# A MECHANISTIC STUDY OF COAL SWELLING AND CHAR STRUCTURE EVOLUTION DURING PYROLYSIS—EXPERIMENTS AND MODEL PREDICTIONS

A Thesis Submitted in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

By

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I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

(Signed) (Jianglong Yu)

TO SHUJUAN AND WALTER ...

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### ABSTRACT

This work presents a systematic study on swelling and char formation during pf coal pyrolysis using both experimental measures and modelling. By using the density fraction samples, i.e. F1.25, F1.30, F1.35, F1.50 and S1.50, prepared using the sinkfloat method, transient observations using a single particle reactor (SPR) and the analysis of drop tube furnace (DTF) chars prepared at atmospheric pressure consistently reveal the heterogeneity of the pyrolysis behaviour and char structures from pf coal. Particles from light density fractions, i.e. F1.25 and F1.30, experience intensive softening and swelling during heating. Apparent bubbling phenomena have been observed in single particle experiments, which is responsible for the coal swelling. On the contrary, particles from heavy density fraction samples, i.e. F1.50 and S1.50, do not exhibit softening and swelling. Correspondingly, the porosity of DTF chars decrease drastically for heavy density fraction samples. It is observed that Group I chars (porous structure) are mainly generated from two light density fraction samples, while Group III chars (solid structure) are yielded from heavy density fractions. The medium density faction sample contains a mixture of different types of chars. The heterogeneity of char characteristics is attributed to the variations in the raw coal properties among different density fractions. The characters of PEFR (pressurized entrained flow reactor) chars prepared at the elevated pressure of 2.0 MPa are examined, and compared with PDTF (pressurized drop tube furnace) and DTF chars. Consistent with previous work, the results suggest that high pressures increase the swelling, the number of bubbles and char porosity, while the population of both cenospheric char and solid char decreases at elevated pressures.

A mathematical model for coal swelling and char structure formation of single coal particles during devolatilization is developed based on a simplified multi-bubble mechanism. The char formation has been considered as two successive steps: the multibubble stage followed by a single bubble stage. During the multi-bubble stage, the rupture of bubbles is a rate-controlled process, during which the volatile release is determined by the bubble rupture rate. When the cenospheric char structure is formed, single bubble model applies. During this stage, the bubble rupture is controlled by the wall stress, and the volatiles are released through both bubble ruptures and direct diffusions of volatiles to the particle surface. The sensitivity study has been carried out, based on which the parameters for the present modelling work have been determined. Comparisons of the model predictions with the experimental data show that the present model predicts the experimental trends of the coal swelling and char structure characteristics under different heating conditions. As an advancement of previous work, the model provides a complete description of the char structure evolution process of pf coal during pyrolysis. From the standard parent coal properties of density-fraction samples, the present model predicts the heterogeneity of the char structure in the same coal, and estimates the distribution of char types, i.e., the Group I, II and III chars. The model predicted results agree with the experimental measurements.

Overall, the experimental observations and model predictions from this study consistently reveal the heterogeneity of char characteristics owing to the heterogeneous nature of coal. In addition to the dominant role of coal macerals, the influence of ash level in coal on char formation is identified. In the meantime, heating conditions under which coal is heated have a significant impact on char formation. Smaller particle sizes tend to have a higher swelling under the present experimental conditions, while the model predicts an increase in the swelling for large particle sizes. High heating rates increase the swelling ratio from both experimental observations and model prediction. Pressure plays a significant role in char formation, and favours the formation of foam char structures with a high porosity. An optimum pressure range has been predicted, which is consistent with the literature data.

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# NOMENCLATURE

$C_b$	Molar concentration of volatiles inside the bubble, $mol/m^3$
$D_e$	Effective diffusivity of volatiles through the porous liquid shell, $m^2/s$
$D_L, D_g$	Diffusivity in liquid phase and in gas phase, $m^2/s$
$E_b$	Bubble escaping rate, bubble/s
$\phi_m$	Metaplast content in coal mass, %
MW <sub>v</sub>	Molar weight of volatile, kg/mol
<i>n</i> <sub>b</sub>	Total number of bubbles inside of the particle
<i>n</i> <sub>m</sub>	Molar mass inside bubbles, <i>mole</i>
<b>P</b> <sub>θ</sub>	The ambient pressure, MPa
$P_b$	Internal pressure of bubbles, MPa
R	Gas constant, 8.314N-m/g.mole.K
$oldsymbol{ ho}_{ heta}$	The true density of the coal particle, $kg/m^3$
<b>r</b> <sub>b</sub>	Bubble radius, m
$R_{p}, R_{p\theta}$	Particle radius and initial particle radius, $m$
Rt	Devolatilization rate, calculated from CPD, wt%/s
$\sigma, \sigma_{\theta}$	The surface tension of the coal melt, $Nm$
Sw, Swc	Wall stress (MPa)
t, dt	Time, s
<b>T</b> , <b>T</b> <sub>c</sub>	Temperature, critical temperature, $K$
Ts, Td	Softening temperature and re-solidification temperature $(K)$
$W_{p0}$	Particle weight, g
yv	Cumulative yield of the volatile, %
$\delta n_b$	Bubble number ruptured at the particle surface
Е, ЕО	Porosity of the coal particle, %
μ, μс	The viscosity of coal melt, Pa.s

# ACRONYMS

a.d.	Air dry basis
С	Cenoshpere
CCSD	Cooperative Research Centre for Coal in Sustainable Development, Australia
CPD	Chemical Percolation Model for Devolatilization
d.a.f.	Dry ash free bassis
d.b	Dry basis
DTF	Drop tube furnace
F	Foam char structure
FG-DVC	Functional Group-Depolymerization, Vaporization, and Cross-linking
IGCC	Integrated Gasification Combined Cycle
L, V, I	Liptinite, vitrinite and inertinite, respectively
MIP	Mercury intrusion porosimetry
MMMF	Moisture mineral matter free basis
NMR	Nuclear Magnetic Resonance
PEFR	Pressurized entrain flow reactor
pf	Pulverized fuel
PFBC	Pressurized Fluidized Bed Combustion
PSD	Particle size distribution
SEM	Scanning electronic microscope
SPR	Single particle reactor
TGA	Thermogravimetry
VM	Volatile matter
WMR	Wire-mesh reactor (also refered to as heated grid, or heating screen)
XRD	X-ray diffraction

### CHAPTER 1. INTRODUCTION

#### 1.1. Background

Coal is the most abundant fossil fuel in the world (Elliott et al., 1981). The majority of coal is utilized through firing for energy supply. For instance, coal is responsible for 56% of all the electricity produced in the U.S. The coal production increased from 613 *MM* ton in 1970 to 1075 *MM* ton in 2000, and about 92% of the coal used in the U.S. today is for electricity generation (Winschel, 2001). Worldwide, coal continues to dominate the energy supply in the future and play an increasing role, in particular, in developing countries.

