rapidly as possible.
around 600 °C and ceasing to contract at 650 °C, so as to smooth the contraction curve of
the coke as much as possible [3].

![Graph showing relationship between average separation of fissures and the maximum value of shrinkage coefficient](image)

**Figure 2.18 Relationship between average separation of fissures and the maximum value of shrinkage coefficient**

Comprehensive study of the effect of contraction on the fissuring and quality of coke was
carried out by Gregory and Horton [65]. They blended a modifier into the coal charge to
control the contraction of the coke. A coke breeze, anthracite and steam coal were used as
modifiers to control the carbonisation behaviour and to improve the quality of the coke
produced. The size and the impact strength of coke was measured to evaluate the effect. It
was concluded that the size and the impact strength of the coke are determined by the
contraction behaviour of the charge in the temperature range following the plastic stage
and up to the final carbonisation temperature. A relationship was evident between the
first peak coefficient of contraction and the mean size of the coke, and between the
second peak and the shatter resistance. They reported that the effectiveness of the
modifiers in improving the size and impact strength of the coke was related to their
ability to reduce the contraction peaks.
2.4.3.2 Effect of coal rank

In general, the contraction coefficient is related to coal rank. Higher rank coals tend to have a low contraction peak after resolidification while lower rank coals tend to have a high contraction peak. Since other factors such as resolidification temperature and coking ability tend to change simultaneously with rank of coal, the relation between coal rank and fissuring is not as clear as the relation between contraction coefficient and degree of fissuring.

Arima et al. [63] studied the effect of the coal charge on the initial size of the coke by carbonising coals of various rank either alone or after blending. They reported that the initial size of coke from single coals tends to increase with increasing Ro, the mean reflectance in oil, of the coal (Figure 2.19). However, the coke size after a mechanical treatment was changed only slightly by Ro when Ro was greater than one. A similar trend was observed in the case of blended coals. These trends can be explained by the fissures in lump coke. They reported that the coke from high Ro coal tends to have many fissures in each relatively large lump. On the basis of their results, it was suggested that the fissures generated in the each lump, as well as the fissures which divide coke into lumps, should be taken into account to control the size of coke.

![Figure 2.19 Relationship between coke size and mean reflectance of coal (single coal)](image-url)
2.4.3.3 Effect of coal particle size

The effect of particle size of coal charge was studied by Mott and Wheeler [47]. They reported that the coke made from a finer coal had more regular structure and there were fewer fractures in it. At the same time, the size of coke was improved as the size of graded coal was decreased.

With regard to additives, the effect of size was examined by Gregory and Horton [65] when attempting to improve coke quality by controlling the contraction behaviour of semicoke using additives. It was found that in terms of the coke mean size alone, coarser additives have a greater beneficial effect per unit weight addition. However, the adverse effect on the shatter and micum indices necessitated crushing additives to a finer level to improve the strength parameters.

To compensate for the adverse effect on surface breakage of lump coke when a low contraction component was blended into the coal charge, Arima et al. [63] also reduced the particle size of the low contraction component so as to decrease the size of micro-fissures in the coke. However, they reported that no difference in either volume breakage or surface breakage behaviour was observed with particles sized below 0.3 mm and in the range of addition up to 10 wt%. They also investigated the effect of coal size, and showed that an initial coke size was reduced by intensified coal pulverisation but that the volume breakage rate was decreased and consequently the coke size after mechanical treatment was increased.

2.4.3.4 Effect of heating condition

Since thermal stress is generated because of shrinkage in the coke, heating conditions which affect the variation of the temperature field in the coke is one of the main factors governing fissure formation. According to the Soule’s theory [66], the fissuring mesh size is inversely proportional to the temperature gradient. Therefore, the more rapid the heating conditions and the higher the temperature gradient, the greater is the number of fissures in the coke.

In the case of coal briquette carbonisation, Dainton and Phillips [67] studied the effects of size of briquette and heating conditions on fissure formation and discussed the mechanism of fissuring in the briquette. It was shown that once the heating rate exceeds the critical rate, the strength of the briquette degrades sharply because of the fissures
generated in the briquette. The critical heating rate varied inversely to the square of the briquette size. In addition, they found that it was possible to prevent the formation of fissures in the briquette by properly controlling the heating pattern. Without damaging the briquette, it was possible to accelerate the heating rate considerably above 630 °C and to save some carbonisation time below 450 °C.

The effect of heating conditions on metallurgical coke was investigated by Kawaguchi et al. [56]. They made coke samples using a 250 kg test oven (430 mm in oven width) under various heating patterns by controlling the wall temperature. The degree of fissure formation in coke across the oven width was observed by means of X-ray computerised tomography. It was reported that fissures penetrate deeper from the oven wall to the centre as the initial oven wall temperature becomes higher and the degree of fissuring across the oven width varies depending on the wall temperature.

2.4.3.5 Other factors influencing fissure formation

It is considered that there are many factors which affect the fissure formation phenomena. However, because of the difficulty of definition and measurement of the degree of fissuring, and the attention given to coke quality parameters such as the micum index, few studies have been carried out to find a relation between the various factors and degree of fissure in coke.

Mott and Wheeler [47] examined the effect of a method of charging on the degree of fissuring in coke. The effect of the method of charging was carried out on the same coals in ovens of the same width to eliminate any effect of the heating rate. Only the method of charging, “gravity charging” or “stamp charging” was varied. Photographs of coke cross-sections indicated that the “gravity charged” coke was less fissured than the corresponding “stamp charged” coke. Since “stamp charging” leads to a higher charge density, this suggests that the degree of fissuring is increased as the density of the charge is increased.

Melnichuk and Khegai [68] developed a novel apparatus, which could measure the quality of coke, i.e. shrinkage, degree of fissuring, and strength of coke from a single specimen to determine the coking ability of coals. The degree of fissuring was determined by dividing a total length of the fissures generated by the observed area. It was suggested
that the degree of fissuring in the coke depends not only on the shrinkage of semicoke but also on the coking property of the coal grains which influences the strength of coke.
2.5 MATHEMATICAL MODELLING OF FISSURE FORMATION PHENOMENA

In the coke oven, coal is carbonised by heat transferred from the oven wall and due to the shrinkage of the semicoke during carbonisation, fissures, which govern the mean size and size distribution of the final product are developed from the oven wall towards the oven centre. To estimate the quality of the product and to optimise it by taking into account the whole carbonisation phenomena, it is necessary to predict the thermal stress raised in the semicoke and the extent of fissure formation therein, which causes fracture, by impact, of the coke during handling. However, to date only a few studies have been carried out to predict the phenomena by means of a mathematical model.

The first one-dimensional mathematical model for stress build-up in semicoke during carbonisation was established by Soule [66]. In his model, the internal stress during carbonisation was calculated on the basis of the following simplifications:

1) the temperature gradient is uniform and constant in the zone covered
2) the coke is mechanically homogeneous i.e. it has a definitive value of elasticity as soon as it resolidifies.

The result of this calculation is shown in Figure 2.20. As the thickness of the semicoke layer increased, the stress generated in the layer developed further and the stress generated in the vicinity of the hottest surface increased. Since the hottest side was always the most stressed, it was assumed the first fractures to appear occurred when the stress reached the rupture limit. They estimated the fissuring mesh, i.e. the average spacing between the fissures, from the calculated stress in the layer on the assumption that the fissures continued to be formed until the stress was reduced below the fracture limit. From the calculation, the mesh size was estimated to be approximately twice the thickness of the coke layer when the rupture took place, and varied from 2 - 5 cm depending on the characteristics of the coal. They concluded that this estimated fissure spacing was in good agreement with the observed range.

Based on the Soule's study [66], further work was carried out by Chagnon and Boyer [69], who developed the model by taking account of the temperature dependence of the Young’s modulus and the creep characteristics of semicoke, and using the temperature curve which approximately corresponded to the carbonisation of dry coal. The
temperature dependence of Young’s modulus was defined by measuring the room temperature Young’s modulus of coke carbonised under various carbonisation temperatures and assuming the Young’s modulus of the plastic coal was zero. The creep coefficient of semicoke used was based on measured values given by Dainton [70]. The results showed that the stress in the semicoke estimated with their improved model was much smaller than that obtained with the original model. Also the pattern of stress development in the vicinity of the wall was different. The stress initially increased passed through a maximum, and then decreased and became negative.

Figure 2.20 State of constrained deformation at different temperature attained by the hottest layer - Drocourt coke, resolidification 505 °C:
A 550 °C; B 575 °C; C 600°C

To determine the optimal heating pattern for formcoke production, Yavorsky et al. [71] developed a mathematical model which allowed them to predict the heating rate and temperature distribution in a briquette during carbonisation. Based on the results derived from the model, they also made an attempt to predict the relative magnitude of the thermal stress. The accuracy of temperature prediction was confirmed by the experimental measurement, and the effect of briquette size and thermal properties on the stress prediction was shown.

The first attempt at a prediction of stress generation in a two dimensional field during carbonisation was made by Konyakhin et al. [72]. In their model, the semicoke layer was considered as sets of rectangular plates and the stress generated in the plates were
calculated as a basic problem in which plates were freely supported round their edges and the stress was generated by a peripheral bending moment (Figure 2.21). However, they gave only a series of mathematical formulations; no numerical results were given.

Maruyama and Yamaguti [73] estimated the thermal stress in a thin coal disk during carbonisation using the Young's modulus measured at the carbonisation temperature and the contraction coefficient during carbonisation. They showed that peaks of thermal stress arose at two points, immediately after resolidification and in the temperature range around 700°C where the coke structure was changing by the dehydrogenation reaction. It seems that these peaks were generated by virtue of the corresponding peaks of the contraction coefficient and the temperature dependence of Young's modulus. It was concluded that the peaks correlated with fissure generation, thus being almost coincident with the mechanism proposed by Chagnon and Boyer [69].

A model which predicts the thermal stress arising during carbonisation and the lump size of products from the whole coke-oven charge was developed by Klose and Knothe [74].
They developed a two dimensional model to take into account the distributions of the heating flue temperature and the bulk density of the coal charge. The thermal stress calculation was based on Kirchhoff's plate theory and when the predicted thermal stress exceeded a breakage strength, they assumed a coke plate broke in half and they then restarted the stress calculation for the smaller plate. The visco-elastic property of semicoke was taken into account by considering the semicoke as a Maxwell body. However, unlike the results of Chagnon and Boyer [69], the predicted stress values of the Maxwell body were larger than those of the elastic body. It was shown that in respect of mean coke size, the prediction by means of the model developed corresponded well to the value measured for pilot [53] and commercial oven cokes.

A new method based on the incremental theory was developed by Fukai et al. [75] to predict thermal stress in the coke layer during carbonisation. The temperature field was calculated during carbonisation, and, based on the temperature change in each time step and the coefficient of contraction, the displacement by contraction was calculated. The thermal stress which arose in the layer was predicted from the strain-displacement and the stress-strain relationships. They showed from the results of experiment and prediction that the thermal stress generated in the coke layer during carbonisation increased as the heating rate increased.

Based on the model developed by Fukai et al. [75], further work was done by Miura et al. [76], who compared the prediction with the x-ray photographs taken throughout the coking process [55]. Their prediction had a good correlation with the experimental phenomena and temperature-dependencies of the thermal properties, the contraction coefficient and the Young's modulus were suggested to be governing factors for thermal stress generation in the coke layer during carbonisation.

Subsequently, based on the behaviour of the fracture mechanics parameter, Yoshino et al. [77] discussed fissure generation in the initial stages of carbonisation. The CTOD (Crack Tip Opening Displacement) was used as the parameter to represent the state in the vicinity of a fissure generated from the coke surface. From the behaviour of CTOD, which increased sharply near the transition point from the first maximum point of contraction coefficient of coke to the second maximum point, temperature at which the fissure on the coke surface initially generated, was suggested (Figure 2.22).
Figure 2.22 Effect of a heating rate on the estimated CTOD

Sato et al. [78] studied the thermal stress in lump coke to elucidate the mechanism of crack generation in lump coke. The stress distribution in the lump coke during carbonisation was calculated by assuming a distance between the fissures which divided coke into lumps and the temperature of the fissure tip when fissure propagation occurs as estimated from the results shown by Yoshino et al. [77], and considering radiative heat transfer within the fissures. From the model, the fissure formation behaviour, for longitudinal cracks, i.e. those generated normal to the oven wall, was successfully estimated. However, the stress considered to cause the transverse fissure, i.e. those generated parallel to oven wall, could not be assessed, since only the compressive stress was predicted by the model.

The model was improved to describe the whole phenomena by taking into account the viscoelasticity of the plastic and the semicoke layers, dilatation of the plastic layer and the pyrolytic reaction dependence of thermophysical properties [79]. By comparison with the measured values of the coke displacement during carbonisation under various heating rates in a laboratory-scale carbonisation furnace, it was shown that the displacement calculated from the dependence of thermophysical properties on the fraction of the pyrolytic reaction was in better agreement with the experimental data than that calculated from the temperature dependence of thermophysical properties as the heating rate increases. The deformation estimated by the viscoelastic model was in better agreement.
with the measured value than that estimated by the elastic model. The results suggested that the effects of heating history and viscoelasticity of semicoke have to be considered for an accurate estimation of the coke deformation behaviour.

Using the modified model, the thermal stress within a coke lump was estimated to investigate the fissure formation behaviour in the coke layer and crack generation in the lump coke [80]. In this study, the fissure propagation was calculated on the basis of the estimated stress intensity factor at the fissure tip and the plane strain fracture toughness. The predicted fissure propagation during carbonisation and the thermal stress arising in the lump coke were in good agreement with the experimental observations made using a laboratory-scale carbonisation furnace.

Since the fracture phenomena during carbonisation is complex, only attempts to predict the mean size of coke have been made. To predict the size and size distribution of products, it is necessary to elucidate further the mechanism of fissure formation in coke during carbonisation.
2.6 PREDICTION OF COKE QUALITY

To optimise the coke production process and to improve the understanding of coal carbonisation, it is important to study coke quality and its prediction. In general, the coke strength indices used in industry have been estimated empirically on the basis of the coal petrography [27, 29]. On the other hand, some basic research which focused on the relation between coal properties and coke structure observed by means of the scanning-electron microscope (SEM) and the polarised-light optical microscope (PLM), and its influence on the coke strength has been conducted [81-89]. In recent years a process simulation model aiming to estimate coke quality from the entire cokemaking process conditions has been developed [90-97].

2.6.1 Coal petrography

A method for coke strength estimation, based on coal petrography has been developed and because of its reasonable accuracy, the method has been widely used in the industry sometimes with minor modification. The application of coal petrography for coke strength prediction was originally developed by Schapiro [29], who estimated the stability factor of coke by the tumbler test from its dependence on a ratio between the reactive and the inert petrographic components in the coal. This method has also been applied to a prediction of the drum index used in the Japanese steel industry [27]. The coke strength was determined from the relation between the coke strength index and two parameters, the composition-balance index and the rank index (also referred to as the strength index). To determine the composition-balance index, the percentage of inerts present in the coal is divided by the optimum percentage of inerts for the best coke strength

\[
Composition\ balance\ index = \frac{100 - \sum x_i}{x_3/a_3 + x_4/a_4 + \cdots + x_21/a_{21}} \tag{2.8}
\]
where \( x_i \) is a fraction of vitrinoi type \( i \) and \( a_3 \cdots a_{21} \) is an optimum inerts ratio for each vitrinoi types. The rank index is calculated from the relationship of the optimum coke strength for a given rank to the inert entities in the coal

\[
\text{Rank index} = \frac{b_3 x_3 + b_4 x_4 + \cdots + b_{21} x_{21}}{\sum x_i}
\]  

(2.9)

where \( b_3 \cdots b_{21} \) is coefficients for each vitrinoi types. By drawing isostability lines based on actual coke tests (Figure 2.23), the coke strength was predicted from the composition-balance index and the rank index.

![Figure 2.23 Composition-balance index, rank index and empirically determined isostability lines](image)

2.6.2 Prediction from the structure of coke

Based on the assumption, that the tensile strength of the fissure free coke material made from a blend of coals is dependent only on the strength of the bonding between regions of
coke derived from the parent coal, Merrick [81] proposed a mathematical model to predict the coke strength from a blend of coals. The overall coke strength $B$ was estimated from

$$B = \sum_{i=1}^{n} \sum_{j=1}^{n} w_i w_j B_{ij}$$  \hspace{1cm} (2.10)$$

where $w_i$, $w_j$ are mass fractions of $i$ and $j$ coals, $B_{ij}$ is the strength of ‘$i$-$j$’ bond. It was shown that the bond strength can be determined from a limited number of tests on binary blends, and can be used to estimate the strength of an arbitrary blend containing several components.

From the observation of fractured surfaces of metallurgical coke by scanning electron microscopy (SEM), which showed the mode of fracture varied in the different textural components [59], the relation between the carbon texture and the tensile strength measured by the diametral compression method was examined [82]. The composition of the coke carbon was measured by applying a point-counting technique to the examination of atomic-oxygen etched surfaces. It was reported that the strength and the textural composition could be related by a single equation derived by the multi-linear regression analysis as follows

$$S=23.4+0.25II+0.37Is+0.34F+0.25Ln+0.33Lf+0.37In+0.30ln+0.16Gc$$ $$+0.28Gm+0.25Gf+0.26Gvf$$  \hspace{1cm} (2.11)$$

where $S$ is a coke tensile strength and $II$, $Is$ etc. are the percentage of the various textural components indicated in Table 2.4.

To expand this method to a multi-component blend, Hays et al. [83] defined the fractional content of the $i$th textural component in the coke from a blend charge $T_i$ by the equation

$$T_i = \frac{\sum_{k=1}^{9} T_{i,k} F_k C_k}{\sum_{k=1}^{9} \sum_{i=1}^{n} T_{i,k} F_k C_k}$$  \hspace{1cm} (2.12)$$
where $T_{ik}$ is the fractional content of the $i$th textural component in the $k$th single-coal coke, $F_k$ is the fractional content of the $k$th coal in the blend and $C_k$ is a correction factor for the $k$th coal. It was shown that from the correlation between the defined $T_i$ and the tensile strength of coke from a blended charge, this approach gave a reasonable prediction.