However, the utilization of coal has also caused severe environmental problems, such as emissions of the pollutant gases, the greenhouse gas and fine particulates. The development of clean and efficient coal utilization technologies have been promoted owing to the increasing political and environmental pressures (Harris et al., 1995). In particular, Integrated Gasification Combined Cycle (IGCC) power generation is considered as a viable technology for clean coal utilization in the future (Takematsu et al., 1991; Harris et al., 1995).

Coal utilization processes, such as combustion or gasification, generally involve several steps (Smoot et al., 1979), i.e. devolatilization of the organic materials leaving char residues behind, homogeneous reactions of volatiles with the reactant gases and heterogeneous reactions of the char with the reactant gases during which ash is formed. The devolatilization process exerts its influence throughout the life of the solid particles from injection to burnout (Solomon et al., 1994), therefore is the most important step, which needs to be considered in modelling the coal combustion (Williams et al., 2002).

While volatiles are generated during devolatilization, the physical structure of char particles change significantly, some accompanied by particle swelling (Howard, 1981). The complexity of the char structure lies in the facts that the char structure itself is highly heterogenous within one individual particle and among different char particles, the chemistry of char is strongly dependent on raw coal properties (maturity and petrographic composition), and the char structure is strongly dependent on heating conditions, e.g., temperature, heating rate and ambient pressure, etc. Understanding of the coal swelling and the char structure formation during pf coal pyrolysis is essential to the development of advanced coal utilization technologies, e.g., IGCC. It is well known that during pulverized coal combustion and gasification, the behaviour of individual coal particles in a given coal vary markedly due to the variation of their maceral composition. Particles with different maceral constituents generate different types of char structure (Benfell, 2001), and the char structure has a significant impact on the subsequent char reactions and ash formation (Wall et al., 1992; Liu, 1999a; Benfell et al., 2000; Wu, 2000<sup>b</sup>; Wall et al., 2002; Wall et al., 2002<sup>a</sup>). This has received wide research interests over the past decades. However, full understanding of char structure formation has not been achieved.

This work presents a mechanistic study of the char structure evolution of bituminous coals during the devolatilization process. Experimental investigations are conducted using a single particle reactor (SPR), a drop tube furnace (DTF) and a pressurized entrained flow reactor (PEFR). These experiments provide information of swelling and bubbling behaviour of coal particles during heating, and effect of heating conditions on the char structures. A mathematical model for coal swelling and char structure evolution has been developed. The model aims at providing mechanistic interpretations to the

swelling behaviour and the structure evolution of char particles, in particular the heterogeneity of char structures, from the standard coal analysis data.

#### 1.2. Outline of the thesis

In the present context of the thesis, chapter 2 provides an overview of previous studies of coal pyrolysis behaviour, in particular, the experimental study and modelling effort on char structure of the bituminous coal in the open literature. Chapter 3 describes experimental approaches used in the present study. Chapter 4 reports experimental observations of pyrolysis behaviour of individual coal particles from density-fractions using the single particle reactor, and provides some mechanistic information for particle swelling and morphology changes. Chapter 5 reports experimental results of the chars prepared in the drop tube furnace (DTF) using density separated coal samples. Chapter 6 details the development of the char structure model based on a simplified multibubble mechanism and the sensitivity study of the model. The model validation is described in chapter 7. In chapter 8, effect of pressure on char formation is discussed based on the analysis of the chars prepared in the pressurized entrained flow reactor (PEFR) in this study and the observations of previous studies conducted in this centre using a pressurized DTF. On the basis of the above investigations, conclusions are drawn in chapter 9. Some important issues are also addressed as suggestions for future work.

## **CHAPTER 2. REVIEW OF LITERATURE**

During devolatilization, coal experiences extensive chemical and physical transformations resulting in solid chars with complex structures, which are strongly dependent upon coal type and heating conditions. To understand the char structure formation, it is important to know the nature of coal itself, and the effect of heating conditions on the devolatilization behaviour and char formation.

#### 2.1 Coal and its heterogeneity—general descriptions

As a sediment rock, coal varies significantly in its chemical and physical properties depending on its maturity and geological environments of the coalification. In standard systems, coal is generally classified by its rank, with fixed carbon content and calorific value as major indicators (Averitt, 1981; Berkowitz, 1985; Smoot et al., 1985; Smith, 1994), and is termed as lignite, sub-bituminous coal, bituminous coal and anthracite. The major transformations in coal properties with increasing the coal rank can be summarized as (Borrego et al., 2000): (1) a drop in moisture and a marked decreases in oxygen content due to the loss of hydroxyl, carbonyl and carboxyl groups occurring in the first place, followed by (2) a removal of aliphatic and alicyclic groups, which causes an important reduction of volatile matter content, with a parallel increase in aromaticity during the bituminous coal stage; (3) the anthracite stage is characterized by a rapid fall of hydrogen content and a particularly strong increase in both the reflectance and the optical anisotropy. An increase in the aromaticity of coal with the rank was reported by Whitehurst et al (Whitehurst, 1978), for which the aromatic carbon content increases from  $40 \sim 50\%$  for sub-bituminous coal to over 90% for anthracite. Figure 2.1 (a) and (b) provides an overview of major coal properties as a function of coal rank (Averitt, 1975; Averitt, 1981; Berkowitz, 1985). Owing to the changes in its properties, the behaviour of the coal of different rank varies drastically during combustion and gasification (Smoot et al., 1979).



(a) Major properties of coal as a function of rank



(b) Reflectance of coal as a function of carbon content

**Figure 2.1.** Major properties of coal as a function of rank after Berkowitz (Averitt, 1975; Berkowitz, 1985).

Coal is well known as a heterogenous substance with a mixture of organic material (the coal matrix) and inorganic material (mineral matters) (Neavel, 1981; Van Krevelen, 1981; Berkowitz, 1985). Macroscopically, coal has a pronounced banded feature, recognized as 'bright', 'predominantly bright', or 'dull' in the appearance (Berkowitz, 1985; van Krevelen, 1993). The identifiable 'banded components' are termed lithotypes. Microscopically, the organic material of coal consists of complex maceral constituents, classified as three groups, i.e. liptinite (exinite), vitrinite and inertinite (micrinite). Since different macerals are derived from different original plant tissues or coalified in different geological environment, there are remarkable distinctions in their chemical and physical properties among the different maceral groups. In general, volatile content, hydrogen content and H/C ratio appear in the order: liptinite<inertinite. With increasing the coal rank, the change in properties, such as chemical composition and

reflectance, of each maceral group follows its own path, as shown in **Figure 2.2** (*a*) and (*b*). For most of the world coals, vitrinite group is the most abundant constituent. There is a tendency that the reflectance of vitrinite is used as the indicator of coal rank (Bailey, 2002). For pulverized coal, marked variations in the maceral composition exist among individual particles from the same coal (Benfell et al., 2000; Benfell, 2001). During heating, particles with different maceral constituents behave differently, including swelling, volatile yields, char structure, reactivity and ash chemistry. Therefore, the microscopic heterogeneity of coal has attracted wide scientific interests in p.f. coal combustion and gasification, in particular for black coal (Benfell, 2001). However, the variation in the property of the different maceral groups diminishes at high rank (**Figure 2.2**). Therefore, it may be expected that, for high rank coal, maceral components from different groups will behave similarly during combustion (Jones et al., 1985; Jones et al., 1985a).