Table 2.4 Classification of textural components

<table>
<thead>
<tr>
<th>Component type</th>
<th>Flat (F)</th>
<th>Lamellar</th>
<th>Intermediate</th>
<th>Granular</th>
<th>Inerts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Normal (Ln)</td>
<td>Flat (Lf)</td>
<td>Normal (In)</td>
<td>Coarse (Gc)</td>
<td>Large (II)</td>
</tr>
<tr>
<td></td>
<td>Flat (If)</td>
<td>Intermediate</td>
<td>Fine (Gf)</td>
<td>Medium (Gm)</td>
<td>Medium (Gm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Granular</td>
<td>Very fine (Gvf)</td>
<td>Fine (Gf)</td>
<td>Very fine (Gvf)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Large (II)</td>
<td>Fine (Gf)</td>
<td>Small (Is)</td>
</tr>
</tbody>
</table>

The approach, which estimates coke strength from textural data, was modified by taking into account the fracture mechanism in the estimation model which used the textural data by the scanning-electron microscope (SEM) [84] and by the polarised-light optical microscope (PLM) [85]. The two fracture modes, intergranular and transgranular, were considered. For intergranular fracture, the coke strength was represented by

$$S = \sum_{i=1}^{9} \sum_{k=1}^{9} F_i F_k S_{i,k}$$

(2.13)

where $F_i$ and $F_k$ are fractional textural contents of the $i$th and $k$th components and $S_{i,k}$ is the intercomponent strength. In the case of transgranular fracture, the coke strength is dependent upon the probability of occurrence of the various textural components in a layer and their strength. Then the strength was given by
where $F_i$ has the same meaning as before and $S_i$ is the transgranular failure strength of a single-component coke. It was concluded that by comparing the results of a standard error of estimations for both mechanisms, the transgranular fracture was indicated as the more probable mode of coke breakage.

These two fracture mechanisms were applied to the blend composition to predict the coke strength from the measured strength of individual blend components [86]. The equations (2.13) and (2.14) were modified to the equations as follows

\[ S = \sum_{i=1}^{n} F_i S_i \]  \hspace{1cm} (2.14)

\[ S = \sum S_{ik} C_i C_k \]  \hspace{1cm} (2.15)

\[ S = \sum S_i C_i \]  \hspace{1cm} (2.16)

where $S_{ik}$ is the strength of the interface between coke components from coal $i$ and $k$, and $S_i$ is the transgranular strength of components from coal $i$. It was suggested that with regard to the coke made in industry where the coal size is relatively large and hence interaction between coal particles is limited, the tensile strength was additively dependent upon the cokes from the individual coals.

Further study has been made by paying attention to the interfaces between the different textural components in the cokes [87]. The interfaces were observed by polarised-light microscopy and classified into four categories, termed transitional, fused, fissured and unfused. Because little evidence of fissuring was detected at the interface, transitional and fused interfaces were regarded as 'good' interfaces and other two were categorised 'poor' interfaces. To convert interface counting data into a parameter, based on the classification, a quality index, $Q$, was defined as

\[ Q = \frac{(T + Fu)}{(Fi + U)} \]  \hspace{1cm} (2.17)

where $T$, $Fu$, $Fi$ and $U$ are the observed percentages of transitional, fused, fissured and unfused interfaces, respectively. However, no clear relation between the interface quality index and the coke tensile strength was observed.
The cohesive condition of two kinds of coal particles was investigated by Aramaki et al. [88] who made an attempt to estimate the strength of coke made from a multi-blended charge from the point of view of the cohesive state between the two coal blend. It was shown that the contact condition of the coal particles depended on maximum fluidity of the test blend, MF, and the difference in the solidification temperature between the two coal blends, ΔST. From this relation, it was suggested that a small ΔST is the necessary condition for good cohesive contact and in case of a large ΔST, a larger MF is required to obtain a good cohesive contact. Based on this study, they developed a mathematical model to estimate the structural strength of coke across the oven width which takes into consideration the effect of the heating rate through the plastic stage [89].

2.6.3 Process simulation model

Recent improvements in computer performance has been promoting the wide development of process simulation in various industrial processes to optimise the operation. An attempt to develop a simulation model of the cokemaking process was made by Merrick et al. [81, 90-94], who constructed a model on the basis of studies of heat and mass transfer in the coke oven and thermophysical properties of coal and coke during carbonisation. Although a model for coke strength prediction was also proposed (see above), the model was not combined with the heat transfer model. Therefore, no prediction of coke strength from the operating conditions was possible using their model. A process simulation model, which predicts all the necessary information regarding coal carbonisation, from temperature to coke quality distribution, by taking into consideration all possible operating conditions (Figure 2.24), was constructed by Nishioka et al. [28, 95, 96]. In their model, heat transfer across the oven width was calculated by the one-dimensional heat conduction model and by introducing a mass transfer model for the dilatation period (Figure 2.25), the coke porosity and quality distribution across the oven width was successfully predicted.

The evaluation of the coke tensile strength was made based on the following strength-porosity relationship for porous materials:

\[ \sigma = \sigma_0 \exp(-cP) \] (2.18)
where $\sigma_0$ is the pore-free strength and $P$ is porosity. The micro strength was introduced to represent a pore-free strength on the basis of the relation shown in Figure 2.26, thus the strength was predicted by

$$\sigma = (11.4Ml - 114) \exp(-4.2P)$$  \hspace{1cm} (2.19)

where $Ml$ is the micro strength.

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### Figure 2.24 Construction of the simulation model

![Construction of the simulation model](image)

---

### Figure 2.25 Transfer model of melting materials in coal

![Transfer model of melting materials in coal](image)
Figure 2.26 Relationship between porosity, micro-strength and tensile strength of various cokes

To establish the dependence of coke strength on operating conditions, the relation between the micro strength and, coal rank and carbonisation temperature was investigated. The following relation between the micro strength and, the mean reflectance of the coal, $R_0$, and the carbonisation temperature, $T$, was obtained.

$$M_{165} = -0.91(R_0 - 1.16)^2 + 6.28 \times 10^{-2}(T - 1000) + 55$$ (2.20)

By using the relationship (Equation 2.21) between the tensile strength of coke and the quality index used in the operation, namely the drum index, DI, it is possible to predict the drum index from the operating conditions by substituting Equations (2.19) and (2.20) into Equation (2.21).

$$DI_{15}^{30} = 100 \exp(-0.81\sigma^{-0.5})$$ (2.21)
Although the quality prediction is restricted to indices which are not governed by the
degree of fissuring, they concluded that it is possible to apply this approach to other
indices used in industry.

Igawa et al. [97] proposed a simulation model which could predict not only coke quality
but also tar quality. In their model, coke quality, in this case the tumbler index, TI, was
estimated from porosity Por and the abrasion index of the coke pore wall Pai. Each
parameter could be estimated from the heating rate, CR, maximum fluidity of coal, MF,
and mean reflectance of coal, $\overline{R_o}$ as shown in Equations (2.23) and (2.24). The tumbler
index could be then be estimated from Equation (2.22).

\begin{align*}
TI &= a_1Pai + a_2Por + a \\
\text{Pai} &= a_4 \rho (a_5CR + a_6) + a_7MF + a_8\left(a_9\overline{R_o}^2 + a_{10}\overline{R_o} + a_{11}\right) + a_{12}\text{CR} + a_{13} \\
\text{Por} &= a_{14} \rho (a_{15}\text{CR} + a_{16}) + a_{17}\text{MF} + a_{18}\left(a_{19}\overline{R_o}^2 + a_{20}\overline{R_o} + a_{21}\right) + a_{22}\text{CR} + a_{23}
\end{align*}

(2.22)

(2.23)

(2.24)
2.7 OUTLINE OF THE RESEARCH

Since fissure formation phenomena has a significant influence on coke quality, considerable attempts have been made to understand fissuring and coke strength as reviewed in this chapter. However, due to the complexity of the phenomena, the total amount of research carried out is relatively small when compared to studies related to other aspect of the coke making process and so the understanding of the mechanism of fissuring is still limited.

Nevertheless, practical studies seeking to identify factors which influence the degree of fissuring in coke have been carried out. Based on the basic knowledge obtained from these studies, operating conditions in industry have been improved by adjusting the coal blend, the particle size of the charge, the carbonisation temperature etc. Although an improved understanding of the coking phenomena and a process simulation model developed on the basis of this understanding allows operators to predict the quality of coke, such as the Micum Index, from operating conditions, only a tentative mean coke size prediction has presently been performed. To develop an advanced model which permits the prediction not only of the mean size but also the size distribution of coke as well as coke strength, further study in this field is needed.

The objectives of these studies should be to improve the understanding of the fissure formation mechanism during carbonisation, to develop means for the estimation of the degree of fissuring in coke, and finally to estimate the mean coke size and size distribution after impact. To achieve these objectives, firstly coke strength development during carbonisation should be addressed since this is one of the most important factors in the fissure formation phenomena.

The strength of coke has been discussed mainly with regard to the final product and few studies have been concerned with the development of coke strength during carbonisation. Previous studies in relation to strength development showed that the strength develops as the carbonisation temperature increases. However, to define the phenomena more strictly, the development of coke strength should be considered in relation to the change in coke structure during the thermal decomposition reaction.

In this study to seek an alternative parameter for precisely describing the phenomena, coke made under various heating conditions and final carbonisation temperatures was
examined. The tensile strength of coke was measured by the diametral compression test and the development of coke matrix strength during carbonisation was assessed after separating three factors, porosity, porous structure and strength of coke matrix which influence the tensile strength, using an empirical formula, which relates the tensile strength and porosity. The change in coke structure during carbonisation was represented by the improved degree of graphitisation, the change in chemical composition of the coke and the true density in relation to the degree of the pyrolysis reaction and the carbonisation temperature.

The influence of temperature history on coke strength development in a commercial coke oven was shown by combining a model for the thermal decomposition reaction during carbonisation and a heat transfer model for a commercial coke oven. Furthermore, the effect of coal rank on the phenomena was investigated by examining cokes from coals of various rank and an attempt was made to find a parameter which governs the strength development phenomena and is applicable to coals of a wide rank range.

Based on the improved understanding of the development of coke strength during carbonisation gained in these experiments, an attempt was made to understand the degree of fissuring observed in cokes made using a laboratory-scale carbonisation furnace under various carbonisation conditions. A tentative model for strength development and thermal stress estimation was developed to understand the mechanism of fissuring during carbonisation. The results observed from the coke with regard to the degree of fissuring are discussed on the basis of the relationship between the estimated strength and stress throughout the carbonisation period.
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3 EVALUATION OF COKE STRENGTH

In the coke oven, coal is carbonised from the oven wall towards the oven centre. Due to shrinkage of the semicoke caused by the thermal decomposition reactions and the consequent structural change in the coke carbon matrix, thermal stress is generated during carbonisation. Principal fissures, which divide the coke cake into lumps, propagate from the oven wall towards the oven centre when the thermal stress generated exceeds the coke strength. Until now, because of the small amount of data available for properties related to fracture mechanics and the strength of cokes, fracture in a coke layer has been mainly discussed on the basis of the development of thermal stress in the coke layer and the available coke strength measured at about 1000 °C [1-4] or an appropriate assumption [5].

However, since the coke strength develops during carbonisation in conjunction with the thermal stress generation, it is necessary to take into account the effect of coke strength development to understand the behaviour fully and to accurately estimate the degree of fissuring.

Furthermore, evaluation of the strength of coke in terms of its porous structure is also important to understand the fissuring mechanism. Since the tensile strength determined by means of the diametral compression test is affected by many factors, such as porous nature, matrix strength and porosity, these factors should be evaluated simultaneously to clarify the effect of each factor and to find a relation between these factors and carbonisation conditions.

In addition, Young’s modulus is also determined by using the data derived from the tensile strength determination. Relations were also sought between the modulus and the factors which influence coke strength.

This chapter describes experimental studies designed to investigate these relationships, to understand the mechanism further and to utilise the knowledge obtained to a mathematical model constructed in the next chapter.
3.1 EXPERIMENTAL

Coke samples were produced to determine the tensile strength of coke made under various heating conditions from a wide range of coals. The general procedures for the coke sample preparation and the measurements made are described in this section. Additional arrangements for each objective will be given in each section.

3.1.1 Coke samples

3.1.1.1 Laboratory scale coke oven

To make a coke sample, carbonised under similar carbonisation condition as a commercial coke oven but also reasonably small so as to prevent property variations in the coke lump, the coal charge was carbonised in a laboratory-scale, test oven heated from two side walls. A charge box, made from steel and insulating-board, sized 160 mm long, 100 mm wide and 100 mm high, was packed (Figure 3.1) with air-dried coal sized less than 3 mm at a charge density of 800 kg/m³. A thermocouple was placed at the centre of the half oven width to measure the average final carbonisation temperature.
The furnace was pre-heated to 200 °C and heated at constant heating rate of 3 °C /min after installing the charge box. To prevent combustion of the coke during carbonisation, especially in the soaking period when generation of pyrolysis gas had decreased, nitrogen was passed through the furnace. After the temperature of charge reached the designed temperature, the charge box was taken out and quenched immediately by means of water.

3.1.1.2 Coal used
The properties of the five coals used are listed in Table 3.1. To permit discussion of the effect of coal rank on strength development during carbonisation and of coking properties on the quality of the coke porous structure, they include coals of a wide rank range with volatile matter content from 20 wt% to 38.9 wt% (db). In this study, coal-D was used as a base coal sample to study strength development under various heating condition and to make clear the effect of heating history on the strength development. All coals were used for the following studies on tensile strength and effective Young’s modulus evaluation.

Table 3.1 Properties of coal

<table>
<thead>
<tr>
<th>Coal</th>
<th>VM wt%db</th>
<th>VM wt% dmmf</th>
<th>Ash wt%db</th>
<th>Fixed C wt%db</th>
<th>Sw.No.</th>
<th>Max. Fluidity log ddpm</th>
<th>Gray-King coke type</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20.0</td>
<td>21.1</td>
<td>5.0</td>
<td>75.0</td>
<td>8.0</td>
<td>2.93</td>
<td>G9</td>
</tr>
<tr>
<td>B</td>
<td>26.6</td>
<td>28.4</td>
<td>6.3</td>
<td>67.1</td>
<td>8.0</td>
<td>4.09</td>
<td>G9</td>
</tr>
<tr>
<td>C</td>
<td>29.4</td>
<td>38.7</td>
<td>21.2</td>
<td>49.4</td>
<td>2.5</td>
<td>1.54</td>
<td>C</td>
</tr>
<tr>
<td>D</td>
<td>35.9</td>
<td>37.2</td>
<td>5.0</td>
<td>59.1</td>
<td>7.5</td>
<td>2.78</td>
<td>G5</td>
</tr>
<tr>
<td>E</td>
<td>38.9</td>
<td>41.6</td>
<td>5.3</td>
<td>55.8</td>
<td>4.5</td>
<td>3.11</td>
<td>G6</td>
</tr>
</tbody>
</table>

3.1.1.3 Carbonisation conditions
Cokes were carbonised at 3 °C/min to final temperatures of 600, 800 and 1000 °C, measured at the centre of the half oven width for all coals (Figure 3.1). With regard to the base coal, coal-D, two heating conditions, with either no soaking or with one hour soaking time to produce coke samples which were carbonised to the same final temperature but with different degrees of carbonisation, were used to investigate the effect of the degree of carbonisation on coke strength. To eliminate the effect of heating rate on the fluidity of the plastic stage of coal, and consequently on the porous structure of coke, every coke made was carbonised under the same heating conditions at least until
the temperature of the coke centre exceeded the resolidification temperature. The carbonisation conditions for coal-D are summarised in Table 3.2.

The additional coke samples produced to examine the effect of the rank and coking properties of the coal were made using coals-A, B, C and E under the same carbonisation conditions as Coal-D but with zero soaking time condition (Table 3.2).

### Table 3.2 Carbonisation condition for coal-D

<table>
<thead>
<tr>
<th>No.</th>
<th>Final temperature [°C]</th>
<th>Heating rate * [°C/min]</th>
<th>Soaking time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

* Heating rate of furnace

### 3.1.2 Coke property analysis

#### 3.1.2.1 Tensile strength

Tensile strength of coke samples was determined using the diametral compression test [6]. Test specimens for each sample were obtained by drilling, using a diamond-tipped core drill, 10 mm diameter cylindrical cores. The cores were drilled in a direction normal to the oven heat flow and at a position approximately midway between the wall and oven centre. Using a diamond-impregnated cutting wheel, discs about 7 mm thick were sliced off these cores. The specimens obtained were cleaned ultrasonically, dried at 100 °C overnight and 30 suitable disc specimens from each sample were selected for testing.

In the diametral compression, a compressive load is applied across one diameter of the test piece and fracture takes place along this diameter caused by a tensile stress generated at right angles to it. The load was applied using an Instron universal testing machine operating at a cross-head speed of 0.5 mm/min. The relation between the applied load \( W \) and the tensile stress \( P \) is given by
\[ P = \frac{2W}{\pi Dt} \]  

(3.1)

where \( D \) and \( t \) are the diameter and thickness of the disc respectively. Using the above equation, the tensile strength of each sample were determined by averaging the individual results from the 30 specimens.

3.1.2.2 Fraction of pyrolysis reaction

To describe the development of coke strength precisely, a parameter based on the degree of carbonisation is required. Coke properties change during carbonisation because of thermal decomposition reactions and so to characterise the extent of carbonisation, the “fraction of pyrolysis reaction” was introduced. The fraction of reaction, \( v \), is defined as

\[ v = \frac{w}{W} \times 100 \]  

(3.2)

where \( W \) and \( w \) are respectively the total percentage weight loss on carbonisation to 1000 °C and the percentage weight loss after carbonising under less severe conditions of temperature or time. Both weight losses were obtained by means of a thermobalance. The total percentage weight loss of coal, \( W \), was defined by measuring the weight loss after carbonising coal at a heating rate of 10 °C/min and holding for two hours at 1000 °C. The percentage weight loss under other carbonisation conditions, \( w \), was calculated from the total % weight loss \( W \) of the coal at 1000 °C and the % weight loss of fractured coke pieces, after tensile test breakage on being reheated at 10 °C/min and holding for two hours at 1000 °C.