Figure 2.2. Hydrogen content (a) and reflectance of macerals (b) as a function of coal rank (Van Krevelen, 1981; Berkowitz, 1985).

The chemical structure, i.e., macromolecular network, of coal is extremely important in terms of coal devolatilization behaviour (Smith, 1994), and is obviously a subject too large to be included in this context. In the meantime, coal has a complex pore structure system, which plays an important role during the pyrolysis or gasification (Simons, 1983). Depending on coal type, the pore structure changes dramatically during heating. Therefore, the physical structure of the solid residue yielded during devolatilization is significantly different from that of the feed coal. For softening coal (in bituminous rank), the original pore structures are blocked due to the high fluidity of the coal developed during pyrolysis (Smith, 1994). The char structure is therefore determined by the devolatilization process (thermoplastic properties of the coal melt, volatile yields, heating conditions), rather than by the original pore structure of the coal.

The presence of ash and of the specific minerals in ash may have several potential effects on the combustion of coal (Smoot et al., 1985): (1) Thermal effect. Large quantities of ash change the thermal behaviour of particles. Ash consumes energy as it is heated to high temperatures and changes phase. (2) Radiative properties. Radiative properties of ash differ from those of char or coal, and the presence of the ash provides a solid medium for radiative heat transfer when the carbon is consumed. (3) Particle size. Char particles, toward the end of burnout, tend to break into smaller fragments. This break-up process is undoubtedly related to the quantity and nature of mineral matter in the char. (4) Catalytic effect. Various minerals in the char have been shown to cause increase in char reactivity, particularly at low temperature. However, this effect is far less prominent at high temperature. (5) Hindrance effect. Mineral matter provides a barrier through which the reactants (e.g., oxygen) must pass to reach the char. Toward the end of burnout, high quantities of mineral matter will impede combustion, particularly due to the softening and melting of the mineral matter. The major research interest on the mineral is associated with the operation of the practical furnace (Takematsu et al., 1991; Kang et al., 1992) or the particulate emissions. Coal pyrolysis behaviour may also be affected by some of the abovementioned effect of minerals.

#### 2.2 Coal devolatilization

Coal devolatilization is referred to as pyrolysis when coal is devolatilized in inert gas environment. Devolatilization and pyrolysis are usually not distinguished from each other in literature due to the similar behaviour of coal in the two processes in terms of char chemistry and volatile composition (Hayhurst et al., 1995). The behaviour of coal during pyrolysis under different heating conditions has been extensively studied and reviewed over the past few decades (Anthony et al., 1976; Suuberg, 1977; Howard, 1981; Gavalas, 1982; Serio et al., 1989; Solomon et al., 1992; Solomon et al., 1994; Cai et al., 1998<sup>a</sup>; Alonso et al., 1999; Mill, 2001; Alonso et al., 2001<sup>a</sup>) (Berkowitz, 1985; Saxena, 1990; Hayhurst et al., 1995; Benfell, 2001). During heating, coal particles experience very complex physical and chemical transformations, yielding volatiles and generating solid residues. Early review provided summaries of the kinetics of the coal pyrolysis (Anthony et al., 1976). The experiments, kinetic rates and mechanisms of coal pyrolysis are more recently reviewed by Solomon et al (Solomon et al., 1992). Products resulting from the coal pyrolysis include gases, tar and solid char. Definition of the pyrolysis products has been summarized in literature (Solomon et al., 1992). Gas component can be defined straightforward, including  $CO_2$ , CO,  $H_2O$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_6H_6$  and some sulphur or nitrogen containing gases. Tar is defined as room temperature condensable components, which separate from the solid product during pyrolysis. The remaining solid is char, which includes extractables with large molecular weight.

Experimental investigations involve a variety of either captive or non-captive techniques, e.g., WMR or heating grid (screen), drop tube furnace or gas flow reactor, TGA and fluidized bed reactor. A summary of pyrolysis experimental conditions for different techniques has been provided by Solomon et al (Solomon et al., 1992) and Gavalas (Gavalas, 1982). Apart from the capacity of and the particle size used in the different experimental techniques, heating conditions, e.g., heating rate, peak temperature and pressure, of different reactor vary significantly. Therefore, one must be very careful when comparing the experimental data from different researchers.

It may be noted that the major concern in the present study is the char structure of black coals, in particular the softening coals. Therefore, the following review is largely

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focused on bituminous coal pyrolysis, although some results from lignites or anthracites may also be mentioned for the purpose of comparisons.

#### 2.2.1 Mechanism of coal pyrolysis

The Mechanism of pyrolysis has been summarized in the literature (Anthony et al., 1976) (Howard, 1981; Gavalas, 1982; Saxena, 1990; Solomon et al., 1992; Smith, 1994). The pyrolysis reactions are complex, broadly involving bond breaking, vaporization and condensation or cross-linking, accompanying the change in density of aliphatic group and aromaticity. Saxena (Saxena, 1990) summarized that pyrolysis reactions commence with the rupture of weak bonds. Since a minimum amount of energy is required to overcome the C-C bond energy, pyrolysis reactions do not commence until the temperature is close to 673K. The C–C bonds at the bridge between the ring systems are much weaker than other C–C bonds, particularly the ones in the aromatic ring structures. Therefore, the pyrolysis begins with the cracking of bridges between the ring systems resulting in the formation of free radical groups (such as -CH<sub>2</sub>, -O- and other larger radicals). These free radicals are highly reactive, and combine in the gas phase to produce the aliphatics (mainly methane) and water, which diffuse out of the coal particle. Since polynuclear aromatic compounds diffuse slowly even at high temperature, they start to condense with the elimination of hydrogen. The ultimate product due to the condensation reaction is coke. In addition, at high temperature, CO is also produced through the cracking of heterocyclic oxygen groups. The following typical reactions take place in stages as the temperature is increased.