3.1.2.3 Coke carbon structure

In order to evaluate the structure of coke made under various carbonisation conditions, the technique of X-ray diffraction was employed. X-ray diffraction can provide information about the atomic arrangement of materials based on the principle of interference of diffracted X-rays. As a consequence of cancellation by interference only the intensity of the diffraction in the direction which satisfy following Bragg’s law is detected:
2d \sin \theta = n\lambda \tag{3.3}

where \( d \) is the interlayer spacing, \( \theta \) is the Bragg angle, \( n \) is the order of diffraction, which is commonly of value 1 for interlayer spacing \( d \) determination and \( \lambda \) is the X-ray wavelength. Consequently, using the equation the interlayer spacing of material can be determined. Furthermore, by measuring the amount of broadening (\( \beta \)) at the half the peak height of the (002) and (100) diffraction peaks, the crystalline stack height (\( L_C \)) and width (\( L_A \)) can be estimated from following equation [7]

\[
t = \frac{\kappa \lambda}{\beta \cos \theta} \tag{3.4}
\]

where value \( t \) can be the crystalline stack height (\( L_C \)) and width (\( L_A \)) by using the values for \( \kappa \) of 0.9 and 1.84, respectively [8].

### 3.1.2.4 Porous structure

The porous structure of the coke was observed by means of image analysis using incident light microscopy. Samples for the image analysis were obtained by mounting the fractured coke samples from the tensile strength test in a block of resin and preparing as polished sections. The porous structure of each sample was determined by examining more than 300 fields, 1.2 mm \( \times \) 1.26 mm, from approximately 20 specimens for each sample. Since the larger pores were of most interest, a low power objective lens, magnification \( \times 4 \), was used to give a pixel size 3.3 \( \times \) 2.9 \( \mu \)m and very small pores under 12 \( \mu \)m were eliminated by image processing (erosion followed by a dilation). The image analysis system was programmed to give measurements of the number, length, breadth, circularity and orientation of pores.

### 3.1.2.5 Other properties

To determine porosity of coke samples, their apparent density and specific gravity were measured. Apparent density was obtained from measurements of size and weight of the specimens used for tensile strength determination, and specific gravity was measured by
means of a helium pycnometer using mis-shaped disc specimens, after crushing. The chemical composition of samples carbonised under various conditions was determined by means of an element analyser capable of measuring the C, H and N content.
3.2 DEVELOPMENT OF COKE STRENGTH DURING CARBONISATION AND THE EFFECT OF TEMPERATURE HISTORY

It is acknowledged that the strength of coke improves with carbonisation temperature [9, 10]. However, coke strength parameters have been measured mainly with regard to the final product, that is, the coke carbonised at about 1000 °C. Even for such coke samples, few mechanical strength parameters are available [6], apart from strength indices derived from empirical industrial tests.

Furthermore, as other properties of coal and coke during carbonisation have been reported to depend not only on the carbonisation temperature but also on other heat treatment factors such as a heating rate, it is assumed that the carbonisation temperature is only one of the parameters which affect strength development during carbonisation.

With regard to the fissuring mechanism, mathematical simulation of the deformation of a coke layer has been successfully performed by taking account of the effect of temperature history using thermophysical properties based on the thermal decomposition reaction [11]. But this effect has not been fully taken into account in the elucidation of the mechanism of fissure formation in coke.

This study was made, therefore, to examine the relationship between coke strength development during carbonisation and the extent of the carbonisation, or the fraction of pyrolytic reaction, as well as carbonisation temperature, under different carbonisation conditions. Coke carbon structural changes during carbonisation were assessed with regard to chemical composition and crystallinity.

On the basis of the relationship obtained for the strength development, the effect of temperature history on the strength development during carbonisation in the commercial coke oven was evaluated by means of mathematical modelling.

3.2.1 Experimental

Coke samples were made from coal-D by means of the laboratory scale test oven described previously. Cokes were carbonised at 3 °C/min to final temperatures of 600, 800 and 1000 °C, measured at the centre of the half oven width, with either no soaking or
with one hour soaking time to make coke samples which had been carbonised to the same final temperature but to different degrees of carbonisation.

The tensile strength of the coke samples was determined using the diametral compression test [6]. The fraction of pyrolysis reaction and the crystallite stack height of the coke carbon matrix, which were defined in the previous section, as well as the chemical composition, C, H and N, of the coke samples were used to discuss the strength development during carbonisation.

3.2.2 Results and discussion

3.2.2.1 Development of strength during carbonisation

A summary of the results obtained is given in Table 3.3. Differences in the data are indicative of the effect of the heating conditions, but as regards the tensile strength of the coke, it is difficult to assess directly the effect of heating conditions from the results, because they are also influenced by any variations in apparent density and in the porosity. Consequently, it is necessary to eliminate these effects in order to ascertain how the development of the strength of the coke carbon material is influenced by the heating conditions.

| Table 3.3 Summary of coke strength and structural data for cokes from coal-D |
|------------------|---|---|---|---|---|---|
|                  | 1  | 2  | 3  | 4  | 5  | 6  |
| Final temperature | 1000 | 1000 | 800 | 800 | 600 | 600 |
| Soaking time      | 1  | 0  | 1  | 0  | 1  | 0  |
| Apparent density  | 939 | 863 | 893 | 887 | 780 | 729 |
| True density      | 1934 | 1949 | 1964 | 1870 | 1668 | 1584 |
| Fractional volume porosity | 0.51 | 0.56 | 0.55 | 0.53 | 0.53 | 0.54 |
| Tensile strength  | 6.3 | 5.0 | 5.1 | 4.1 | 3.2 | 2.3 |
| Standard deviation | 1.01 | 0.99 | 1.13 | 0.84 | 0.80 | 0.66 |
| Strength of matrix | 101.3 | 99.5 | 96.1 | 70.3 | 56.4 | 41.4 |
| Fraction of reaction | 97.5 | 96.5 | 95.7 | 92.1 | 88.3 | 85.1 |
| Crystalline stack height | 13.7 | 13.6 | 11.5 | 10.5 | 9.4 | 9.3 |

To eliminate the effect of porosity, the strength of the coke matrix was estimated using an empirical formula for porous materials, which relates strength and porosity, as follows [12]
where $\sigma$ and $\sigma_0$ are respectively the tensile strength of the porous material and the matrix material, $P$ is the volume porosity and $c$ is a porous structure coefficient which represents the porous structure of the material. Although this equation is an empirical equation and there is no strict physical meaning, the porous structure coefficient $c$ has been related to the shape of pores [13, 14] and to the pore size distribution [15].

The porous structure coefficient $c$ was determined by statistical regression using data from all the samples, by assuming that the porous structure e.g. pore size and shape but not the volume porosity had a similar effect for all the samples. The assumption was made on the basis that the samples were prepared under the same heating conditions apart from final temperature and soaking time, and so the heating conditions during the plastic stage of the carbonisation process, the stage which governs the pore structure development [16], was considered to be identical throughout. Accordingly, the strength of the coke matrix for each heating condition and the porous structure coefficient $c$ were determined from Equation (3.5).

![Figure 3.2](image-url)  

**Figure 3.2** Relation between carbonisation temperature and strength of the coke carbon matrix

*Figure 3.2* shows the relationship between the carbonisation temperature and the estimated strength of the coke matrix. As a whole, the strength of the coke carbon matrix
improves as the carbonisation temperature increases. There is a good correlation between the carbonisation temperature and the development of the coke matrix strength for the cokes prepared with no soaking time at the final temperature. This is in agreement with the general understanding of the coke strength development [9, 10]. However, considerable improvements in the strength of the coke carbon matrix were observed in the cases of soaking at the final carbonisation temperatures of 600 and 800 °C. It is well known that heating conditions influence many coal coking properties such as dilatation [17], the softening temperature and the resolidification temperature [18] and the development of the strength of coke carbon matrix is similarly influenced.

This leads to the conclusion that the coke matrix strength develops even during soaking at a constant temperature and thus the explanation of the strength development by carbonisation temperature only is insufficient if other carbonisation conditions differ.

In order to take into consideration these effects in estimating the strength development during carbonisation, a parameter, which can represent the effect of the heating conditions in their entirety, is necessary. For this purpose, the fraction of the pyrolysis reaction defined earlier was used as the required parameter, so that the effect of arbitrary heating conditions, namely the temperature history, can be taken into consideration.

![Figure 3.3 Relation between fraction of reaction and strength of the coke carbon matrix](image-url)
As shown in Figure 3.3, the fraction of the pyrolysis reaction parameter correlates well with the strength of the coke matrix, especially so in comparison with the relation using carbonisation temperature as the parameter (Figure 3.2). It is concluded that the fraction of reaction is clearly better than the carbonisation temperature as a means of assessing the development of coke strength. This is because the fraction of reaction is based on much more fundamental carbonisation phenomena and therefore as long as the prediction of the progress of the pyrolysis reaction is reasonably accurate, it is possible to estimate the property changes during carbonisation under different heating conditions.

Figures 3.4, 3.5 show the changes in the chemical composition, H/C, and the crystallite size, stack height $L_c$, during carbonisation, respectively. As the pyrolysis reaction progresses, the hydrogen content decreases and as a result the ratio of hydrogen to carbon in the coke matrix decreases continuously in the latter half of the thermal decomposition reaction. This hydrogen release causes a reordering of the carbon structure [18] leading to a more graphite-like structure, which is indicated by the increase in a size of the crystallite stack height shown in Figure 3.5.

It is apparent that the chemical composition and the carbon structure govern the physical properties of the coke matrix. Therefore, the strength of the coke matrix develops during carbonisation as the pyrolysis reaction progresses. Since the pyrolysis reaction strongly depends on heating conditions [17] and these are unlikely to be constant in the commercial coking process, the carbon structure can be different for coke formed at the same temperature. This effect might cause a significant error in estimating fissuring, since a fissure generates when the generating stress exceeds the developing strength. To describe carbonisation strictly as regards changes in physical properties, it is necessary to take into consideration the effect of heating conditions. Although the carbonisation temperature is a reasonable parameter when other heating conditions are constant, it can cause a considerable error when the heating conditions are irregular as shown in Figure 3.2. On the other hand, the parameter introduced in this study provides the means of describing the phenomenon more precisely on the basis of the reactions which cause structural change in the coke carbon matrix.
3.2.2.2 Effect of temperature history on coke strength development

In the commercial coke oven the heating rate varies across the oven width and hence the temperature history of the coke varies. An estimation of the possible difference in the coke strength development during carbonisation in a commercial coke oven caused by this difference in temperature history is significant since the strength developing factors

Figure 3.4 Relation between H/C of coke carbon and fraction of reaction

Figure 3.5 Relation between crystallite stack height of coke carbon and fraction of reaction
affect both final coke quality and fissure formation, i.e., the size distribution of the product. Therefore, a mathematical model was developed to evaluate the effect of temperature history on the coke strength development in a commercial oven.

The temperature field in a commercial coke oven, for an oven width of 460 mm and a wall thickness of 100 mm, was estimated as a one dimensional non-steady state heat conduction problem. Although the effect of radiation heat transfer in a fissure is considerable with regard to total coking time [5], a simple model, which is capable of predicting a typical heating pattern in a commercial oven was chosen in this study. Initial conditions for the oven wall and the coal charged are 1200 and 60 °C, respectively. The flue temperature was assumed to be constant at 1200 °C through the coking period and gives the boundary condition at the flue side wall surface. The thermal conductivity and thermal diffusivity were estimated by empirical formulae which take account of the effects of the heat of reaction during carbonisation and depend on the carbonisation temperature [19, 20]. The calculation starts from the temperature field and then the pyrolysis reaction is calculated in each time step.

The fraction of the coal thermal decomposition reaction was estimated using the Arrhenius type gas generation rate parameters, for the pyrolysis gas species \( H_2, CO, CO_2, CH_4, C_2H_4, H_2O \) and tar [21]. The fraction of reaction \( \nu(\theta) \) under an arbitrary heating condition at temperature \( \theta \) was defined as

\[
\nu(\theta) = \frac{\sum W_i \int \left( \frac{d\nu_i(\theta)}{dt} \right) dt}{\sum W_i^*} \times 100
\]  

(3.6)

where \( W_i^* \) and \( \nu_i \) represent the total mass of gas generated and the fraction of reaction for the \( i \) th gas species, respectively. Thus the properties were determined by the fraction of reaction obtained from Equation (3.6).

Figure 3.6 compares the estimated fraction of pyrolysis reaction under various constant heating rates with the fraction of reaction measured thermogravimetrically. Due to the relatively low heating rate, 2.5 and 5 °C/min, in the experimental conditions for the gas releasing rate parameter determination [21], differences between the measured and estimated values tend to increase as the heating rate increases. Nevertheless, the model
estimates the effect of heating conditions reasonably well and hence it was considered possible to evaluate the effect of temperature history in the commercial coke oven using this gas generation model.

![Figure 3.6 Effect of heating rate on pyrolysis reaction](image)

![Figure 3.7 Relation between strength of coke matrix development and fraction of reaction](image)
The development of the strength of the coke matrix was estimated on the basis of the calculated history of the fraction of reaction during carbonisation and the relation between fraction of reaction and strength of the coke matrix (Figure 3.7). This relationship for the strength of the coke matrix development was derived from the estimated strength of the coke matrix shown previously in Figure 3.3 and the estimated fraction of reaction at the resolidification temperature, and assuming the strength development takes place from the resolidification point.

![Figure 3.8 Estimated temperature history across oven width](image)

**Figure 3.8** Estimated temperature history across oven width

*Figure 3.8* shows the estimated temperature history in the coke oven from the oven wall to the oven centre. The different lines represent non-dimensional fractional distances from the oven wall. By using the effective thermophysical properties, which take account of the effects of the change in state from a packed bed to a porous material through a plastic stage, the heat of reaction, the porous structure and the carbon structure change, the model is capable of simulating a typical temperature history measured in the commercial coke oven [18]. The overall heating rate tends to be faster at the heated wall side and becomes slower towards the oven centre. Even at the same position in the oven width direction, the heating rate is never constant and changes significantly during carbonisation. At the plastic stage temperature range of around 300 to 500 °C, the heating rate was estimated to vary from more than 10 °C/min at the vicinity of the oven wall to
around 2 °C/min near the oven centre. This suggests that a temperature dependence of the strength development during carbonisation measured at a constant heating rate of around 3 °C/min could result in considerable error when applied to the case of the commercial coke oven.

Because of this temperature history difference, the extent of the progress of the pyrolysis reaction, the fraction of reaction, at the same temperature was estimated to be different at each position across the oven width as shown in Figure 3.9. Because of the rather complicated temperature history across the oven width, the estimated relationship between the fraction of reaction and the carbonisation temperature is complex since the trends vary according to position. Nevertheless, the progress of the pyrolysis reaction tends to be delayed in relation to the carbonisation temperature at the "near wall" and "oven centre" positions where the heating rate is relatively high.

![Figure 3.9 Effect of temperature history on pyrolysis reaction](image)

To evaluate the effect of temperature history on the coke strength development during carbonisation, the strength of the matrix was converted using Equation (3.5) to the tensile strength of porous coke at a constant fractional porosity of 0.55 across the oven width. As shown in Figure 3.10, the estimated tensile strength differs across the oven width at the same temperature due to the difference in the extent of the pyrolysis reaction.
The difference was estimated to be up to approximately 2 MPa during carbonisation. This difference has usually been neglected in estimations of the strength development based on the carbonisation temperature. Since the tensile strength of a wide range of cokes rarely differs by more than 2 MPa [22] and fissuring is considered to occur simultaneously with strength development, this tensile strength difference caused by the difference in the temperature history could exert a significant effect on the phenomena of fissure generation. Therefore, it is suggested that the difference in temperature history across the oven width has a significant effect on the strength development in addition to that of the porosity difference across the oven width [6].

![Figure 3.10 Effect of temperature history on development of coke tensile strength](image)

Figure 3.10 Effect of temperature history on development of coke tensile strength
3 EVALUATION OF COKE STRENGTH

3.3 EFFECT OF COAL PROPERTIES AND POROUS STRUCTURE ON TENSILE STRENGTH OF METALLURGICAL COKE

Since coke is a brittle material, the tensile strength of coke has been studied mainly to evaluate the mechanical strength of coke in terms of its porous nature [6, 23, 24]. To evaluate and discuss the nature of the strength of a porous material, it is necessary to take into consideration the effect of the porosity and to separate the effects of the matrix strength and the porous nature. It was previously reported that a qualitative evaluation of the coke matrix strength was possible by using empirical equations which explained the tensile strength in terms of the matrix strength and porosity [25]. Amongst the various equations used, that based on the results of Ryshkewitch [26] and examined by Knudsen [12] has been widely applied to many studies of the strength of porous materials since the equation separates the effect of porous structure from the tensile strength as well as the effects of matrix strength and porosity (Equation 3.5)).

Some studies have used the equation to obtain a better understanding of the strength of coke on the basis of coke being a porous material. The porous structure of coke has been determined to establish a relationship between the porous structure coefficient c in the equation and the porous structure as observed by optical microscopy and image analysis [13]. By assuming an identical porous structure, attempts were made to evaluate the coke matrix strength in relation to the coke carbon texture [22] and to model the coke tensile strength by estimating the matrix strength in relation to the micro-strength index [27]. The effects of the coking properties of the coal and the carbonisation conditions on the porous structure represented by the porous structure coefficient c were discussed by assuming identical matrix strength for a metallurgical coke [28]. However, no study appears to have been made to evaluate both the porous structure and the matrix strength simultaneously for cokes made from coals covering a wide range of coking properties. Furthermore, it is recognised that coke has a strength anisotropy due to the anisotropy of the porous structure [29]. Since this strength anisotropy could influence crack propagation and the direction of the crack path, and these cracks affect the coke strength index and mean size of coke, it is important to assess this effect in relation to the porous structure.
In this section, cokes made from coals with a wide range of properties were examined. The effects of the porous nature and the coke matrix strength on the tensile strength were evaluated separately using an empirical equation which relates strength and porosity and the effects of the coal properties were also assessed. The porous structure was qualified by means of optical microscopy and image analysis and coke matrix strength was evaluated in the light of the carbon structure estimated by X-ray diffraction. The strength anisotropy is discussed with regard to the porous structure by relating the tensile strength and crack path angle, i.e., the angle between the crack path and average pore orientation measured during image analysis.

3.3.1 Experimental

3.3.1.1 Coke samples
Coke samples from the five coals shown in Table 3.1 were produced using the laboratory scale carbonisation test oven. The samples were evaluated on the basis of the measurements described previously and the parameter introduced in this section.

3.3.1.2 Degree of carbonisation
Crystallite stack height, \( L_c \), and width, \( L_a \), of the coke carbon matrix were estimated by means of X-ray diffraction [30] to evaluate the coke carbon structure of each coke sample. To represent the nature of the coke carbon matrix, the following parameter was defined:

\[
\text{Carbon structure factor} = \frac{L_a}{L_c} \quad (3.7)
\]

This factor is defined on the basis of the concept of graphitic and non-graphitic carbon as introduced by Franklin [31]. Although coke samples considered in this study were carbonised at a relatively low temperature for the division into graphitic and non-graphitic carbon, it was assumed that the carbon structure factor does represent the nature of the coke carbon. According to the definition, as the carbon structure factor increases, the nature of carbon approaches that of non-graphitic carbon and tends to have a cross-
linked carbon structure. The carbon structure factors were determined for cokes made from each coal at the three final temperatures of 600, 800 and 1000 °C.

3.3.1.3 Quality of porous structure
To evaluate the effect of the porous structure on the strength, the following parameters were introduced, using the data measured by image analysis:

a) Pore size distribution factor
Defined as the gradient of the linear relation obtained by regression analysis when the pore size and the cumulative number of pores are plotted in a log-log plot. As the factor becomes larger, the pore size distribution range becomes narrower.

b) Pore rugosity factor
This parameter was defined to evaluate the degree of irregularity of the pores, since a sharp pore shape can be a stress concentration point and affect the strength [16]. The rugosity was calculated from the pore circularity defined by

\[
Pore\ circularity = \frac{4\pi (pore\ area)}{(pore\ perimeter)^2}
\]

(3.8)

The circularity of the pores compared with that of an equivalent ellipse, i.e., with the same aspect ratio, then gives a measure of the pore rugosity.

\[
Pore\ rugosity\ factor = \frac{(Pore\ circularity)}{(Pore\ circularity\ of\ equivalent\ ellipse)}
\]

(3.9)

Because of its strong dependence on resolution, pore perimeter is strongly affected by the pore size. Therefore, the parameter was calculated for pores with length in the range between 200 to 300 μm. When a pore has a rough surface, the perimeter is longer than that of an ideal ellipse of same aspect ratio and the pore circularity is smaller. Therefore, when the pore rugosity factor becomes smaller, the pore shape has a rough surface and deviates from an ideal elliptical shape.

c) Crack path angle
This is the angle between crack path and average pore orientation. It is equivalent to the pore orientation as measured by the image analysis procedure when the crack path in the
fractured specimen is set along the Y-axis of the measuring field as shown in Figure 3.11.

![Crack path angle](image)

**Figure 3.11 schematic diagram of the crack path angle definition**

3.3.2 Results and discussion

3.3.2.1 Evaluation of the coke matrix strength and the porous structure

To evaluate the porous nature and the matrix strength separately, and to exclude the effect of porosity, the empirical formula for porous materials, which relates strength and porosity [12, 26], used in previous section was applied (Equation 3.5). Although the equation is an empirical one and has no strict physical meaning, it has been used widely to evaluate the strength of porous materials in relation to porosity and hence the effect of the porous structure [14]. Therefore, it was considered that this equation is capable of quantitatively estimating the matrix strength and effect of the porous structure [25]. Based on the same procedure used in the previous section, the porous structure coefficient c, which represents the porous structure, was determined by the statistical regression technique using approximately 90 data points for the coke samples made from same coal by assuming that the porous structure coefficient c was identical for each coke made from the same coal. This was assumed because the samples were prepared under...
the same heating conditions apart from the final temperature. Therefore the heating conditions during the plastic stage which, in conjunction with coking properties, governs the porous structure [16], was considered to be identical in all cases. The strength of the coke matrix for each final temperature was also determined by this procedure. A summary of the results obtained for the cokes carbonised to 1000 °C is given in Table 3.4.

<table>
<thead>
<tr>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density [kg/m³]</td>
<td>911</td>
<td>910</td>
<td>801</td>
<td>863</td>
<td>829</td>
</tr>
<tr>
<td>True density [kg/m³]</td>
<td>1981</td>
<td>2044</td>
<td>2060</td>
<td>1949</td>
<td>2017</td>
</tr>
<tr>
<td>Fractional volume porosity [-]</td>
<td>0.54</td>
<td>0.56</td>
<td>0.61</td>
<td>0.56</td>
<td>0.59</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>4.31</td>
<td>5.36</td>
<td>4.70</td>
<td>4.96</td>
<td>4.60</td>
</tr>
<tr>
<td>Strength of matrix [MPa]</td>
<td>55.6</td>
<td>58.9</td>
<td>385.0</td>
<td>97.5</td>
<td>122.5</td>
</tr>
<tr>
<td>Porous structure coefficient [-]</td>
<td>4.77</td>
<td>4.37</td>
<td>7.25</td>
<td>5.38</td>
<td>5.64</td>
</tr>
</tbody>
</table>

3.3.2.2 Coke matrix strength and carbon structure

In considering the effect of the coke carbon structure on the coke matrix strength, a relationship between the carbon structure factor, which represents the nature of the carbon in relation to graphitic or non-graphitic carbon, and the estimated strength of the coke matrix at 1000 °C was examined. Figure 3.12 shows the relationship for coals A, B, D and E. In this figure coal-C was excluded since it contained a considerable amount of mineral matter and this could not be taken into consideration in the carbon structure factor, which is defined only by the X-ray diffraction of the coke carbon. The large amount of mineral matter content and the associated poor coking quality resulted in a weak porous structure and led to a large estimated coke matrix strength. Although the estimated matrix strength for coal-C could be taken as a qualitative value in relation to the other coals, it is difficult to discuss this difference in terms of the carbon structure factor defined in this study.
The coke matrix strength increases with increase of the carbon structure factor. In other words, the coke carbon matrix is stronger when the carbon is more non-graphitic. This can be explained on the basis of the carbon structure model which describes the non-graphitic carbon as having a highly cross-linked structure [31]. It was reported that the non-graphitic carbon has a strong system of cross-linking in the carbon structure and this binds the crystallites in a rigid mass, so that the resulting carbons are termed hard carbon [30, 31]. Furthermore, the measured high Knoop hardness of coke is concluded to be attributable to the three dimensional network structure [32]. Since the hardness of materials has a correlation with their tensile strength [33], the strength of coke can be expected to be higher when the coke carbon has a cross-linked structure. Therefore, it is possible to conclude that the estimated matrix strength is able to represent the coke carbon matrix strength, at least qualitatively.

Figure 3.13 shows the relationship between the volatile matter (dmmf) and the carbon structure factor. Since a lower rank coal tends to have a smaller Lc, crystallite stack height, the carbon structure factor derived from the Equation (3.7) becomes larger. This tendency suggests that the carbon from the lower rank coal approaches that of a non-graphitic carbon and this is in accord with previous studies regarding graphitisation of carbon and carbonisation [17], where non-graphitic properties were associated with low-
rank coal. Hence, it is concluded that the carbon structure factor defined in this study is capable of representing the nature of the coke carbon.

![Graph showing relationship between coal rank and carbon structure factor](image)

**Figure 3.13 Relationship between coal rank and carbon structure factor**

However, from the results shown in Figures 3.12 and 3.13, it appears that the coke carbon matrix is stronger for the coke made from lower rank coal in the range of coal rank used in this study. This is different to the general understanding, which associates a strong coke matrix to the coke made from medium rank coal, i.e., with a maximum vitrinite reflectance around 1.0-1.2 % [27] or higher rank coal (in a coal rank range around VM 20-40 dmmf wt%) [32, 34]. Apart from the study which measured the coke matrix strength as the Knoop hardness number [32], the coke matrix strengths were estimated using tensile strength data on the basis of an identical porous structure for various coke samples [27], and using mercury pressure porosimetry and modelling of the coke porous structure as an ideal and identical porous structure for every coke sample [34]. Accordingly, these results are considered to contain an effect of the porous structure, which is strongly influenced by coking properties, and therefore they differ from the real coke carbon matrix strength. Even the data based on the Knoop hardness showed considerable scatter so that it is not obvious from the hardness/coal carbon content plot at which carbon content the maximum strength occurs from 85 to 90 wt% (d.a.f.) of the coal carbon content [32]. Since, the high Knoop number was considered to
be associated with the three dimensional network structure of carbon, the coke which has a cross-linked carbon structure, namely, close to that of the non-graphitic carbon can be considered to have a strong matrix strength. Consequently, it was concluded that the coke matrix strength is stronger when the coke carbon has a cross-linked structure and this feature tends to be associated with a coke made from a lower rank of coal.

3.3.2.3 Effect of coking properties on the porous structure of coke

As a porous material, the coke strength is governed by the matrix strength, the porous nature and porosity. In this study, the effect of porous structure on the tensile strength was represented by the porous structure coefficient $c$ in the Equation (3.5). A higher coefficient $c$ means that coke is weaker at same porosity and matrix strength condition.

![Figure 3.14 Effect of coking properties on porous structure coefficient](image)

The relationship between the porous structure coefficient $c$ and the coking properties, maximum fluidity and the swelling number, is shown in Figure 3.14. The lines shown in the figure were derived from the relationship between the porous structure coefficient $c$ and the coking qualities, the maximum fluidity and swelling number, by statistical regression. The porous structure coefficient $c$ decreases, in other words, by definition the porous structure improves as the maximum fluidity and the swelling number increase. Although number of the plots in the figure is restricted to obtain a concrete relationship
between the porous structure coefficient \( c \) and the coking qualities, it is possible to use the relationship to estimate the porous structure coefficient \( c \) in the mathematical model, since differences between the coefficient appear to be well explained by these two coking properties. A possible explanation for the relationship is to consider the quality of the porous structure on the basis of the relationship of an adhesive force and a force pushing particles together. In this case the maximum fluidity indicates the quality of adhesion and the swelling number indicates the force for adhesion. Therefore, it is necessary to have a good quality in both coking parameters to obtain better porous structure. On the basis of this concept, the porous structure is considered to be improved by a high heating rate and high charge density which improve the fluidity and state of adhesion between particles, respectively [28]. Although these considerations apply in this instance, it is recognised that there is likely to be optimum values of these parameters. Such considerations may be applicable if a wider range of coals was used.

3.3.2.4 Relationship between measured porous structure and estimated coefficient

Measurements of coke porous structure by optical microscopy have been used in attempts to find an explanation for coke strength differences. However, there has been little in the way of quantitative evaluation of the porous structure, i.e., number, size and shape of pores, and its relationship with the porous structure coefficient \( c \) in Equation (3.5) [13, 15]. Therefore, in this study an attempt was made to quantify the porous structure using optical microscopy and image analysis with the aim of establishing a parameter which has a strong correlation with the porous structure coefficient \( c \).

Figure 3.15 shows the relationship between the pore size distribution factor defined previously and the porous structure coefficient \( c \). There is a good correlation between two parameters, with a poor porous structure being associated with a wide pore size distribution. Differences between the pore size distribution factor for the various cokes were mainly attributable to the differences in the proportion of the smallest pores, i.e., with pore length less than 20 \( \mu \text{m} \), a low pore size distribution factor being caused by a large proportion of such small pores in the pore size distribution. On the basis of the relationship between the porous structure coefficient \( c \) and the coking properties, it is deduced that the large proportion of small pores in the coke porous structure is
attributable to poor coking properties and represents a consequent inferior adhesion between coal particles, which might lead to unfilled gaps between particles.

The poor coking properties were used to explain the poor coke strength in relation to pore shape [16], where a rough pore shape caused by lack of fluidity was associated with poor strength whilst a smooth pore shape was associated with high strength because of the possible stress concentration at sharp edges in a pore [35]. However, no qualitative evaluation for such concept has been made. It is to represent this irregularity of the pores in the coke that the pore rugosity factor was introduced.

![Figure 3.15 Relationship between pore size distribution factor and porous structure coefficient](image)
The effect of the pore irregularity on the porous structure coefficient $c$ is shown in Figure 3.16. In the figure, an effect of pore aspect ratio was neglected since all average aspect ratios of each sample were within 0.61 to 0.64 and the effect of this variation was considered to be small. The figure shows that as the pore shape becomes smoother, the porous structure becomes better.

As shown in Figures 3.15 and 3.16, the measured coke porous structure clearly indicates that the adhesion of the coal particles is vital for a good porous nature and hence a strong coke. To obtain a good porous nature, enough adhesive and force to fuse particles together are necessary to fill the space between particles and to prevent sharp edges in pores at which stress concentration could take place.

### 3.3.2.5 Effect of pore orientation on tensile strength

It is well known that coke has a porous structure anisotropy due to the coking pressure generated during carbonisation. Pores tend to distort through the plastic coal and semicoke being compressed towards the hot walls by the coal swelling pressure during carbonisation [36] and consequently the coke strength should differ in the directions normal to and parallel to the oven wall. It was reported that the compressive strength of coke specimens compressed at right angle to the long axis to the coke lump, that is in the
direction parallel to the heat flow, was 1.36 times greater than that measured in the direction normal to the heat flow [29]. The effect of the anisotropy of the porous structure on the tensile strength is here considered on the basis of the relationship between the crack path angle and the tensile strength. By the definition, a crack path angle of $90^\circ$ represents the strength for the propagation of fissures normal to the oven wall and when it is $0^\circ$ for fissures parallel to the oven wall. Although the strength anisotropy is considered to be influenced by the extent of the pore distortion, the aspect ratio of the pores, this effect was neglected in this study since the pore aspect ratio obtained was similar for all the coke samples.

To evaluate the effect of the crack path angle on the tensile strength and the effect of quality of the porous structure on the strength anisotropy, the tensile strength, normalised to an identical porosity of 0.55, was examined for specimens with good (coal-B), medium (coal-D) and poor (coal-C) porous structure represented by the porous structure coefficient $c$. The results inevitably showed variability since many factors affect the tensile strength, but they suggest that the tensile strength improves when the crack path angle increases. This leads to the conclusion that the coke is more resistant to the penetration of a longitudinal fissure, which is normal to the oven wall, than a transverse fissure, which is parallel to the oven wall, under an identical stress condition. There are indications that this strength dependency on the crack path angle becomes less marked when the coke porous structure becomes poor, but further study is necessary to confirm this idea that the difference in coke strength anisotropy in relation to the porous structure quality affects the mechanism of the fissure formation in coke lumps.
3.4 DETERMINATION OF THE EFFECTIVE YOUNG’S MODULUS ON THE BASIS OF THE DIAMETRAL COMPRESSION TEST

Since the Young’s modulus is one of the more important factors influencing the fissure formation phenomena, an attempt was made to determine the modulus for the coke samples used in the previous section. The Young’s modulus was estimated using the method proposed by Klose and Suginobe [37] from data obtained when the tensile strength was measured. The determined values of the Young’s modulus for the cokes made from five coals used in this study will be utilised in the next chapter when the stress generated in each coke sample is estimated by constructing a mathematical model.

3.4.1 Theory

To determine the effective Young’s modulus from the diametral compression test, Klose and Suginobe [37] derived a theoretical relation between the deformation and the stress from a general model of two cylinders by assuming the contact between a disc sample and parallel discs in the test is identical to that of two cylinders with the diameter of one cylinder tending towards infinity (Figure 3.17).

![Figure 3.17 The Hertz contact problem of two disc shapes (cylinders)](image-url)
The relation between force and deformation was derived as follows

\[
\frac{2}{\pi FH} = -E_{\text{eff}} \frac{d}{dF} \left( \frac{V_s}{F} \right)
\]

(3.10)

where \(F, H\) and \(V_s\) are force, sample height and total deformation, respectively. \(E_{\text{eff}}\) is the effective Young's modulus and is defined as

\[
E_{\text{eff}} = \frac{E_1}{1 - \nu_1^2}
\]

(3.11)

where \(E_1\) and \(\nu_1\) are Young's modulus and Poisson's ratio of coke.

A differential form of Equation (3.10) for two points \(A(V_{s,1}, F_1)\) and \(B(V_{s,2}, F_2)\) in the force/deformation curve (Figure 3.18) gives

\[
\frac{4}{\pi H(F_1 + F_2)} = -E_{\text{eff}} \frac{F_2 - F_1}{F_2 F_1}
\]

(3.12)

Using five to seven points from the force/deformation curve, it is possible to determine the effective Young's modulus by a statistical regression technique.

To obtain physically meaningful data, the effective Young's modulus was determined from measured points which fulfil the following condition

\[
\frac{a}{R} = 2a = \frac{8F}{\pi DHE_{\text{eff}}} \leq 0.1
\]

(3.13)

where \(a, R\) and \(D\) are half length of the contact plane, cylinder radius and sample diameter, respectively. This condition was derived from the applicability of Equation (3.10) on the basis of the theory. The equation is applicable only to the case where the stresses are located within a limited area close to the contact surface and the condition for this limitation is \(a/R \leq 0.1\).
Figure 3.18 Example of force/deformation curve for the determination of the effective Young's modulus

3.4.2 Results and discussion

Data obtained for the five cokes are summarised in Table 3.5. Only a proportion of the 30 specimens used to obtain mean tensile strengths quoted earlier fulfilled the requirements of the Equation (3.13). For each coke the number of specimens used to obtain the effective Young's modulus is shown and the tensile strengths listed are average values obtained from the same specimens.

Table 3.5 Determined effective Young's modulus

<table>
<thead>
<tr>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of specimens</td>
<td>23</td>
<td>20</td>
<td>25</td>
<td>12</td>
<td>19</td>
</tr>
<tr>
<td>Effective young's modulus [GPa]</td>
<td>0.518</td>
<td>0.300</td>
<td>0.567</td>
<td>0.327</td>
<td>0.371</td>
</tr>
<tr>
<td>Standard deviation  [GPa]</td>
<td>0.272</td>
<td>0.161</td>
<td>0.251</td>
<td>0.156</td>
<td>0.162</td>
</tr>
<tr>
<td>Tensile strength [MPa]</td>
<td>4.33</td>
<td>5.39</td>
<td>4.72</td>
<td>5.24</td>
<td>4.41</td>
</tr>
</tbody>
</table>

Amongst individual specimens of each coke, the determined effective Young's modulus varies considerably, however the standard deviations listed are similar to those quoted in
the literature [37]. Therefore, it is concluded that this is either due to the heterogeneity of coke or is a characteristic of the method of determination but nevertheless these moduli are representative of the property of each coke. Besides, the determined values were similar in magnitude to previously published results using this method.

Figure 3.19 shows the relation between the effective Young's modulus and the tensile strength. Plotted data include those of cokes carbonised at 600 and 800 °C. This relation has been studied by other researchers and, generally only a weak correlation has been obtained [9, 23]. Although the degree of correlation varies for each coke and, for some cokes, the effective Young's modulus even decreases as the tensile strength increases, the effective Young's modulus as a whole tends to increase as coke becomes stronger. This weak and imperfect correlation is considered to stem partly from the method used and partly from the quality of the coke specimens. The effective Young's modulus seems to correlate with the number of specimens which reflects the quality of the coke disc specimen surface to some extent, since the data with an evidence of edge crushing during the diametral compression test were excluded from the estimation.