Cracking: 
$$R-CH_2-R' \rightarrow R-R' + -CH_2$$

Saturation:

 $-OH + H' \rightarrow H_2O$ 

 $-CH_2 + H' \rightarrow CH_4$ 

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Tar production:  $-R-CH_2 + H' \rightarrow R-CH_3$ 

Condensation (cross-linking) reactions:

The R radical is obtained from benzene, naphthalene, phenantherene etc. Oxides of carbon are produced by the following reaction:

$$R-COOH \rightarrow R-H + CO_2$$

Obviously, hydrogen is a key elemental composition in terms of pyrolysis reactions, in particular for tar evolution. The hydrogen in coal is used up partly to produce hydrocarbons and water, and is partly liberated as molecular hydrogen. The hydro-aromatic hydrogen is consumed in three different reactions: (i) in saturating the OH and O radicals to produce water, (ii) by the CH<sub>2</sub> radicals to produce the aliphatics, and (iii) in saturating the larger radicals to produce tar molecules. On the other hand, the aromatically bonded hydrogen is liberated as molecular hydrogen, during the condensation of aromatic nuclei, to produce coke. During gasification process, the objective is to use the hydrogen in coal as efficiently as possible by devolatilization. But the structure of coal is such that it preferentially evolves hydrogen as chemical water and light aliphatics depleting the remaining carbon of much needed hydrogen. Hence pyrolysis always produces tar and char due to the inefficient use of intrinsic hydrogen. Excess hydrogen during hydro-pyrolysis significantly enhances tar and hydrocarbon production (Anthony et al., 1976; Suuberg, 1977; Howard, 1981).
During pyrolysis,  $T_d$  is commonly identified as the active thermal decomposition temperature of coal, beyond which massive weight loss takes place. Berkowitz (Berkowitz, 1985) pointed out that significant thermally-induced structural changes occur without generating major amounts of volatile reaction products below  $T_d$ . These structure changes have important association with the pyrolysis reactions occurring later on. The overall decomposition process is therefore viewed as three successive stages: (i) limited thermal alteration of the original molecular structures (mostly by condensation reactions) at temperatures below  $T_d$ ; (ii) active decomposition, leading to generation and discharge of the bulk of the volatile matter, primarily in the form of tars and light oils, between  $T_d$  and ~550°C; and (iii) secondary degasification, resulting in formation and evolution of a variety of hydrocarbon gases, elemental hydrogen and oxides of carbon over an extended temperature range beyond ~550°C.

An important concept in coal pyrolysis may be the functional group (Whitehurst, 1978). Gavalas (Gavalas, 1982) summarized functional groups and their roles in coal thermal decomposition. The reactivity of coal in pyrolysis can be characterized by the following functional groups, i.e., aromatic nuclei, hydro-aromatic structure, alkyl chains, alkyl bridges and oxygen containing groups, etc. The thermal reactions, e.g., bond dissociation, hydrogen abstraction and hydrogen addition, were also described accordingly.

Nine steps of the pyrolysis reactions were proposed to interpret the volatile evolution by Solomon et al (Solomon et al., 1992). As coal is heated, there are three processes, which occur in the temperature range 200-400°C. These processes are disruption of hydrogen bonds (Step 1), vaporization and transport of the non-covalently bonded 'molecular phase' (Step 2) and low temperature cross-linking in coals with more than 10% oxygen

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(Step 3), which coincides with CO<sub>2</sub> or H<sub>2</sub>O evolution. During primary pyrolysis, the weakest bridges can break producing molecular fragments (depolymerization) (Step 4). The fragments abstract hydrogen from the hydro-aromatics or aliphatics, thus increasing the aromatic hydrogen concentration (Step 5). These fragments will be released as tar if they are small enough to vaporize and be transported out of the char particle (Step 6) under typical pyrolysis conditions, and do not undergo moderate temperature crosslinking reactions before escaping from the particle. The moderate temperature crosslinking reactions (Step 7) are slightly slower than the bridge breaking reactions and appear to correlate with CH<sub>4</sub> evolution. The other event during primary pyrolysis is the decomposition of functional groups to release gases (Step 8), mainly CO<sub>2</sub>, light aliphatic gases and some CH<sub>4</sub> and H<sub>2</sub>O. The release of CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>O may produce crosslinking, e.g., CH<sub>4</sub> by a substitution reaction in which the attachments of a larger molecular weight release the methyl group, CO<sub>2</sub> by condensation after a radical is formed on the ring when a carboxyl is removed, and H<sub>2</sub>O by the condensation of two OH groups or an OH group and a COOH group to produce an either link. The crosslinking is important to determine the release of tar and the visco-elastic properties of the char. The end of primary pyrolysis occurs when the donatable hydrogens from hydroaromatic or aliphatic portion of the coal are depleted. During secondary pyrolysis, there is additional gas formation (Step 8), methane evolution (from methyl groups), HCN from ring nitrogen compounds, CO from ether links and  $H_2$  from ring condensation (Step 9).

Another comprehensive reaction mechanism of pyrolysis was proposed by Jüntgen (Jüntgen, 1987) and overviewed by Smith (Smith, 1994). This mechanism includes the desorption of water at 393 K, distillation of the mobile phase beginning at 523~623 K

forming an aliphatic tar, the formation of tar and gases by the degradation of the macromolecule beginning up to 673 K, and the formation of char by condensation reaction with simultaneous evolution of H<sub>2</sub> and CO at high temperature. This overall picture provides interpretations to some low heating rate experimental data.

Pyrolysis of lignite is comprized of five principal devolatilization phases suggested by Suuberg et al. (Suuberg et al., 1979). Pyrolysis behaviour of softening coals have been described as three stages (Solomon et al., 1988), illustrated in Figure 2.3. Coal undergoes a reduction of hydrogen bonding during stage I, and sufficient labile bond breaking of the macromolecular network occurs to form primary gas and liquid components, which are often referred to as metaplast. The metaplast is generally accepted to be responsible for the coal fluidity (van Krevelen, 1953; van Krevelen et al., 1956; Fitzgerald, 1957; Oh, 1985; Solomon et al., 1992<sup>a</sup>). Bond breaking competes with bond stabilization, which forms char during stage I. Much of the material that is associated with the mobile phase and extractable with suitable solvents is released in this stage. Stage II is featured by bulk evolution of tar, which is considered the lowmolecular-weight component of the metaplast. The remaining high-molecular-weight components in the metaplast re-attach to the char structure by cross-linking reactions, which is important to evolution and the property of char. In FG-DVC model (Solomon et al., 1988<sup>a</sup>; Solomon et al., 1990; Solomon et al., 1992), tar formation is viewed as combined depolymerization and vaporization process. Gas formation is correlated with functional group composition of the coal. Thus coals with different functional group composition will behave differently during pyrolysis. During stage III, char evolves CO and H<sub>2</sub> while continuing to cross-link with further ring condensation.



Figure 2.3. Pyrolysis process of softening coal (after Solomon et al., 1988).