Figure 3.19 Relation between effective Young's modulus and tensile strength

To evaluate the effective Young's modulus in relation to porosity, porous nature and the Young's modulus of the coke matrix, and to find its relation to the previously determined
tensile strength of the coke matrix and the porous structure coefficient, an attempt was made to estimate the Young’s modulus of the coke matrix and the porous structure coefficient on the basis of a following equation [38]

\[ E_{\text{eff}} = E_{\text{eff}0} \exp(-c_E P) \]  

(3.14)

where \( E_{\text{eff}}, c_E \) and \( P \) are the effective Young’s modulus of the coke matrix, the porous structure coefficient and porosity, respectively. Each parameter was determined using data of cokes carbonised at 600, 800 and 1000 °C using the statistical regression technique.

![Graph showing the relation between porous structure coefficient and tensile strength and effective Young's modulus](image)

**Figure 3.20** Relation between the porous structure coefficient of the tensile strength and the effective Young’s modulus

**Figure 3.20** shows the relation between the porous structure coefficients for the tensile strength, \( c \), and the effective Young’s modulus, \( c_E \). Apart from coal-D for which a particularly small number of specimens was used for the effective Young’s modulus determination, there is a correlation between the coefficients. This could suggest that the effect of porous nature on both properties is similar. However, due to smaller number of data used in determining the effective Young’s modulus, the correlation coefficient of the
statistical regression technique was relatively small compared to that for the tensile strength determination. Therefore, the relation found is regarded only as a tentative result. The effective Young’s modulus of the coke matrix also has a correlation with the tensile strength of the coke matrix if the result of D coal is excluded, as shown in Figure 3.21. In the figure, a tentative regression line was drawn to go through the origin.

![Diagram](image)

Figure 3.21 Relation between the tensile strength and the effective Young’s modulus of the coke matrix
3.5 CONCLUSIONS REGARDING EVALUATION OF COKE STRENGTH

In the second section of this chapter, strength development during carbonisation has been studied to estimate the effect of temperature history during carbonisation. Because coke strength development is related directly to the degree of thermal decomposition of the coal, and the consequent structure change in the coke carbon matrix, the final carbonisation temperature is, in itself, an insufficient parameter for describing the strength development during carbonisation. Therefore, the development of the strength of coke during carbonisation depends not only on carbonisation temperature, but also on other heat treatment parameters, e.g., rate of heating. It is possible for the effect of temperature history to be taken into account by using the fraction of pyrolysis reaction as a characteristic parameter. Based on this treatment, the strength development under arbitrary heating conditions can be estimated, as long as the estimation of the pyrolysis reaction is reasonably accurate.

The effect of temperature history on the strength development in the commercial coke oven was demonstrated by means of a mathematical model, which makes it possible to estimate the temperature history and the pyrolysis reaction during carbonisation, and the relationship, derived in this study, between the fraction of reaction and the strength of coke matrix. The development of the strength of the coke matrix during carbonisation, even to the same final temperature, in a commercial coke oven was calculated to differ considerably across the oven width. Since this variation caused by the temperature history is almost the same as that amongst a wide range of 1000 °C cokes, it is considered that this could affect the formation and propagation of fissures in coke during carbonisation.

In the third section, the effect of coal properties on the tensile strength of coke was evaluated by separating the tensile strength into the matrix strength factor, the porous nature factor and porosity.

The matrix strength of coke carbon was evaluated in relation to the graphitic and non-graphitic carbon structures present. A coke with a larger carbon structure factor has a stronger matrix strength due to cross linking of the carbon structure. The carbon structure factor depends on the rank of coal and for the range of coal rank used in this study, the coke made from lower rank coal tended to have a larger carbon structure factor. Thus, the
coke matrix strength tended to be stronger for lower rank coal over the limited range of coal rank studied.

It was clearly demonstrated that the porous structure coefficient \( c \) was governed by the coking properties. For the range of coal used, the porous structure improved as the maximum fluidity and the swelling number of the coal used increased. The quality of the porous structure can be evaluated on the basis of the pore size distribution and the irregularity of the pores as defined in this study. Both parameters were considered to represent the state of adhesion between coal particles.

The strength of coke varies depending on the orientation of the pores and it is considered that the consequent strength anisotropy affects the fracture phenomena, such as the direction of the crack path. This strength anisotropy is influenced by the quality of the porous structure and the effect of porous structure anisotropy is more apparent when the porous structure, represented by the defined porous structure coefficient, is smaller.

In the last section, the effective Young's modulus was determined by the diametral compression test method. The values obtained were similar to the previously reported Young’s modulus value for cokes and thus it was concluded that these results for each coke sample can be used for stress estimation using the mathematical model in the next chapter.

Tentative evaluation of the relationship between Young's modulus and tensile strength, including the relations for estimated porous structure coefficient and the Young’s modulus value of pore free matrix, was made. Because only a small number of data were available to determine these parameters, it was difficult to obtain a firm results. Nevertheless, a reasonable relation was obtained for these cokes, which had a reasonable number of data points for the effective Young’s modulus determination.
3 EVALUATION OF COKE STRENGTH

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NOMENCLATURE

a  Half length of the contact plane (mm)
c  Porous structure coefficient (-)
c_E  Porous structure factor for Young's modulus (-)
D  Cylinder-(sample-)diameter (mm)
E  Young’s modulus (GPa)
E_{eff}  Effective Young’s modulus (GPa)
E_{eff,c}  Effective Young’s modulus of coke matrix (GPa)
F  Force (kN)
H  Cylinder-(sample-)height (mm)
L_a  Crystallite stack width (Å)
L_c  Crystallite stack height (Å)
P  Tensile stress (MPa)
P  Porosity (-)
R  Cylinder-radius (mm)
t  Thickness of disc (mm)
t  Time (s)
v_s  Total deformation (mm)
W  Applied load (Kg)
W  Total weight loss (%)  
W’  Total gas weight generation (kg/kg-coal)
w  Weight loss at a certain point of carbonisation (%)

Greek symbols

v  Fraction of reaction (%)  
v  Poisson’s ratio (-)
θ  Temperature (K)
θ  Crack path angle (°)
σ  Strength (MPa)
Subscripts

0  coke carbon matrix

i  i th gas species
4 ELUCIDATION OF FISSURE FORMATION PHENOMENA

In the previous chapter, coke strength was evaluated in relation to the degree of carbonisation and the structures of the coke matrix and the pores in the coke. An objective of this part of the study is to discuss and to make an attempt to elucidate the fissure formation phenomena during carbonisation using the improved understanding of coke strength described in chapter 3. To utilise the knowledge obtained in the previous chapter and to relate it to the fissuring in coke, coke samples large enough to have fissures and made from the coals used in the previous experiment were studied. To produce the coke samples, a large laboratory-scale furnace was used to prepare samples under various carbonisation conditions. A mathematical model was constructed to discuss the fissuring phenomena observed in relation to the coke strength.

4.1 EXPERIMENTAL

Coke samples large enough for the observation of the degree of fissure formation were produced using a large test oven. Five coals identical to those previously used in the small scale test oven experiments were used to permit discussion of the effect of coal properties on fissuring, based on the previous results. Coke samples were carbonised under various heating conditions to elucidate the effect of heating condition on fissure formation phenomena.

4.1.1 Coke samples

4.1.1.1 Large scale test oven
Coke samples were made by means of a large scale carbonisation furnace shown in Figure 4.1. The $330 \times 430 \times 30$ mm coal charge, contained in a stainless steel charge box, was heated between oven walls $430$ mm apart to simulate the behaviour of a $30$ mm thick horizontal slice of the charge in a commercial coke oven. The coal charge size was designed to produce enough coke sample to investigate fissure formation phenomena. In
accord with nomenclature used in commercial coke making, the distance between the heated walls is here described as the oven width and the dimension of the charge perpendicular to the width as the length. The thickness of the charge was chosen to avoid a three dimensional fissure network in the coke so that fissures could be evaluated easily and objectively in two-dimensional manner.

![Diagram of Large scale carbonisation furnace](image)

**Figure 4.1 Large scale carbonisation furnace**

### 4.1.1.2 Coal used

The five coals used in previous experiments were again used to examine the effect of coal properties and coke strength on fissure formation. Properties of the coal used are given in Table 3.1 (page 64).
4.1.1.3 **Carbonisation conditions**

Since heating conditions as well as coal properties are significant factors in fissure formation, the carbonisation was performed under various heating conditions to study the effect on the phenomena. For a base heating condition, after placing the charge box in the furnace, it was heated to 1100 °C as fast as possible and kept at that temperature until the end of carbonisation. Two other furnace temperatures, 1150 and 1200 °C, were studied using coal-C to evaluate an effect of the final furnace temperature. Slower heating conditions, 3 and 5 °C/min, were also applied to coals A and E. For these conditions, the furnace temperature was controlled to heat up at 3 or 5 °C/min, after reaching 400 °C as quickly as possible, and then maintaining the final furnace temperature for one hour. The heating conditions examined in these experiment are summarised in **Table 4.1**.

<table>
<thead>
<tr>
<th></th>
<th>Base</th>
<th>1150, 1200 °C</th>
<th>3, 5 °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>*</td>
<td></td>
<td>0*</td>
</tr>
<tr>
<td>B</td>
<td></td>
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<td>C</td>
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<td>D</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* only 3 °C/min

Under all conditions, air-dried coal, sized under 3 mm, was charged to a packing density of 800 kg/m³. Nitrogen gas was introduced into the lower part of the furnace to prevent combustion of the coke during carbonisation. Carbonisation was terminated when the temperature at the centre of the coke sample reached 850 °C or after carbonising for 23 hours. After the termination of carbonisation, insulating bricks, which covered the charge box, were removed and the box was quenched immediately by means of nitrogen gas.

To avoid an effect on the degree of fissuring of friction between coke sample and the charge box, papers were placed at the bottom and top of the coal charge. The effect of the paper was examined before making the samples for evaluation by placing the paper at the middle of the coal charge. Since the coke was clearly divided into two lumps by the paper
installed and the fissuring behaviour was independent in each coke lump, the beneficial
effect of paper was confirmed and the normal coke samples were considered to be free
from the friction with the bottom and top walls.

4.1.2 Property distribution across the oven width

4.1.2.1 Degree of fissuring in the coke
To clarify the effect of heating condition across oven width, the degree of fissuring in
each coke sample was evaluated by counting the number of longitudinal fissures, i.e.
those which penetrated the coke perpendicular to oven wall, at various distances from the
heated wall. The number of fissures was converted into the average distance between
fissures by dividing original coke length (coal length) by the number of fissures as
follows

\[
\text{Average distance between fissures} = \frac{\text{Charge box length}}{(\text{Number of fissures} + 1)}
\]  
(4.1)

Transverse fissures, generated parallel to the oven wall, were rare and so they were not
counted.

4.1.2.2 Micro strength index
The micro strength index of coke was determined using the standardised method. It
provides a measure of the mechanical strength of coke [1]. This index has been
considered to represent the strength of coke matrix, at least to some extent [2, 3]. The
procedure for the measurement is as follows [1].
Two grams of coke, graded between 14 and 25 mesh sieves, are placed in a stainless steel
tube, whose internal diameter and height are 1 in. and 12 in. respectively, together with
twelve 5/16 in. diameter steel balls. The tube is rotated longitudinally at a constant speed
of 25 rpm for 800 revolutions by means of electric motor. The index is determined by
weighing the particles remaining on 25 mesh sieve and expressing it as percentage of the
original weight of coke (M.S.I.25). Similar indices are obtained using 72 mesh (M.S.I.72)
and 125 mesh sieves (M.S.I.125).
4.1.2.3 Other properties
To determine the porosity of the coke samples, apparent density and specific gravity were measured. Samples for measurement were cut from the coke lumps at various position across the oven width.

4.1.3 Results

4.1.3.1 Temperature distribution in coke during carbonisation
The temperature distribution in the coke during carbonisation was studied to establish whether the carbonisation progressed under one dimensional heat flow conditions as in a commercial coke oven. Figure 4.2 shows temperature histories measured in the vicinity of side wall ("Wall side" in the figure) and at mid length ("Centre") at the centre of oven width. The temperature histories are almost identical and therefore it is concluded that coal was carbonised under one dimensional heat flow and the degree of fissuring observed in the coke sample is considered to be free from edge effects of the side wall. In other words, the coke samples made using the test oven should be similar to samples from a commercial coke oven.

![Figure 4.2 Temperature distribution in coal/coke during carbonisation](image-url)
4.1.3.2 Number of fissures in the coke samples

Pictures of cokes samples carbonised under base heating conditions are shown in Figure 4.3. The number of fissures in the coke samples was assessed by counting the number of fissures visible on four surfaces of each coke lump, these are, right side surface facing upward and downward, left side surface facing upward and downward, and obtaining an average value.

Figure 4.3 Coke samples obtained from various coals
Figure 4.4 shows a relationship between a number of fissures in the right and left side lumps of cokes from all the coke samples. The number of fissures in the two sides correspond reasonably. This result suggests that the number of fissures generated and counted in the cokes has a consistent tendency and, therefore, at least, a qualitative meaning.

It has previously been reported that the degree of fissuring was in general agreement with that estimated from the apparent density method and by the extended drum test [4]. Since the coke sample obtained in the present work is thin enough to observe the degree of fissuring through the lump, visual observation in this case accurately reflects the degree of fissuring.

![Figure 4.4 Number of fissures in right and left side lump](image)

**Figure 4.4 Number of fissures in right and left side lump**

4.1.3.3 Effect of coal properties on degree of fissure formation

Figure 4.5 shows the temperature history under the base heating condition at the centre of the charge for all the coals. It is clear that the temperature history of the cokes are almost identical. Thus any difference in the degree of fissuring observed in these experiments is attributable to the properties of the coal.
The degree of fissuring in the cokes shown in Figure 4.6, expressed as an average distance between fissures, varies from coal to coal and with position across the oven width. The number of fissures tends to increase (distance between fissures in the figure decreases) near the oven wall because of the higher heating rate compared to that near the centre of the charge. The average distance between fissures has no obvious relation with
volatile matter content, which, to some extent governs shrinkage and hence influences the stress imposed in a semicoke during carbonisation.

On the other hand, the difference in the micro strength index shown in Figure 4.7 does seem to correlate reasonably well with the degree of fissure formation. The degree of fissure and the micro strength index place the cokes in a similar order. In other words, weak coke in terms of the micro strength index tends to have more fissures than strong coke.

It can be concluded that the degree of fissure is influenced by the strength of coke as well as the stress generated in the coke. Thus, coking properties, heating conditions and volatile matter are the main governing factors of the fissure formation during carbonisation.

![Figure 4.7 Micro strength index distribution in coke lump](image)

**Figure 4.7** Micro strength index distribution in coke lump

**Figure 4.8** shows true density distribution across the oven width. The densities measured were almost identical to the results obtained in the previous chapter and therefore any effect of oxidation can be concluded to be negligible. Decline of the densities of coals C and D in the vicinity of the oven wall are attributable to an increase in microporosity which is inaccessible to the measuring media, in this case helium [5].
4.1.3.4 Effect of heating conditions

(a) Effect of heating rate

To assess the effect of the heating rate, coal samples were carbonised at 3 and 5 °C/min in addition to the base condition. **Figure 4.9** shows the temperature rise of the furnace and the resulting heating pattern of coal in the vicinity of oven wall.
Degree of fissure formation in the coke lump made from coal-E under each heating condition is shown in Figure 4.10. Despite the considerable difference in heating rate in the vicinity of the oven wall shown in Figure 4.9, the general manner of fissuring is similar for every heating condition. Furthermore, at some part across the oven width, especially near the oven wall where heating rate difference is considered to be greater, more fissures are generated under slower heating conditions. This tendency is impossible to explain only in terms of the thermal stress generated in coke during carbonisation, since generally the stress increases when the heating rate is faster.

![Figure 4.10 Effect of heating rate on degree of fissure](image)

(b) Effect of final furnace temperature

To investigate further the effect of heating conditions, coke samples were carbonised to two different final furnace temperatures, 1150 and 1200 °C. The measured degree of fissuring in the coke samples is shown in Figure 4.11. Since heating conditions near the oven wall for all conditions were identical until the temperature exceeded 1100 °C, the degrees of fissure formation are almost identical in the vicinity of the oven wall. However, near the oven centre, more fissures are generated when final furnace temperature is higher due to the higher heating rate.
To discuss and to elucidate the fissure formation mechanism in relation to the heating conditions and coal properties, it is necessary to develop a mathematical model which takes into consideration as many parameters as possible.
4.2 MATHEMATICAL MODELLING

4.2.1 Temperature field

4.2.1.1 Analytical field
The temperature field was calculated for the analytical field shown in Figure 4.12. The test oven was assumed to be symmetrical and therefore a quarter of the longitudinal section of the oven (Figure 4.1) was defined as an analytical field. The measured furnace temperature \( T_b \) was taken as the boundary condition at the heating element and heat loss at top and bottom surfaces was taken into consideration. Other surfaces were assumed to be adiabatic. The basic procedure of the calculation was identical to that described in literature [6, 7]. A two-dimensional non-steady-state equation of heat conduction is formulated by finite element formation using the Galerkin method. Temperature distribution in the analytical field was calculated for each time step until the end of the carbonisation period.

![Figure 4.12 Analytical field for temperature model](image-url)
4.2.1.2 Thermophysical properties of coal during carbonisation

The thermophysical properties of coal and coke were estimated on the basis of the empirical formulae of effective heat conductivity and heat diffusivity which take into account the effects of heat of reaction during carbonisation [8, 9].

The effective heat conductivity is given by following equations [8].

\[ \lambda_{\text{eff}} = \lambda_c \exp\{A(\theta - \theta_c)\} \]
\[ \theta_c = 71.3R_o + 668 \]
\[ \lambda_c = 3.11 \times 10^{-2} R_o + 0.147 \]
\[ A_{\alpha\text{cd}} = 5.88 \times 10^{-1} R_o + 6.88 \times 10^{-1} \]
\[ A_{\alpha\text{cd}} = 5.53 \times 10^{-4} R_o + 3.32 \times 10^{-3} \]

where \( \theta_c \) is the transition temperature, \( \lambda_c \) is the effective heat conductivity at the temperature \( \theta_c \), and \( R_o \) is the mean reflectance of vitrinite in oil. The coefficient \( A \) differs in the temperature ranges lower and higher than the temperature \( \theta_c \). In this study Gregg River coal (VM=23.8 wt% d.b., \( R_o=1.22 \)) was used to calculate the thermal conductivity by means of Equation (4.2). Since the measured temperature history of all the coke samples was almost identical, this value was used for all coals.

For the same reason the thermal diffusivity during carbonisation of all samples was assumed to be similar to that of Goonyella coal (VM=25 wt% d.b.) [9] estimated from following equation

\[
\kappa_{\text{eff}} = \begin{cases} 
0.858 \times 10^{-6} \exp\left(-7.29 \times 10^{-2} \frac{\theta - 676}{676}\right) & 450 < \theta \leq 676 \\
0.858 \times 10^{-6} \left(\frac{2.53 \times 10^{-6}}{0.858 \times 10^{-6}}\right)^{\frac{\theta - 676}{782-676}} & 676 < \theta \leq 782 \\
2.53 \times 10^{-6} \exp\left(3.23 \frac{\theta - 782}{782}\right) & 782 < \theta < 1100
\end{cases}
\]

These three equations roughly correspond to the three states of coal during carbonisation, namely a packed bed of coal, plastic stage and semicoke.
Since thermophysical properties change during carbonisation as a result of the pyrolysis reaction and the consequent structural change in the semicoke, it is considered that the properties are better defined on the basis of the extent of the pyrolysis reaction [7]. A method to convert the temperature dependent thermophysical properties to the extent of reaction dependent properties is described in a later section.

4.2.1.3 Properties of brick

Properties for brick were based on the properties of kaolin insulating brick [10] and a measured temperature history of the furnace when fully loaded with brick. The temperature dependence of the heat conductivity of brick was derived from the reported properties at 500 and 1150 °C and the specific heat was determined from the properties at 100 and 1500 °C as follows

\[ \lambda_b = (1.69 \times 10^{-4} + 0.065) \times 1.730735 \]  
\[ C_p = (7.143 \times 10^{-5} + 0.19086) \times 4184 \]

(4.4)  
(4.5)

Since the brick used in this study was not exactly the same as the brick considered in the literature, a correction coefficient for the heat conductivity was introduced to make the predicted temperature history agree well with the measured one. Using a correction coefficient of 0.7 the predicted temperature rise was in good agreement with the measured temperature history, as shown in Figure 4.13. The density of the brick was measured to be 511.43 kg/m³.

4.2.1.4 Heat loss condition

The heat transfer coefficient at the surfaces of the brick was calculated by following equation [10].

\[ h = 0.88 \Delta t^{1/4} L^{-1/4} \]

(4.6)

where \( \Delta t \) is temperature difference between brick surface and atmosphere and \( L \) is the length of surface. Since in the experiment the surface facing upwards was covered with insulating board, the coefficient 0.88, which is the coefficient for a horizontal flat surface
facing downward, was used for the calculation. The atmosphere temperature was taken as 137 °C, on the basis of the temperatures at the top and bottom surfaces throughout the carbonisation.

![Figure 4.13 Temperature history of brick in the furnace](image)

**Figure 4.13** Temperature history of brick in the furnace

4.2.2 Heating rate dependence of properties

The values used for effective thermal conductivity and thermal diffusivity, Young’s modulus, the coefficient of contraction and the viscosity for coal, plastic and semicoke layers were measured at constant heating rate. It is well known, however, that not only these values but also the softening temperature [11] and resolidification temperature [12] are influenced by the heating rate which also changes the temperature dependency. In this study, therefore, these properties are assumed to vary with the fraction of the thermal decomposition reaction as it changes with time [7]. The numerical values for the properties were obtained from the relation, defined previously, between the fraction of reaction and the properties using the values measured under constant heating conditions.
The fraction of the coal thermal decomposition reaction is estimated using the volatile gas generation rate parameter \([13]\). The fraction of reaction \(\nu(\theta)\) at an arbitrary heating condition at temperature \(\theta\) is defined as

\[
\nu(\theta) = \frac{\sum W_i^* \int \left( \frac{dV_i(\theta)}{dt} \right) dt}{\sum W_i^*} \times 100
\]

(4.7)

where \(W_i^*\) and \(V_i\) represent the total volatile gas mass generation and the fraction of reaction, respectively. Thus the numerical values of the properties can be calculated from the fraction of reaction obtained using Equation (4.7). The contraction coefficient, viscosity and strength of coke matrix, which will be described later, can also be defined on the basis of the fraction of reaction.

\[4.2.3\] Stress field

\[4.2.3.1\] Creep analysis

The analytical field is assumed to be a viscoelastic body, includes the creep phenomena, and is formulated by incremental theory in the two-dimensional plain strain system. In this study, only the material property non-linearity is taken into account since the effect of the geometrical non-linearity is relatively small as regards the coke deformation behaviour during carbonisation. The analytical field is shown in Figure 4.14. The field was determined as a quarter of the cross section of the total coke sample based on the symmetry of boundary conditions. The stress field was solved by using the temperature distribution from the temperature model. The two dimensional temperature distribution in coke was neglected since the measured difference is small. Therefore, the temperature at any position across the oven width was assumed to be identical from the oven centre to the side wall and the temperature history at the mid height of coke sample across oven width was used for stress estimation during carbonisation.
The principle of virtual work and the constitutive equation in incremental form are formulated by the finite element method based on the method of Yagawa and Miyazaki [14]. By neglecting the surface force and the volumetric force and arranging the equations, the following finite element formulas are derived.

\[
\begin{align*}
[K^e]\{\Delta d\} &= \{\Delta f^e_c\} + \{\Delta f^e_h\} + \{\Delta r\} \quad (4.8) \\
[K^e] &= \int[B]^T[D^e][B]dV \\
\{\Delta f^e_c\} &= \int[B]^T[D^e]\{\Delta \varepsilon^c\}dV \\
\{\Delta f^e_h\} &= \int[B]^T[D^e]\{\Delta \varepsilon^h\}dV \\
\{\Delta r\} &= -\int[B]^T\{\sigma\}dV
\end{align*}
\]

\([K^e]\) is the stiffness matrix, \(\{\Delta f^e_c\}\) and \(\{\Delta f^e_h\}\) are the pseudo-nodal force vectors due to creep strain and thermal strain respectively. \(\{\Delta r\}\) is a residual force vector which is conserved and added to the next time step calculation to improve the accuracy of the solution. The thermal strain increment \(\{\Delta \varepsilon^h\}\) is determined using the contraction coefficient defined later on the basis of experiment. The creep strain increment \(\{\Delta \varepsilon^c\}\) is calculated by
Equation (4.9) converts the creep strain increment measured in uniaxial creep testing to the multi-axial state, $\dot{\varepsilon}$ being the equivalent creep strain rate, $\bar{\sigma}$ and $\{\sigma^{'}\}$ the equivalent stress and the deviation stress, respectively, and $\Delta t$ is the time increment. In general, the creep law, which is derived experimentally takes account of stress, temperature, time and accumulated creep strain dependence (e.g., Norton-Baily equation [14]), is applied as the equivalent creep strain rate. However, there has been no study of the creep law of the plastic and semi-coke layers during carbonisation. In this study, because the plastic and semi-coke layers are represented as a Maxwell viscoelastic body [15], both layers are assumed as the Maxwell body. In this case, the equivalent creep strain rate in Equation (4.9) is defined as

$$\dot{\varepsilon}^e = \frac{1}{\eta} \sigma = \frac{1}{E \tau_M} \sigma$$  \hspace{1cm} (4.10)$$

where $\eta$ is viscosity, $E$ is Young’s modulus, and $\tau_M$ is the relaxation time which represents the time period for the stress to decrease to $1/e$ of its initial value under constant strain. In this study the viscosity $\eta$ of the plastic and semi-coke layers is decided on the basis of the experimental results of Waters [16] and Dainton [15], respectively. Since Dainton used only one coal to measure the viscosity of the semi-coke layer, the same relation between viscosity of semi-coke and the fraction of the pyrolysis reaction was used for all coal conditions in the model. The property was not given in relation to Young’s modulus and the relaxation time, since Young’s modulus can be different even for the coke made from same coal due to the difference in porous structure.

In the incremental method for creep analysis, to continue the calculation with stable solution, it is necessary to keep the creep strain increment below a certain proportion of the elastic strain increment by using the time step $\Delta t$ small enough to achieve this. Therefore, in terms of the plastic layer, where the viscosity is extremely low, the stability of the calculation must be taken into account. To maintain the stability of the calculation,
the time step $\Delta t$ is examined by the Chang-Rashid condition [14] in relation to the creep strain increment.

$$\Delta t = \frac{x \bar{\varepsilon}}{E \bar{\varepsilon}^n} \quad (0 < x \leq 0.1) \tag{4.11}$$

where $x$ is a constant. Using this condition, the proper time step $\Delta t$ for stable calculation for the plastic layer is estimated with the viscosity of plastic layer taken as $10^3$ Pa s, based on the minimum value of the experimental results of Waters [16], the Young’s modulus as 2 MPa, based on the experimental result of Fitzgerald [17] and $x$ as 0.1. From Equation (4.11), it seems necessary to set the time step smaller then $10^{-4}$ s for stable calculation. However, the application of such a small time step for the this experimental condition, which takes more than twenty hours to terminate the carbonisation, is impracticable because of excessive calculation time. In this study, therefore, the minimum time step for practicable calculation is set first as 10 s, and the viscosity of plastic layer is assumed to be constant at $2 \times 10^8$ Pa s. In this case, the relaxation time is 100 s for the plastic layer.

Substituting the creep strain increment obtained by Equations (4.9) and (4.10) in Equation (4.8) and superimposing each element equilibrium equation to construct the global equilibrium equation, the first order simultaneous equation, the displacement increment, the strain increment and the stress increment in each time step are determined by solving the equations.

4.2.3.2 Young's modulus

Although, in the previous chapter, the Young’s modulus of the cokes used in this study were estimated from the data of the tensile strength determination using the diametral compression test, the data has not been directly applied in the model because the modulus can be different when the porous structure is different. Therefore, the Young’s modulus of semicoke during carbonisation was estimated in relation to the estimated tensile strength of coke to take into account the effect of porous structure, to some extent. This allows the effect of heating conditions across the oven width and the consequent difference in the porous structure to be taken into account. On this basis Young’s modulus is calculated from the line shown in Figure 4.15, which is derived from linear
relation between the tensile strength and Young’s modulus when they are plotted on the log-log scale.

![Graph showing the relation between tensile strength and Young's modulus](image)

**Figure 4.15 Relation between tensile strength and Young’s modulus**

Young’s modulus of the plastic stage is assumed to be 2 MPa, based on the experimental value of the coefficient of rigidity for the plastic layer [17] and the application of the relation $E = 2(1 + \nu)G$ based on the assumption that the Poisson’s ratio for the plastic layer is 0 by presuming the plastic layer to be a foaming material.

With regards to a packed bed of coal, there is no reasonable Young’s modulus since it is not a continuous body. However, to carry out the calculation it is necessary to give it a value. In this study the packed bed of coal was assumed to be a porous body and having a modulus given by the following equation

$$E = E_0(1 - 1.91P + 0.91P^2)$$

(4.12)

where $E_0$ and $P$ are the Young’s modulus of a porous free material and porosity, respectively. Based on the value for compressed coal briquettes [18] the Young’s modulus of the porous free material was assumed to be 100 MPa.
4.2.3.3 Poisson’s ratio

The Poisson’s ratios of a packed bed of coal and the plastic layer were assumed to be 0. The Poisson’s ratio of semicoke was assumed to 0.3 based on previous experimental results [19].

4.2.3.4 Contraction coefficient of coals

Since the coefficients of contraction for the coals used in this study were not available, the coefficients were calculated on the basis of the relation between the coefficient of contraction at the two peaks and coal rank obtained using data available in the literature [20, 21]. The relation between volatile matter content and the coefficient of contraction of each peak is shown in Figure 4.16.

![Figure 4.16 Effect of coal rank on coefficients of contraction](image)

The first peak (Peak 1), which takes place just after resolidification, has a strong dependency on the rank of coal, while second peak (Peak 2) is almost identical for a wide range of coals. The temperature at the first peak strongly depends on the temperature of resolidification and it has been reported that the difference between the temperatures at resolidification and the first peak is approximately 5 °C [20]. On the other hand the temperature at the second peak seems approximately constant as shown in Figure 4.17.
Figure 4.17 Effect of coal rank on temperature of the second contraction peak

Using the relations shown in Figures 4.16 and 17, the coefficient of contraction for all the coal used in this study were calculated by the Spline complement to fit the peaks derived from the relations (Figure 4.18).
4.2.3.5 Dilatation during plastic stage

Swelling and particle bonding in the plastic layer occur simultaneously when the coal bed exceeds the softening temperature and fusion of active constituents and generation of pyrolysis gas take place [22]. Nishioka [23] defined the true dilatation to indicate actual amount of dilatation as

\[ D_T = 100\frac{(V_D - V_C)}{V_C} \]  

(4.13)

where \( V_C \) and \( V_D \) represent a volume of coal before dilatation and an apparent volume of coal after dilatation, respectively. Since the true dilatation is defined on the basis of the true coal volume before dilatation and the apparent volume of coal after dilatation, it is possible to measure the true dilatation for an arbitrary packing condition of the coal. Based on the measured true dilatation under various heating rate, the heating rate dependence of the true dilatation [23] is represented as

\[ D_a = 1.114D_0(\log \alpha + 0.42) \]  

(4.14)

where \( \alpha, D_a \) and \( D_0 \) represent the heating rate, true dilatation at the heating rate \( \alpha \) K/min and true dilatation at a heating rate of 3 K/min, respectively. By measuring the value \( D_0 \) in Equation (4.14) experimentally, the true dilatation at an arbitrary heating rate can be estimated from the equation.

Since the true dilatation of the coal samples used was unknown and only the swelling number of the coals was available, the true dilatation was calculated from the relation between the swelling number and the maximum dilatation measured using a Ruhr dilatometer (Figure 4.19) and the relation between the maximum dilatation and the true dilatation (Equation (4.16)).

The relation between the swelling number and maximum dilatation for the coals of volatile matter content from 32.4 to 38.4 wt% dmmf is shown in Figure 4.19.
From the data plotted on the figure, the following relation was derived as it is shown in the figure as a solid line

\[ \text{Maximum dilatation} = 10^{0.277\text{SwN}} - 27.186 \]  
\[ (4.15) \]

where SwN is the swelling number.

From the definition of each value [23] the relation between the maximum dilatation and the true dilatation is as follows

\[ D_r = \left( \frac{\text{Maximum dilatation} + 33}{0.67} \right) \]  
\[ (4.16) \]

Using the above relations, the true dilatation for all the coals used in this study can be estimated.

A total dilatation strain is determined by using the true dilatation from Equation (4.14) and the following equation

\[ \varepsilon^D = \left( \frac{D_r}{100 + 1} \right)(1 - P) - 1 \]  
\[ (4.17) \]
where $P$ represents the porosity of the plastic layer during dilatation. It was assumed that the dilatation takes place in the same direction to the temperature gradient because of the viscosity gradient in the layer.

The porosity of the plastic layer and semicoke is defined as a function of temperature as follows

$$P(\theta) = 1 - \frac{\rho_{\text{app}}(\theta)}{\rho_{\text{true}}(\theta)}$$

(4.18)

where $\rho_{\text{app}}$ and $\rho_{\text{true}}$ represent the apparent density and the true density of coke. The porosity can be estimated by defining the value of $\rho_{\text{app}}$ and $\rho_{\text{true}}$ for each element.

According to the method of Miura et al. [13], $\rho_{\text{true}}$ was estimated from the relation between the true density and the weight fraction of hydrogen in the coal.

$$\rho_{\text{true}}(\theta) = 1.03\omega_H(\theta)^4 - 18.9\omega_H(\theta)^3 + 1.38 \times 10^4\omega_H(\theta)^2 - 5.32 \times 10^3\omega_H(\theta) + 2.23 \times 10^3$$

(4.19)

where the weight fraction of hydrogen $\omega_H(\theta)$ is calculated using the following equation and the total weight generation $W_i$ of the $i$ th composition obtained when Equation (4.7) is solved

$$\omega_H(\theta) = \left(\omega_H^0 - 100\sum f_k W_k\right) / \left(1 - \sum W_i\right)$$

(4.20)

In this equation, $\omega_H^0$, $k$ and $f_k$ represent the weight fraction of hydrogen in the coal, the gas species in pyrolysis gas, which contains hydrogen, and the weight fraction of hydrogen in each gas species. The initial fraction of hydrogen in the coal is estimated in relation to the volatile matter content (d.b. wt%) of coal based on the Miyazu’s equation [24].

$$\omega_H^0 = 2.82 + 0.106\text{VM} - 0.0008\text{VM}^2$$

(4.21)
On the other hand, $\rho_{\text{app}}$ is calculated, using the change of element volume by dilatation and contraction during creep analysis, and weight decreases by the thermal decomposition reaction by

$$
\rho_{\text{app}}(\theta) = \frac{w_c(\theta)}{v_c(\theta)} \quad (4.22)
$$

$$
w_c(\theta) = w^0_c - \sum W_{le} \nu_{le}(\theta) \quad (4.23)
$$

### 4.2.4 Estimation of the coke strength development during carbonisation

The tensile strength was chosen as the strength parameter to represent strength development, since in the previous chapter the tensile strength was measured and evaluated for the cokes made from same coals used in this study. It is a suitable parameter for assessing the fracture of coke, since coke behaves as a brittle material. The tensile strength can be described in terms of the strength of the coke matrix, the nature of the porous structure and porosity as follows

$$
\sigma = \sigma_0 \exp(-cP) \quad (4.24)
$$

where $\sigma_0$, $c$ and $P$ are the strength of coke matrix, porous structure coefficient and porosity. By estimating each parameter in the equation, the tensile strength during carbonisation for various conditions can be obtained.