Figure 2.4 presents experimental results of evolution rate and cumulative weight loss of volatile products for a bituminous coal using the TG-FTIR as a function of temperature, reproduced from the literature (Solomon et al., 1992). TGA has been used extensively, and provided a virtual insight of coal pyrolysis characteristics, in particular, when combined with the analysis of GC and FT-IR techniques. In general, the pyrolysis process at slow heating rate (<1 K/s) is summarized (Saxena, 1990; Smith, 1994) as the following: Occluded carbon dioxide and methane are driven off at about 473 K. Above this temperature, internal condensation occurs among the macromolecular structure of low rank coals with the evolution of carbon dioxide and water. In the range  $473 \sim 773$ K, methane begins to evolve with its higher homologues and olefins; most of the oxygen in coal structure is eliminated as water and oxides of carbon. The decomposition of both nitrogen structure and organic sulphur species begins in this temperature range. The evolution of hydrogen begins at  $673 \sim 773 K$  with a critical point at about 973 K characterized by a rapid evolution of hydrogen and carbon monoxide. In the temperature range 773 ~ 973 K, the volume of gases such as  $H_2$ , CO, CH<sub>4</sub> and nitrogen increases with increasing temperature, while most hydrocarbons decrease. Tar formation begins at around 573  $\sim$  673 K with a maximum yield occurring at approximately 773  $\sim$  823 K. For some bituminous coals, the tar evolution rate curves

often show a small peak or shoulder at a lower temperature before the main peak, due to the non-covalently bonded guest molecules (Smith, 1994), while the higher temperature peak is due to the release of coal fragments during the break-up of the macromolecular coal structure by bonds breaking, evaporation and transport. Character and composition of the tars vary with temperature and coal types.



**Figure 2.4.** Evolution rates and cumulative yields of Illinois No.6 coal during pyrolysis from TG-FTIR analysis (reproduced from (Solomon et al., 1992)).

Proportions of gases and tars vary widely with coal rank (Fletcher et al., 1992; Fletcher et al., 1992<sup>a</sup>; Smith, 1994). In general, low rank coals exhibit high gas yields and low tar yields, high volatile bituminous coals exhibit high tar yields and moderate gas yields, and high rank coals exhibit moderate tar yields or low tar yields and low gas yields.

### 2.2.2 Product yields and heating conditions

The practical devolatilization of coal is a kinetic process. Experimental data shows that the yields of pyrolysis products are strongly dependent on heating conditions, e.g., temperature, heating rate, particle size, system pressure, presence of hydrogen, etc (Kimber et al., 1967; Badzioch et al., 1970; Anthony, 1974; Solomon, 1977; Suuberg, 1977; Suuberg et al., 1979; Jamaluddin et al., 1986; Cai et al., 1993; Solomon et al., 1993<sup>a</sup>; Griffin et al., 1994; Yeasmin et al., 1997; Mill et al., 1998; Yeasmin et al., 1998), and have been extensively reviewed in literature (Anthony et al., 1976; Howard, 1981; Gavalas, 1982; Berkowitz, 1985; Saxena, 1990; Solomon et al., 1992).



**Figure 2.5.** Effect of temperature on pyrolysis weight loss at different residence times (after Anthony et al., 1976).

*Effect of temperature.* The earlier observed trend that the amount of ultimate weight loss of pyrolysis increases with increasing peak temperature (Kimber et al., 1967; Anthony, 1974; Solomon, 1977; Suuberg, 1977) has continuously been confirmed by latter investigations (Jamaluddin et al., 1986; Cai et al., 1993; Griffin et al., 1994; Yeasmin et al., 1998). Most of the above observations were conducted at high heating rates compared to TGA. A critical parameter, i.e., residence time, needs to be considered when comparing the data. In the early review, Anthony et al (Anthony et al.,

1976) summarized the effect of temperature on pyrolysis weight losses at different residence times by comparing data from different workers, shown in **Figure 2.5.** The weight loss at different temperature was normalized with the observed weight loss at 1000 °C as 100%. Obviously, the data of long residence time provided solid supports on the temperature effect. A later review by Howard (Howard, 1981) provided additional informative data suggesting further devolatilization occurs beyond 1000 °C on short residence time based on results from US coals by a number of investigators. Data from drop tube furnace (Jamaluddin et al., 1986; Yeasmin et al., 1998) showing an increase in the weight loss with increasing the furnace temperature from 800 °C to 1400 °C also supported this point. Additional information of vields of pyrolysis products, e.g. H<sub>2</sub>O, CO,  $CO_2$ , Tar and  $H_2$ , from a bituminous coal with increasing the pyrolysis temperature were illustrated by Gavalas (Gavalas, 1982) based on data for the Ohio No.2 coal investigated by Solomon et al (Solomon, 1977). An increase in the tar yield of bituminous coal has been reported more recently (Griffin et al., 1994) as the peak temperature increases below 1100 K during pyrolysis at a heating rate of 1000 K/s using a heating screen reactor investigating the pressure effect. Figure 2.6 presents product yields from a sub-bituminous coal measured by Suuberg (Suuberg, 1977) at a heating rate of 1000 K/s.

*Effect of heating rates* on pyrolysis weight losses have been proved significant in the past studies, and reported extensively (Kimber et al., 1967; Anthony, 1974; Anthony et al., 1976; Suuberg, 1977; Suuberg et al., 1979; Howard, 1981; Berkowitz, 1985; Solomon et al., 1993<sup>a</sup>). Anthony (Anthony, 1974; Anthony et al., 1976) investigated and compared volatile yields of a bituminous coal in a wide range of heating rates using different reactors (crucible, wire-mesh and electrical strip furnace), and found that when

heating rate increased from 1 to  $10^4 \text{ Ks}^{-1}$ , the total volatile yields increased around 11%. High heating rate may shift the pyrolysis reactions to a much higher temperature range. Therefore the devolatilization occurs at a much higher rate (Suuberg, 1977; Howard, 1981). High heating rate causes more extensive thermal fragmentation of coal molecule structure and suppresses secondary reactions (Berkowitz, 1985), loss of fixed carbon (Kimber et al., 1967) and less carbon deposition occurs. Virtual observations are excess yields of volatiles over the proximate volatile matter content at high heating rates, resulting in a Q factor greater than 1 due to some of the fixed carbon being carried into the gas phase (Kimber et al., 1967). A comparison of experimental volatile yields with proximate volatile matter content was provided by Howard (Howard, 1981). The Q value ranges from 1.3 to 1.5 for weakly-swelling coal and from 1.4 to above 1.8 for highly-swelling coal (Badzioch et al., 1970). This effect has been observed the strongest for the intermediate rank coal, i.e., the bituminous coal, where the yield of tar exhibits a maximum (Howard, 1981). Other experimental evidences also show that higher heating rates result in higher devolatilization weight loss, in particular, for intermediate rank coals, as presented in Figure 2.7 (Eddinger et al., 1966). It may be concluded from most experimental data that excess volatile yields are primarily due to higher tar yields at high heating rate. In the meantime, the maximum rate of devolatilization increases almost linearly with heating rate for some coals (Khan, 1985; Khan et al., 1989) as pyrolysis reactions take place at a higher temperature range at higher heating rate. However, the experimental data that bear on this mater are not without contradictions (Berkowitz, 1985), for example, some of the data contain a mixture of effect of temperature and heating rate. Some experimental data also showed Q factors less than 1 (Howard, 1981), possibly due to the incomplete pyrolysis of coal.