#### 4.2.4.1 Strength of coke carbon matrix

The strength of coke matrix is estimated using the relation between the fraction of the pyrolysis reaction and the previously estimated strength of matrix for each coke made from coals carbonised in the small scale furnace experiments. The strength of the coke matrix is obtained from following equation. This was obtained by assuming the strength develops after resolidification.

$$
\sigma_0 = a \nu^2 \left( \nu - \nu_{\text{fold}} \right)^2 \quad (4.25)
$$
where \( a \) is a coefficient and \( \nu_{\text{fr}} \) is the fraction of reaction at resolidification. The strength of matrix for each coke was calculated using Equation (4.25) and compared to experimental values in Figure 4.20.

![Figure 4.20](image)

**Figure 4.20** Relation between the fraction of reaction and the strength of the matrix

### 4.2.4.2 Porous structure coefficient

The porous structure coefficient is calculated from the maximum fluidity (MF) and the swelling number (SwN) using the following equation

\[
\text{Porous structure coefficient} = -0.619 \times \text{MF} - 0.245 \times \text{SwN}
\]  

Equation (4.26)

The equation is based on the previous results from the small scale furnace [25]. The results obtained from above equation and the experimentally-obtained coefficients for the cokes are shown in Figure 4.21. The coefficient obtained is in good agreement with the coefficient for a wide range of coking properties.
It is well known that the coking properties are affected by heating conditions. The effect of heating rate during the plastic stage was taken into account by the reported relation between heating rate and coking properties.

(a) Heating rate dependence of the maximum fluidity
The maximum fluidity of coal at various heating rates can be calculated using the equation proposed by Aramaki et al [26] i.e.

\[ MF_{a} = MF_{0} - 1.894 \log \left( \frac{3}{HR} \right) \]  

where \( MF_{a} \) and \( MF_{0} \) are the maximum fluidity at a heating rate of \( \alpha \) °C/min and 3 °C/min, respectively. HR is the heating rate during the plastic stage.

(b) Heating rate dependence of the swelling number
Because there is no relation available to estimate the effect of heating rate on the swelling number directly, the effect was estimated from the effect on the true dilatation. Using the equations which relate the maximum dilatation and the swelling number (Equation
ELUCIDATION OF FISSURE FORMATION PHENOMENAS (4.15), the maximum dilatation and the true dilatation (Equation (4.16)) and heating rate and the true dilatation (Equation (4.14)), the effect of heating rate on the swelling number can be derived.

A flow sheet for the coke property estimation model is shown in Figure 4.22.
4.3 RESULTS AND DISCUSSION

4.3.1 Temperature model

4.3.1.1 Evaluation of the model

Figure 4.23 shows the comparison between measured temperature histories and prediction by the model described in the previous section. The predicted temperature history is in good agreement with measured one especially at the temperature range of 200-700 °C where coke quality in terms of pore structure is determined and most fissuring is considered to take place. Therefore, the calculated results from the model developed is capable of simulating the temperature history during carbonisation sufficiently well to discuss stress generation and strength development.

![Figure 4.23 Comparison of measured and calculated results](image)

Figures 4.24 and 4.25 show comparisons between measured temperature histories and predictions under various heating conditions used in this experiment. Errors in prediction apparent in the figures are considered to be mainly attributable to the thermophysical properties used in the model. Nevertheless the predictions are satisfactorily in agreement with measured temperature histories and so can be used to describe the heating conditions for the purposes of the model.
4.3.1.2 Effect of heating conditions

(a) Effect of heating rate

Figure 4.26 shows effect of heating rate on temperature history at various stages of carbonisation. The parameters, HR35, HR56 and HR68 plotted in the y axes are heating rates between 300-500, 500-600 and 600-800 °C, respectively. Each temperature range roughly corresponds to the temperature ranges of the plastic stage of coal, and the first
and second peaks of the contraction curve of semicoke. In other words, HR35 affects the pore structure of semicoke and HR56 and HR68 are related to the thermal stress generated in semicoke caused by contraction during carbonisation.

![Graphs showing effect of heating rate on fissure formation](image)

**Figure 4.26** Effect of furnace wall heating rate on the heating rate at various stages of carbonisation

The effect of heating rate on the degree of fissuring is shown in **Figure 4.27**. The effect is shown as the difference in distance between the fissures formed at the shown heating rate and under base heating condition. The distance between fissures under heating rates of 3 and 5 °C/min, which are slower heating rates than the base condition, decreased near the oven wall. This means that number of fissures generated in the coke increased at slower furnace heating rates. Since thermal stress generated in coke decreases as heating rate decreases, the results are difficult to understand directly from the estimated heating conditions across the oven width as shown in **Figure 4.26**. This shows that the heating
rate near the oven wall under 5 and 3 °C/min rates is considerably slower than the base condition for all carbonisation stages. Therefore, a change in the coke strength during carbonisation in relation to the heating condition is a possible cause for the contradictory results obtained.

**Figure 4.27 Effect of heating rate on degree of fissuring**

**Figures 4.28 and 4.29** show the difference in estimated heating rate through the plastic stage and the difference in the micro strength index of cokes made at the specified heating rate and under the base heating condition, respectively. It can be recognised that the strength of coke tends to degrade when the heating rate through the plastic stage is slower.

**Figure 4.28 Effect of heating rate on the heating condition around plastic stage**
The results from the small scale carbonisation furnace can provide a possible explanation for this tendency. According to the results, coke pore quality is governed by two parameters, the maximum fluidity and the swelling number of coal and both properties are known to improve when heating rate through the plastic stage is faster \([26, 23]\). Therefore, it is reasonable that the coke is weaker when heating rate in the plastic stage is slower. The vague correspondence between Figures 4.28 and 4.29 is considered to be attributable to a non-linear relation between heating rate and coke strength and errors in both calculation and strength measurement. Nevertheless, it is apparent from the similarity between Figures 4.27 and 4.29 that the coke strength is one of the main factors influencing the fissuring phenomena.

To represent effects of heating rate on coke quality and thermal stress in one parameter, the following simple parameters were introduced.

\[
dHR56/HR35 = \frac{HR56}{HR35} - \frac{HR56}{HR35} \text{ (base)} \quad (4.28)
\]
\[
dHR68/HR35 = \frac{HR68}{HR35} - \frac{HR68}{HR35} \text{ (base)} \quad (4.29)
\]

These parameters are designed to represent the ratio between positive (coke quality) and negative (thermal stress) effects of heating rate on fissure formation and how these change when the heating rate differs from the base heating condition. Accordingly, a
positive value of both parameters means an increase in the effect of thermal stress over coke strength improvement and consequently more fissures are likely to generate. **Figure 4.30** shows the distribution of the parameters across the oven width. Despite the lower heating rates considered, both parameters are positive near the oven wall. This means that changes in heating rates in the temperature ranges of 500-600 and 600-800 °C are relatively small compared to that near the plastic temperature range and therefore fissures are likely to be generated because of the poorer coke strength.

**Figure 4.30 Effect of heating rate on the parameters**

The trends shown in **Figure 4.30** are in good agreement with that in **Figure 4.27**. Therefore, the change in the degree of fissure formation due to a change in heating rate
can be understood in terms of the effects of heating rate on coke strength and thermal stress.

(b) Effect of final furnace temperature
The effect of final furnace temperature on the fissuring phenomena can also be discussed on the basis of the predicted heating conditions across the oven width. Figure 4.31 shows heating rates at various carbonisation stages with three furnace wall temperatures, 1100, 1150 and 1200 °C. Unlike the effect of heating rate, the effect of furnace wall temperature on the heating rate at various stages of carbonisation appears mainly near the middle of the oven width.

Figure 4.31 Effect of furnace wall temperature on various carbonisation stages

The effect of furnace wall temperature on the degree of fissuring is shown in Figure 4.32 as the difference between the mean separation of fissures in cokes made using base
heating conditions and with other furnace wall temperatures. The measured distance between fissures was relatively small near the oven wall and the oven centre, but wider at the middle of the oven width when the final furnace temperature was higher than that in the base condition. Since the heating rate at middle of the oven width is faster compared to the base condition, this result is also difficult to explain purely on the basis of the thermal stress generated under the estimated heating conditions across the oven width, i.e. if the effect of coke strength is ignored.

![Figure 4.32 Effect of furnace wall temperature on degree of fissuring](image)

This trend is considered to be caused by a change in coke strength due to the change in heating rate through the plastic stage. Figures 4.33 and 4.34 show the heating rate through the plastic stage and the measured micro strength index across the oven width. With a higher furnace wall temperature, the heating rate at the middle of the oven width increases significantly from the base condition and as a consequence the micro strength index increased. It is assumed that this coke strength improvement prevents fissure generation and causes the increase in the distance between fissures at the middle of oven width shown in Figure 4.32.

To understand changes in degree of fissuring near the oven wall and the oven centre, parameters defined in Equations (4.28) and (4.29) are used. As shown in Figure 4.35, the decrease in distance between fissures near the oven wall can be explained by these parameters. However, the parameters fail to explain the increased tendency for fissuring near the oven centre.
Thus it has been shown that it is possible to predict the effect of heating conditions on fissure formation on the basis of the concepts introduced in this study, i.e. that the heating conditions affect not only the thermal stress, but also the coke strength. The degree of fissure formation is governed mainly by the relationship between these two factors. However, since these parameters are simple and do not represent coke quality and thermal stress precisely, their capability to explain the measured degree of fissuring has limitations. Therefore, a more complete model, which is capable of predicting coke
quality and thermal stress while taking into account the effect of heating conditions is required before the mechanism can be discussed further.

![Graph](image)

**Figure 4.35** Effect of furnace wall temperature on the parameters

### 4.3.2 Stress and strength model

#### 4.3.2.1 Evaluation of the strength model

Since, for each sample, the tensile strength distribution across the oven width could not be obtained, it is not possible to evaluate the strength estimation model from the measured strength. Therefore instead of the tensile strength, the micro strength index,
which could be obtained from a relatively small amount of specimen, was used to evaluate the strength model. For comparison with the measured micro strength index across the oven width and to evaluate the strength model, the micro strength index distribution across the oven width was estimated using the estimated strength of the coke matrix and the coke porous structure coefficient from the strength model. The micro strength was estimated from the following equation obtained from a simple statistical calculation based on the data from the previous experiments.

$$\text{MSI}=0.01481\sigma_0-9.05495C+96.113 \quad (4.30)$$

where $\sigma_0$ and $C$ are the strength of coke matrix and the coke porous structure coefficient, respectively.

The results obtained are shown in Figure 4.36. The estimated micro strength indices are in fairly good agreement in cases of coals C, D and E. However, in the case of coals A and B, the model overestimated the effect of heating rate near the heated wall. This probably stems from differences in the heating rate dependency of the coking properties of the coal. In the model, effect of heating conditions affects the coking property from strong coking coal to poor coking coal equally. However, if the coking property of coal is sufficiently strong, it might not be improved by the higher heating rate to as great an extent as that of a poor coking coal. Therefore, the over-estimated strength of cokes made from coal-A and B can be explained by the their stronger coking properties. Nevertheless, the strength model is capable of adequately estimating the coke strength across oven width, taking into account the effect of the heating rate.

### 4.3.2.2 Evaluation of the porosity model

A comparison of the calculated and measured porosity is shown in Figure 4.37. The model is capable of estimating part of the porosity variation across the oven width, but as a whole, there is a clear difference between the estimated and measured porosity. This difference is attributable to the error in estimating the true density and the apparent density of coke across the oven width.

Figure 4.38 shows the estimated true density. Although the level of the estimated true density is in reasonable agreement with the measured one and it was possible to estimate...
the difference caused by coal rank, the model failed to predict the difference in true density across the oven width.

Figure 4.36 Estimated and measured micro strength index
Figure 4.37 Estimated and measured porosity
Figure 4.38 Estimated and measured true density
This can be attributable to the coal pyrolysis model, since the true density is estimated on the basis of the change in hydrogen content during carbonisation. The error stems from the slow heating rate during carbonisation in the experiment especially at the later stage of the carbonisation due the rather large oven width. Since the pyrolysis model used in the model was based on the experimental data obtained at a heating rate of around 3-5 °C/min, errors caused by the slow heating rate can be considerable after the long carbonisation period of the experiment. In the model, the pyrolysis reaction terminated at the final stage of carbonisation even at the centre of the oven and consequently constant true density distribution across oven width was estimated.

Figure 4.39 shows the estimated apparent density of coke. The model failed to estimate the apparent density distribution across oven width observed in the measurement. This is especially true for the centre of the carbonisation box, where all estimated results indicated an increase of apparent density while the measured apparent density decreased for most of the cokes. This is considered to caused by the boundary condition used in the model. In the model, the boundary condition at the oven centre was constrained initially and freed after resolidification. Due to the contraction of semicoke at the centre, in the model the coke lump starts to deform concavely at the centre, while in the experiment the coke deformed in a concave shape to some extent, but still porous coke remained at the centre of the charge. Because of this porous coke at the centre, the measured apparent density always decreased at the centre of the charge. Furthermore, the model estimates the apparent density on the basis of the deformation of each of the finite elements, which form the coke lump, and therefore mass transfer during carbonisation was neglected. However, it has been reported that the mass transfer caused by softening and coking pressure during carbonisation affects apparent density [22]. To achieve accurate apparent density estimation, the effect of mass transfer in the semicoke during carbonisation should be included.

In addition to the incompleteness of the model, the measured results can contain errors, since, for all measurements, the amount of specimen available for measurement was limited and properties can vary within each coke lump even in the oven length direction. Nevertheless, the model can provide a base for discussion of the effect of heating conditions on strength, porosity, true density and apparent density, and the consequent
effect on the fissuring phenomena, even if it is too simple model to describe the rather complex phenomena perfectly.

Figure 4.39 Estimated and measured apparent density
4.3.2.3 Evaluation of the fissuring phenomena on the basis of the model

Based on the model, the degree of fissuring in coke samples across an oven width was evaluated in relation to the strength and stress during carbonisation. During carbonisation, coke strength develops as pyrolysis reaction progresses. Thermal stress, which causes fissures in coke, is also generated as the pyrolysis reaction proceeds and the consequent contraction of the semicoke takes place. Therefore, the fissure formation mechanism should be discussed by taking into account the process of carbonisation. In this study an attempt was made to estimate these phenomena namely, development of coke strength and thermal stress generation during carbonisation as explained. A parameter was introduced on the basis of the idea that the degree of fissuring is related to a ratio between strength and stress at each stage of carbonisation. The degree of fissuring, that is, number of fissures generated, was considered to be determined by the maximum value of the ratio between strength and stress through the carbonisation. The parameter is defined as follows

**Max. Stress/Strength:** Maximum value of the stress/strength ratio from resolidification to the end of carbonisation.

This parameter was compared to the degree of fissuring measured in the experiments in relation to the coking properties and the heating conditions.

4.3.2.4 Effect of coal properties

Estimated Max. Stress/Strength distributions across the oven width for all cokes made from coals A to E are shown in Figure 4.40. The distributions across the oven width of the stress, temperature and fraction of reaction at the time when the maximum value of the ratio occurs are shown in Figure 4.41. The ratio varies markedly from coal to coal and the stress, temperature and fraction of reaction at the maximum value of the ratio also differs amongst the cokes. This is due to differences in coal properties in the model, such as contraction coefficient, resolidification temperature and coefficients for the strength determination. Since the ratio was calculated every time step during carbonisation from resolidification, small difference in strength development and stress generation could lead to significant changes in the ratio and the stress, temperature and fraction of reaction at
the maximum ratio. In the case of coal-B, the stress, temperature and fraction of reaction at the maximum ratio change suddenly across the oven width. This is considered to indicate that the maximum point could occur at several stages of carbonisation and the ratio could be changed by a small change in the calculation condition.

![Graph showing effect of coking property on the maximum stress/strain ratio](image)

**Figure 4.40** Effect of coking property on the maximum stress/strain ratio

Trends of the maximum stress/strength ratio distribution across the oven width for all cokes shown in Figure 4.40 are different from the measured fissure spacing shown in Figure 4.42, where the fissure spacing is smallest at the heated wall side and increases towards centre of the charge. Since fissure propagation was omitted in the model, this difference is considered to be caused by change in stress field due to the non-existence of fissures in coke and consequent stress relaxation. Also, the parameter introduced in this study is perhaps too simple to explain every aspect of the fissuring phenomena.
Nevertheless, an average value of the estimated maximum ratio between stress and strength across oven width shown in Figure 4.40 correlates well with an average of the measured fissure spacing across the oven width as shown in Figure 4.43. This clearly indicates that fissure spacing does depend on the maximum ratio between stress and strength during carbonisation and a larger ratio leads to a smaller fissure spacing in the coke.

Apart from the studies carried out by Soule [27], and Klose and Knothe [28], there has been no study which achieved a prediction of fissure spacing or coke size based on mathematical modelling. Since, in the coke-making industry, coke size is controlled by the properties of the coal charge as well as the heating conditions, it is especially
important to predict the effect of the coal qualities on the fissuring phenomena. In this respect, the model demonstrated in this study is the only model which is capable of predicting the effect of the coal properties.

Figure 4.42 Effect of coal property on fissure spacing

Figure 4.43 Relation between the maximum stress/strength ratio and measured fissure spacing
4.3.2.5 Effect of heating conditions

(a) Effect of heating rate

Effect of heating rate on the maximum ratio between stress and strength is shown in Figure 4.44. Although the thermal stress during carbonisation is expected to be smaller under slower heating conditions, the maximum ratio is estimated to be larger under the slower heating rate experienced near the heated wall. This can be explained by the balance between the effect of heating rate on stress and strength during carbonisation.

![Graph showing effect of heating rate on stress-strength ratio](image)

**Figure 4.44** Effect of heating rate on the maximum ratio between stress and strength

As shown in Figure 4.45, the estimated stress at the maximum ratio is smaller when the heating rate is slower. This suggests that the extent of strength deterioration under slower heating rate is more significant compared to that of the thermal stress change and therefore the maximum ratio under slower heating condition is considered to be larger near the heated wall side. The effect of heating rate on strength is shown in Figure 4.46 as a change in the micro strength index. Although the model failed to predict the positive change in the micro strength index at the centre of the oven width, it predicted the tendency of strength deterioration near the heated wall.
The effect of heating rate is shown as the difference in the maximum stress/strength ratio from the base heating condition in Figure 4.47. This can be compared to Figure 4.27, which shows the measured effect of heating rate on the degree of fissuring, but positive and negative values of the parameter in the figure are in the sense opposite to that in Figure 4.27. A positive difference in Figure 4.47 means a larger ratio between stress and strength and hence smaller fissure spacing, which is a negative difference in Figure 4.27. The overall trends in these two figures correspond to some extent and this indicates that the model is capable of predicting the effect of heating rate on the degree of fissure formation, at least to some extent. This result suggests that the effect of heating rate on
the degree of fissuring should be considered not only on the basis of the thermal stress generated, but also on the strength development during carbonisation. The heating rate condition at the heated wall mainly affects the heating rate near the heated wall and the effect becomes less significant towards the furnace centre. The difference in the maximum stress/strength ratio also becomes smaller at the centre of the furnace.