**Figure 2.6**. Product distributions from Pittsburgh Seam bituminous coal during pyrolysis heated to different peak temperatures (after Suuberg, 1977).



**Figure 2.7.** Effect of heating rates on the devolatilization weight loss of a subbituminous coal (after Eddinger et al (Eddinger et al., 1966; Berkowitz, 1985)).

Effect of pressure on coal devolatilization behaviour have attracted wide interests in the recent years owing to the development of pressurized coal utilization facilities, e.g., IGCC (Takematsu et al., 1991; Harris et al., 1995) or PFBC (Wang et al., 1998). Wall et al (Wall et al., 2002; Wall et al., 2002<sup>a</sup>) provided a recent review on impacts of the operating pressure on a variety of aspects of coal reactions during pf coal conversion, including pyrolysis behaviour of coal. In general, pressure significantly influences the volatile matter yields, coal particle swelling and the structure of the resulting char residues. This further influences the char reaction rate (Liu, 1999<sup>a</sup>) and the ash formation mechanism (Wu, 2000<sup>b</sup>). A pronounced reduction of the total weight loss and tar yields at elevated pressures and temperatures has been observed using different reactors (Anthony, 1974; Suuberg, 1977; Mill, 2001). The early investigations carried out using Pittsburgh bituminous coal (Anthony, 1974) showed that the total volatile matter yield decreased with increasing operating pressure, and the effect was more distinguishable at high temperature. Measurements on Pittsburgh No.8 coal by Suuberg et al (Suuberg, 1977) revealed that as pressure increases the total volatile matter and tar yields decrease whilst total gas production increases, as shown in **Figure 2.8**. The published data regarding the pressure effect on the total volatile yield at various conditions in the open literature have been summarized in the literature (Shan, 2000), as shown in Figure 2.9. More recently, Mill (Mill, 2001) measured weight losses of Australian coals using a pressurized WMR, and compared the results with CPD model predictions.





**Figure 2.8.** Yields of volatile products vs. pressure during pyrolysis of Pittsburgh No.8 coal at 1000°C (after Suuberg, 1977).



Figure 2.9. Volatile yields as a function of operating pressure (after Shan, 2000).

It has been clear that pressure suppresses the formation and release of tar, and shifts the molecular weight of tar to a lighter fraction. On the other hand, high pressure promotes secondary reactions, hence increases the total yield of hydrocarbon gases. Because tar is the predominant product of the volatiles, the total volatile matter yields decrease significantly at high pressure (Howard, 1981; Berkowitz, 1985). In general, effect of pressure is to increase the solid and gas yields at the expense of tar production (Khan et al., 1989). The effect of secondary reactions may not be significant for non-plastic coal, according to Lewellen's study (Lewellen, 1975) on the Montana lignite. His results showed that total volatile yields of this coal did not vary over a wide range of pressures and heating rates.

The effect of particle size is usually not an object of study, therefore very little experimental data have been accumulated (Howard, 1981). Badzioch et al (Badzioch et al., 1970) found no significant effect on the weight loss of particle size based on rather limited observation of coals with the mean size of 20, 40 and 60  $\mu$ m, and attributed the results to that the heating rate of the particle was controlled mainly by the heating rate of the carrier gas, so that the coarser particles heated only at slightly lower rates than the fine particles. Mathews and co-workers (Mathews et al., 1997) concluded that the particle size dependence of the measured volatile matter, after correction for effect of mineral matter, is due almost entirely to differences in maceral composition, based on the observations of two pure bituminous coal vitrinite in the size range of 60~400 US mesh (37~250  $\mu$ m). However, in an inert ambient gas, Anthony (Anthony, 1974; Lewellen, 1975) found the yields of volatiles fell somewhat with increasing particles size over the range 53~1000  $\mu$ m for Pittsburgh Seam bituminous coal. Gavalas (Gavalas, 1982) observed significant particle size effect during the pyrolysis of a sub-

bituminous coal. The yield of gases showed a substantial increase with particle size, while tar yield generally decreases. This observation is also consistent with Suuberg's results (Suuberg, 1977). The effect of particle size on volatile yields may be interpreted by the mass transfer and secondary reactions. Larger particle sizes restrain the volatile transport out of particle, and promote secondary reactions, which increases light gas yields and decreases the tar yield. Overall, the effect of particle size is considered similar to that of the pressure (Howard, 1981). However, this effect may not be significant over the size range less than 100  $\mu m$ .

#### 2.2.3 Devolatilization models

The kinetics of devolatilization deals with how fast volatiles evolve and discharge from the coal under specified conditions (Berkowitz, 1985). Extensive modelling effort has been focused on determining the kinetic rates. An earlier review by Gavalas (Gavalas, 1982) summarized the kinetic modelling effort on describing coal pyrolysis, including the first order reaction (Anthony et al., 1976; Howard, 1981), the competing reactions (Solomon et al., 1979; Suuberg et al., 1979), and the detailed Chemical Models (Gavalas, 1982). The first order reaction models describe the total weight loss with one set of kinetic rates, i.e., the rate constant k and the activation energy E. Individual volatile product yields (i.e., tar, light gases) are also described with several independent first order reactions. The competing reactions are based on the experimental observations showing a negative correlation between the ultimate yields of tar and gases, which is believed due to the competition between purely chemical steps or to secondary reactions in conjunction with mass transfer limitations. The detailed chemical model developed by Gavalas et al (Gavalas, 1982) describes pyrolysis on the basis of functional groups and their elementary reactions.

Many recent studies have suggested that the chemical structure of coal can be considered as a macromolecular network to which concepts of cross-linked polymers may be applied (Solomon et al., 1993<sup>a</sup>). A number of investigators have applied statistical methods to predict how the network would behave when coal is subjected to thermally induced bridge-breaking, cross-linking and mass transport processes, and developed network models with different features. Macromolecular network models include the functional group-depolymerization, vaporization and cross-linking (FG-DVC) model (Solomon et al., 1987; Solomon et al., 1988; Solomon et al., 1988a; Serio et al., 1989a; Solomon et al., 1990), the distributed-energy chain (FLA SHCHAIN) model (Niksa et al., 1986; Niksa, 1986<sup>a</sup>; Niksa et al., 1986<sup>b</sup>) and the chemical percolation model for devolatilization (CPD)(Grant et al., 1988; Grant et al., 1989; Fletcher et al., 1990; Fletcher et al., 1992; Fletcher et al., 1992a). Network models of coal thermal decomposition approximating the breaking-down of the macromolecular network have demonstrated success in modelling the devolatilization behaviour of coal, and have been reviewed in the literature (Solomon et al., 1990; Smith, 1994; Shan, 2000). Network code for devolatilization has been incorporated in modelling of coal combustion to improve the design of combustion plants (Williams et al., 2002). In the present study, the CPD model is employed to predict transient yields of volatiles during pyrolysis. However, detailed descriptions of the devolatilization models are beyond the context of this review.

## 2.2.4 Changes in physical properties

When coal is subjected to heating, significant changes in the physical properties occur. Two physical properties, i.e., the viscosity and pore structure of coal during plastic stage, are believed extremely important, as they govern the rate of mass transport process (Gavalas, 1982) which determines the apparent yield of the volatiles. Some coals, such as caking (or coking) coal, develop significant fluidity (Habermehl et al., 1981; Berkowitz, 1985), and may be considered to behave as a Newtonian fluid (Attar, 1978). These coals are also referred to as softening or plastic coals, which are in the intermediate rank. The thermoplastic properties of the coal affect the size of the char particle and its pore distribution (Solomon et al., 1994). During devolatilization, coal particles swell to different extents, and therefore generate solid residues with different physical structures. Another important physical property, which is not well understood, is the surface tension of the coal during plastic stage (Oh, 1985). In the following, the viscosity or thermo-plasticity is discussed. The change of pore structures and the surface tension is discussed in the subsequent sections.

The mechanism and experimental measurements of the coal thermo-plasticity has been an object of discussion for long time because of its importance in the coke production (Habermehl et al., 1981). Thermoplastic phenomena are obviously associated with thermal decomposition of the coal, however the fluidity is very difficult to be correlated to other individual associated plastic phenomena, such as dilatation, softening, contraction, or swelling (Berkowitz, 1985). Crossing-linking reactions are critically important to the development of fluidity and the tar formation (Suuberg et al., 1985; Smith, 1994). The occurrence of low temperature cross-linking reactions provides interpretations to the absence of fluidity in lignites (Suuberg et al., 1985; Suuberg et al., 1985<sup>a</sup>). Some evidences show that fluidity has a direct correlation to cross-linking density of the coal during heating. Different theories of softening, such as physical melting, thermo-bitumen and physico-chemical process, are hypothesized to interpret the thermoplastic behaviour of softening coal (Berkowitz, 1985; Khan et al., 1989). It has been generally accepted that the metaplast pre-exists in coal and developed during thermal decomposition is responsible for the coal thermo-plasticity (Fitzgerald, 1957; Van Krevelen, 1981; Oh, 1985; Fong et al., 1986; Solomon et al., 1992<sup>a</sup>). The thermal decomposition of coal upon heating is therefore conceptually simplified as a two-step reaction, "coal→metaplast→coke" (van Krevelen et al., 1956; Suuberg et al., 1979; Solomon et al., 1988<sup>a</sup>). A number of viscosity models have been developed based on the metaplast theory to predict the viscosity of coal, which is generally a function of metaplast fraction, under different heating conditions (Fong et al., 1986; Oh et al., 1989; Solomon et al., 1992<sup>a</sup>; Solomon et al., 1993). On the macromolecular basis, Lynch et al (Lynch et al., 1988) describe the transient nature of bituminous coal thermo-plasticity as three overlapping processes, i.e., a physical mobilization of aromatic-rich structure, thermochemical decomposition of the macromolecular structure and a rapid condensation to produce a rigid semi-coke.

A review of the relevant literature (Khan et al., 1989) demonstrates that the thermoplastic properties of coal are complicated functions of coal properties, such as rank and petrographic composition, as well as pyrolysis conditions, such as heating rate, particle size and pressure. Petrographic composition is a critical property governing coal thermoplastic behaviour(Van Krevelen, 1981; Kidena et al., 1998; Nomura et al., 2000; Nomura et al., 2001; Kidena et al., 2002). Sung (Sung, 1977) cited Neavel's conclusion of maceral study that the plasticity of bituminous coal is primarily attributed to the presence of exinite and vitrinite maceral components. This coincides with earlier observation of van Krevelen et al (van Krevelen et al., 1956; Van Krevelen, 1981). Inertinites exhibit no plasticity upon heating at conventional heating rate of 3 °*C/min*, while exinites become extremely fluid, whereas vitrinites take an intermediate position.

Both vitrinite and exinite develop the highest fluidity at intermediate rank, where the vitrinite carbon content is around 86~88% (as shown in **Figure 2.10**). In the meantime, an additive relation is also found when vitrinite and exinite are mixed, while the inertinite has a strong depressing effect on the fluidity (Van Krevelen, 1981). More recently, Nomura and Kidena (Kidena et al., 1998; Nomura et al., 1998; Nomura et al., 2000; Kidena et al., 2002) studied the nature of plastic phenomena of vitrinite-rich and inertinite-rich fractions of two bituminous coals using a number of techniques. They reported that inertinite-rich fractions exhibited little fluidity in a plastic range. 13<sup>C</sup> NMR analysis suggests they have larger size of aromatic clusters, lesser amount of substituents (alkyl- and oxygen functional groups) on aromatic rings and higher density of cross-linking than vitrinite-rich fractions. Vitrinite-rich fractions of the same coal exhibited higher fluidity due to relatively higher concentration of aliphatic chains and bridges and branched aliphatic moieties and alicyclic parts, along with low aromaticity and much transferable hydrogen.



**Figure 2.10**. Maximum Gieselar plasticity of vitrinites and exinites as functions of carbon content (3 °*C/min*) (after Van Krevelen, 1981).

Heating rate has a crucial impact on the coal fluidity (van Krevelen et al., 1956; Chan et al., 1991; Smith, 1994). At low heating rate range (<10 K/min), both the maximum fluidity and the temperature range of the plastic region increase with increasing the heating rate (Van Krevelen, 1981), as presented in **Figure 2.11** (a). Fong et al (Fong et al., 1986) developed a fast plastometer measuring viscosity of coal under rapid heating conditions ( $40 \sim 800 \text{ K/s}$ ). The results demonstrate significant impacts of heating rates on the temperature range, the duration of the plastic region and the temperature of the maximum fluidity, as shown in Figure 2.11 (b). It may be noted from Figure 2.11 (b) that the maximum fluidity decreases with increasing the heating rate. This implies that the coal plasticity will not increase infinitely with heating rate. An optimal value for the maximum fluidity may exist. Smith (Smith, 1994) suggested that plastic properties become more pronounced at high heating rates up to a point; if the heating rate becomes too high, coals cannot plasticize or fluidize because cross-linking reaction temperatures are attained and the cross-linking reactions are initiated before diffusion processes can manifest a fluid-like behaviour. However, the heating rate range for the optimum fluidity is not clear. On the other hand, low rank coal (lignite), which does not exhibit fluidity at conventional heating rates, may develop fluidity if it is heated at extremely high heating rates  $(>2\times10^4 \text{ K/s})$  when low temperature cross-linking becomes significantly reduced (Solomon et al., 1990a; Smith, 1994). Chan et al., 1991) studied thermo-plastic behaviour of a range of coals at pressurized carbonization conditions, and found that at low heating rate (~20 K/min), plastometry torque decreases with increasing the heating rate for all coals investigated, while effect of pressure is more complicated. It may be noted that the rheological properties of the coal also play an important role in the coal thermoplastic properties at high heating rate (Waters, 1962; Khan, 1985; Khan et al., 1989).