![Figure 4.47 Effect of heating rate on the maximum stress/strength ratio](image)

**Figure 4.47** Effect of heating rate on the maximum stress/strength ratio

(b) Effect of final furnace temperature

The effect of final furnace temperature on the estimated maximum ratio between stress and strength is shown in Figure 4.48. As with the effect of heating rate, the final furnace temperature influenced the ratio in the opposite way to that generally expected. Usually, a higher final furnace temperature is expected to lead to a higher heating rate and hence more fissure generation in the coke. However in this case, the estimated maximum ratio between stress and strength decreases when the final furnace temperature increases, because in this case only the final furnace temperature varies with heating conditions and as the initial heating rate is identical for all final furnace temperatures, the estimated maximum ratios start to show differences from 0.2 fractional distance from the wall. The difference remains until 0.7 fractional distance from the wall and then the ratio becomes almost identical for all conditions.
The change in the ratio also indicates that the final furnace temperature has more effect on strength than on stress. Since the thermal conductivity of coal and coke changes significantly during carbonisation and that of coke is much higher than that of plastic coal, the effect of final furnace temperature could lead a larger effect on the heating rate of plastic coal than that of the semicoke. A higher heating rate at the plastic stage improves the quality of porous structure, which is one of the most important parameters for coke strength. In Figure 4.49, the estimated and measured micro strength index is compared. It is possible that the estimated effect of final furnace temperature is in agreement with the measured one, if an error in the micro strength measurement is considered.

Estimated changes in the maximum ratio from the base heating condition is shown in Figure 4.50. It is difficult to explain the negative change in fissure spacing shown in Figure 4.32 on the basis of the estimated result. Nevertheless the overall trend in estimation is in agreement with that in the measurement.
Figure 4.49 Comparison between estimated and measured strength index

Figure 4.50 Effect of final furnace temperature on the maximum stress/strength ratio
An average value of the estimated maximum stress/strength ratio and the measured fissure spacing across the oven width for all heating conditions shown in Figures 4.44 and 4.48 are plotted in Figure 4.51. In this figure the results for coal-A, which is carbonised under the base heating condition and heated at 3 °C/min, are added. The line placed in the figure is derived from Figure 4.43. The plotted results correlate with the line to some extent and therefore, the concept introduced in this study is also applicable to the effect of heating condition on the fissuring phenomena.

Figure 4.51  Relation between the maximum stress/strength ratio and measured fissure spacing (Effect of heating conditions)
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NOMENCLATURE

[B] Strain-displacement matrix

$C_p$ Specific heat (J/kg K)

c Porous structure coefficient (-)

$D_T$ True dilatation (%)

$D_0$ True dilatation at 3 K/min (%)

$D_\alpha$ True dilatation at $\alpha$ K/min (%)

[D] Stress-strain matrix

$\{d\}$ Displacement of node

E Young's modulus (MPa)

$f$ Weight fraction of hydrogen in coal (-)

$\{f_c^r\}$ Pseudo-nodal force vector due to creep strain

$\{f_{th}^r\}$ Pseudo-nodal force vector due to thermal strain

G Coefficient of rigidity (MPa)

HR Heating rate (K/min)

$h$ Heat transfer coefficient (W/m$^2$ K)

[K] Stiffness matrix

L Length of surface (m)

MF Maximum fluidity (Log ddpm)

MSI Micro Strength Index (-)

P Porosity (-)

$R_0$ Reflectance of coal (-)

$\{r^f\}$ Residual force vector

SwN Swelling Number (-)

t Time (s)

V Volume (m$^3$)

VM Volatile matter (wt%)

$v_e$ Element volume (m$^3$)

$W^*$ Total gas weight generation (kg/kg-coal)

w Weight (kg)
Greek symbols

Δ Increment

\{\varepsilon\} Strain

\{\dot{\varepsilon}\} Equivalent strain rate

\eta Viscosity (Pa s)

θ Temperature (K)

κ Thermal diffusivity (m²/s)

λ Thermal conductivity (W/mK)

ν Fraction of reaction (-) or (%)

ν Poisson’s ratio (-)

ρ Density (kg/m³)

σ Strength (MPa)

σ Stress (MPa)

\{\sigma\} Stress

\{\overline{\sigma}\} Equivalent stress

\{\sigma'\} Deviation stress

τₘ Relaxation time (s)

ωₜ Hydrogen content (wt%)
eff Effective value
i i th gas species
th Thermal
true True value
5 GENERAL DISCUSSION

The aims of this study were to improve the understanding of the fissure formation mechanism during coal carbonisation, to develop means for the estimation of the degree of fissuring of the coke and ultimately to control coke quality under efficient operating conditions. To achieve these objectives, firstly coke strength development during carbonisation and its relation to the coking properties were studied, since this is one of the most important factors in the fissure formation phenomena. Then using the understanding obtained of coke strength development and the effect of coking properties, an attempt was made to understand the fissure formation phenomena observed in an experimental coke oven by constructing a mathematical model and introducing various concepts to explain the phenomena.

Regarding the strength of coke in relation to the fissure formation, it is clearly important to take into account its development during carbonisation, since fissures in coke have been reported to start to propagate in the temperature range 500 to 600 °C [1, 2]. Previously, no study has been carried out to elucidate the fissuring mechanism while taking account of the effect of strength development during carbonisation and its relation to the simultaneously-generated thermal stress. As shown in this study, the coke strength develops as carbonisation progresses, and the structure and nature of the coke evolves. To represent this strength development phenomena, some studies have used carbonisation temperature as a parameter [3-7]. Under constant heating conditions or if the general trend of strength development is the prime concern of the study, carbonisation temperature is probably a sufficient parameter to evaluate the coke strength change during carbonisation. However, if the strength development is examined in order to elucidate the fissure formation phenomena, carbonisation temperature alone is not a sufficient parameter, since it can lead to errors as large as those caused by a large difference in coking properties. As demonstrated in this study using the mathematical model, the error in estimating coke strength during carbonisation caused by using the carbonisation temperature as the parameter increases as the heating rate increases. It is impossible to estimate the strength development precisely on the basis of the carbonisation temperature especially in the case of the commercial coke oven, where
heating conditions across the oven width differ markedly and change as the temperature level changes.

To take fully into account the effect of heating condition during carbonisation, a fundamental parameter, which is directly connected to the carbonisation phenomena, is needed. For this purpose the fraction of the pyrolysis reaction was introduced in this study. Since the nature of coke changes in direct relation to the progression of the pyrolysis reaction, the fraction of reaction is considered to be an ideal parameter to represent the coke strength development during carbonisation. As shown in this study, this newly introduced parameter is better than the formerly-used carbonisation temperature to represent changes in the nature of coke, especially as the estimation of the pyrolysis reaction is reasonably accurate.

It was shown by mathematical modelling that the coke strength development varies considerably across the oven width in a commercial coke oven, even when heated to the same final temperature, because of differences in the previous temperature history. Since fissures in coke first generate from the heated-wall side and propagate towards the oven centre, the strength distribution across the oven width is a vital factor. Using the fraction of reaction as the parameter to represent strength development, it is possible to improve the accuracy of the prediction of the coke strength in the mathematical model.

As a porous material, coke strength is evaluated by an empirical equation (Equation (3.5)). Although this equation has no strict physical meaning, the equation has been used for coke strength evaluation [8, 9] and the meaning of the porous structure coefficient $c$ has been examined in relation to the shape of pores [10, 11] and to the pore size distribution [12].

In this study, the meaning of the equation is investigated further in order to further understand the strength of coke by evaluating the strength of the coke carbon matrix as well as the porous nature of coke. Previous studies determined either the strength of the coke matrix [8] or the porous structure coefficient [9], the other factor being assumed to remain constant for all coke samples. Thus the results inevitably contain some effect of the other factor and it can cause major errors in results. In this study, therefore, both the strength of coke matrix and the porous structure coefficient were evaluated simultaneously.
Although the results obtained in this study may not be sufficient to claim general applicability, the results clearly indicate the meaning of each parameter in relation to the structure of coke carbon, the coking properties and the measured porous structure. As shown in Figure 3.12, the strength of coke carbon matrix is related to the carbon structure factor, which as defined in this study represents the degree of graphitisation of coke carbon. From the result it can be concluded that coke carbon with a non-graphitic structure is stronger than that which has a graphitic structure. This result is supported by the concept introduced by Franklin [13], who described the non-graphitic carbon as having a cross-linked structure and termed it hard carbon. It is also shown that the strength of the coke carbon matrix increases as coal rank decreased in the range examined in this study. The strength of coke is usually expected to be weaker as a rank of coal carbonised becomes lower and this seems contradictory to the results obtained in this study. However, the lower strength of coke from lower coal rank can be attributed to poorer coking properties and consequent poor porous structure. In addition, there seems to be no previous experimental data which claim the strength of coke matrix falls as the rank of the coal becomes lower.

Since coke breaks in a brittle manner, it is possible to evaluate coke strength in relation to the theory introduced by Griffith [14]. According to the theory of brittle fracture, the stress to break a material is defined as follows

$$\sigma_c = \frac{1}{Y} \sqrt{\frac{2E\gamma}{C}}$$

(5.1)

where $\sigma_c$ is the fracture stress, $E$ the Young’s modulus, $\gamma$ the surface energy, $C$ the length of the critical crack and $Y$ the shape factor. As is clearly shown in the equation, to improve the strength of a brittle material, it is necessary to decrease the size of the critical crack.

The quality of coke porous structure, as represented by the porous structure coefficient in the empirical equation (Equation (3.5)), was evaluated in relation to the pore size distribution factor and the pore rugosity factor defined in this study. It was shown that a poor porous structure is associated with cokes having a proportion of the smallest pores, i.e., with pore length less than 20 $\mu$m, and/or pores with rough surface. This results can
not be reconciled with the Griffith theory directly, since the smallest pores are not considered to be detrimental in the theory. However, as explained in this study, if the large proportion of the smallest pores reflects poor adhesion between coal particles, the results can be adapted to the theory. In the diametral compression test, fatal fracture in a coke sample has been considered to take place after minor flaws grow under stress to critical size [15]. The rough surface of pores enhances the stress concentration at the pores while poor adhesion between coal particles, represented by a high proportion of the smallest pores, makes initial minor fractures easy to propagate. Thus the generation of major flaws can be favoured by the poor porous nature as defined in this study.

Previous attempts have been made to establish a mathematical model to simulate every phenomena during carbonisation, especially in relation to a prediction of coke quality, i.e., the strength indices [9, 16-22]. With regards to the fissuring phenomena, the few studies reported have demonstrated an estimation of the fissure spacing of the coke mass and consequently the mean coke size [23, 24]. Since the coal carbonisation process is a complex phenomena and there are so many properties and parameters to be used to establish a mathematical model, inevitably many assumptions have to be made to perform modelling. For modelling of the fissuring phenomena, mechanical properties of coal through to coke during carbonisation, i.e., Young’s modulus, fracture toughness, Poison’s ratio and viscosity, are necessary. However, there is very little data available, even for the properties of a carbonised coke. Thus the calculation has been performed with a constant fracture toughness throughout the carbonisation period.

As discussed earlier, fissuring can take place just after resolidification and so prediction of fissure propagation on the basis of the strength of carbonised coke samples can lead to a major error. In this study, therefore, development of coke strength during carbonisation is taken into account. Since a fissure is generated only when the developing thermal stress exceeds the developing coke strength, the degree of fissuring was evaluated in relation to the ratio between the stress generated and the coke strength developed during carbonisation. The concept that fissuring takes place during carbonisation when the developing thermal stress exceeds the developing coke strength proved to be applicable to explain the fissuring phenomena, since a reasonable correlation was observed between the maximum stress/strength ratio during carbonisation and degree of fissuring observed in a coke lump. The relations shown in Figures 4.43 and 4.51 may not seem particularly
precise, but this is inevitable if the data is obtained by counting the fissures visible in the coke and only a limited sample is available. Since the results shown on the figures can be included in a single relation, the concept is capable of evaluating the effect of heating conditions, as well as coal properties, on fissuring phenomena. Although the concept introduced is simple, it is based on the fundamental mechanism of fissuring and should be taken into consideration in further modelling of the phenomena.

However, in simulating the phenomena, the model developed in this study also includes some assumptions and limitations. Since, in the model, propagation of the fissures in coke lump is neglected in the stress field estimation, and consequently stress relaxation could not be taken into account, the stress field estimated during carbonisation inevitably differs from the real stress field. This is considered to be one reason why the maximum stress/strength ratio across an oven width has no reasonable correlation with the measured distribution of the distance between fissures in the coke across the oven width. Because in this study, actual experimental data for coke strength estimation is limited, further coke strength data should be measured for various coke samples to improve understandings of the coke strength development phenomena during carbonisation. However, since it is difficult to obtain enough coke strength data due to difficulties in the measurement, ultimately a modelling of the coke strength development phenomena during carbonisation should be achieved on the basis of the coal properties and carbonisation conditions.
REFERENCES

6 CONCLUSIONS

1. The final carbonisation temperature has been shown to be an insufficient parameter to describe the strength development during carbonisation when the heating conditions are not constant. This is because the strength development directly relates to the thermal decomposition reaction and consequent structural changes in the coke carbon matrix. Therefore, the development of the strength of coke during carbonisation depends not only on carbonisation temperature, but also on other heat treatment parameters, i.e., the temperature history. It is possible for the effect of temperature history to be taken into account by using the fraction of pyrolysis reaction as a characteristic parameter. Based on this treatment, the strength development under arbitrary heating conditions can be estimated, as long as the estimation of the fraction of pyrolysis reaction is reasonably accurate.

2. The effect of temperature history on coke strength development in a commercial coke oven has been demonstrated in this study by means of a mathematical model, which made it possible to estimate the temperature history and the fraction of pyrolysis reaction during carbonisation, with the derived relationship between the fraction of reaction and the strength of coke matrix. The development of the strength of coke matrix during carbonisation in a commercial coke oven differed considerably across the oven width even for the same carbonisation temperature. Since this difference in strength caused by the temperature history is almost the same as the difference in strength of cokes made from a wide range of coals, it is considered that the effect of temperature history could influence the formation and propagation of fissures in coke during carbonisation.

3. The effect of coal properties on the tensile strength of coke has been discussed by separating the effect on the tensile strength of the matrix strength factor and the porous structure factor. The matrix strength of coke carbon was evaluated on the basis of graphitic or non-graphitic nature of the coke carbon structure. It appears that the coke with a larger carbon structure factor, i.e., a carbon structure closer to that of non-graphitic carbon, tends to have a stronger matrix strength due to the cross-linking of layers within the carbon structure. The carbon structure factor depends on the rank of
coal and, for the range of coal rank used in this study, the coke made from lower rank coal tended to have a larger carbon structure factor. Thus, the coke matrix strength tended to be stronger for coke from lower rank coal over the limited range of coal rank studied.

4. It was clearly demonstrated that the porous structure was governed by the coking properties. For the range of coals used, the porous structure improved as the maximum fluidity and the swelling number of the coal increased. The quality of the porous structure can be evaluated on the basis of the pore size distribution and the smoothness of the pores as defined in this study. Both parameters were considered to represent the state of adhesion between coal particles.

5. Young's modulus of coke was determined from results of the diametral compression test. Although the number of the samples was not enough to provide accurate values, the effective Young's moduli obtained for all coke samples were similar to previously obtained results and are considered adequate for the thermal stress estimation. It was shown that Young's modulus was related to the tensile strength. Using this relationship it is possible to take into account the effect of coal properties and heating conditions when estimating the Young's modulus.

6. For cokes produced in the experimental oven, the average distance between fissures had no obvious relation with volatile matter content, which governs the extent of shrinkage and hence the stress imposed on a semicoke during carbonisation. On the other hand, difference in the micro strength, seems to provide a reasonable correlation to the degree of fissure formation. It was considered that either stress imposed on the coke or the strength of the coke by itself can not describe the degree of fissure formation accurately. Thus, it is important to take into account the factors influencing both strength of coke and the stress generated in coke, i.e., coking properties, heating conditions and coal volatile matter, in order to estimate fissure formation in coke during carbonisation.

7. Both the heating rate and the final temperature of the heated wall in the experimental furnace affect the degree of fissure formation in the coke. It was shown that more fissures were generated in the coke when using a slower heating rate, even though a lower thermal stress is expected to be generated. In the case of a higher furnace
temperature, the degree of fissuring in the coke near the centre of the oven width decreased, possibly because of the higher heating condition during the plastic stage.

8. The effect of heating conditions on the fissure formation phenomena can be estimated to some extent from the heating rates in the temperature ranges of 300-500 °C (HR35), 500-600 (HR56) and 600-800 °C (HR68). Each temperature range roughly corresponds to the temperature ranges of the plastic stage of coal, and the first and second peaks of the contraction curve of semicoke. In other words, HR35 affects the pore structure of semicoke and HR56 and HR68 affect the thermal stress in semicoke caused by contraction during carbonisation. The change in the degree of fissure formation is explained by the parameters dHR56/HR35 and dHR68/HR35, which represent the ratio between the effect of heating rate on thermal stress change and the change in coke strength from the base heating condition.

9. The model established for coke strength estimation is capable of estimating the tendency of the coke quality to change across the oven width. However, for the coke made from the good coking coal, the estimated results had rather large errors compared to those for the poor coking coal. This indicated that the linear relation used in the model between coking properties and heating rate is not accurate and causes errors in estimation if the coking properties are good.

10. An attempt was made to explain the degree of fissuring generated across the oven width on the basis of the maximum ratio between estimated thermal stress and strength. It was clearly shown that the model and the parameter introduced is capable of estimating the effect of coal properties on the overall degree of fissure formation.

11. Although the model could estimate general trends of the change in the degree of fissure formation across the oven width in relation to the heating conditions, it failed to predict the detailed behaviour across the oven width. Since the coke sample is not large enough to detect small change in heating conditions, the results are partly attributable to the coke sample rather than the model. Nevertheless the model and the parameter introduced are relatively simple concepts with which to describe the complicated phenomena of fissure formation and further development/modification is required to achieve this.