**Figure 2.11**. Fluidity of coal during plastic stage as a function of heating rates; (*a*) Low heating rates (after Van Krevelen, 1981); (*b*) High heating rates (after Fong et al., 1986).



**Figure 2.12**. Gieseler fluidity as a function of pressure in  $N_2$  gas (after Khan et al., 1989) (Lancet et al., 1981).

Increased Gieseler fluidity at elevated pressures at the heating rate of 3 *K/min* has been observed by Lancet et al (Lancet et al., 1981), and the effect appears stronger at the low-pressure range of up to 1.5 *MPa*, as presented in **Figure 2.12**. However, Fong et al (Fong et al., 1986) reported a decrease in fluidity under the pressure of 3.5 *MPa* at

heating rate 350 K/s. An enhancement of repolymerization reactions, hence an increased resolidification rate, has been suggested for the decrease of fluidity at elevated pressures. Considering the occurrence of the pressure range for the increased fluidity is below 1.5 *MPa* in Lancet's results, obviously, more experimental investigations are needed to clarify the contradicted observations on pressure effect.

## 2.3 Char structure of bituminous coal

The chemistry of char includes the elemental composition, proximate composition, internal structure (i.e., porosity, pore distribution), char particle size, surface area and surface morphology, etc. Apparently, the change in internal structure of the char is one of the most important issues during coal devolatilization, and is closely associated with the swelling phenomenon of coal during plastic stage. The extent to which the pore structure changes, hence the ultimate char structure, is coal type dependent, e.g., rank properties and maceral composition, and is strongly affected by the conditions under which coal is devolatilized, e.g., heating rate, temperature, system pressure and particle size. The scope of the following review is largely focused on the char structure, referred to the ultimate structure of the solid char after resolidification, of such coals that undergo plastic stage during which significant physical alterations occur.

### 2.3.1 Importance of the char structure

The importance of char structure arises from the following three aspects:

i) The change of the internal structure of the char during pyrolysis determines the mass transport of the volatiles. During devolatilization, the pore openings of the softening coal will be blocked at the onset of the plastic stage due to the high fluidity contributed by the metaplast. Therefore the volatiles will be trapped inside coal particles to form bubbles. The release of volatiles and the ultimate structure of char will be

largely determined by the behaviour of the bubbles (Oh, 1985; Solomon et al., 1993; Smith, 1994), rather than by the original pore structure of the feed coal (Lewellen, 1975). According to the multi-bubble mechanism (Oh, 1985), the volatile is transported through the movements of bubbles during plastic stage. When a large number of bubbles exist in the coal fluid, volatiles diffuse into bubbles instead of diffusing directly out of particle surface. This causes the growth of bubbles and swelling of the coal particle. When bubbles reach the particle surface, they overcome the force balance to burst and release the volatiles. This mechanism has been generally accepted to interpret the bituminous coal swelling phenomena during heating. The observations in the present study conducted on the single particle reactor confirm that the bubble growth and rupture is the dominant phenomenon during the whole plastic stage (Yu et al., **2001**).

ii) The ultimate char structure plays a significant role in char reactivity during the subsequent char oxidation after devolatilization, in particular during char gasification (Alvarez et al., 1993; Liu, 1999<sup>a</sup>). Based upon analysis of three British bituminous coals, Koranyi (Koranyi, 1989) found that a good correlation exists between char reactivity and their micro-porosity. Hurt et al (Hurt et al., 1991) studied the roles of micro-porosity, and concluded that  $CO_2$  gasification reactions took place primarily outside the micro-pore network on the surfaces of larger pores. The pore distribution determines the diffusion of reactants within the particle, which is often a rate-limiting step for char oxidation (Solomon et al., 1994). The morphology of the char types formed during pyrolysis will affect the overall combustion efficiency (Oka et al., 1987; Lester et al., 1996). Hampartsoumian et al (Hampartsoumian et al., 1989) studied the effect of the porous structure of char on the rate of gasification, and suggested an estimated effectiveness factor for investigating the influence of the pore diffusion

limiting of reactant gases at different conditions. Menendez et al (Menendez et al., 1993) listed the most important char characteristics with increasing combustion temperature, successively, as the following: i) the surface area and the surface structure, i.e. the total surface which may be accessible to reacting gases; ii) the porosity which influences the rate of access of the reacting gas to the surface; and iii) the size of the char particle. These parameters are crucial in modelling considerations of pf combustions and gasification. Apparently, highly porous chars have experienced much more extensive devolatilization during heating resulting in a loss of its most materials. Therefore, during the char oxidation, these chars will burnout at a rather early stage compared to solid ones, even they burn at a similar rate (Wu, 2000<sup>b</sup>; Wall et al., 2002).

iii) The char structure has a significant impact on ash formation and pollutant emission during coal conversion. An important aspect in the char reaction is the fact that porous char particles are easily fragmented during combustion. Kantorovich et al (Kantorovich et al., 1998) investigated the role of the pore structure in the fragmentation of highly porous char particles, and suggested that the reason for local fragmentation under non-uniform oxidation is the increase in the local macro-porosity. The tendency of the fragmentation of the different chars has a major impact on the chemistry of the final ash particles, therefore is crucial to the performance of reactors (Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>). Kang et al (Kang et al., 1992) studied the effect of char structure on ash formation during pf combustion, and concluded that the fragmentation of char induced by macro-pores can influence the final ash PSD due to the less occurrence of the ash coalescence. Using a pressurized drop tube furnace, Wu et al (Wu et al., 2000; Wu, 2000<sup>b</sup>) reported that finer ash particles were generated under elevated pressures due to higher yields of highly porous chars. Textural properties (i.e., pore distribution and active surface area) of bituminous coal chars are also found to have some important effect on the  $NO_x$  emissions (Arenillas et al., 1999).

## 2.3.2 Classification of char structure

## 2.3.2.1 Pore system of coal and char

The pore structure is a rather complex system, and is highly heterogeneous, in terms of pore dimensions and spatial configurations in both coal and char. Pores are described to have a random spatial distribution in the carbon matrix with linkages and intersections occurring between each other (Simons, 1983). Pore size of porous solid systems is generally expressed by either the diameter of the opening, assuming cylindrical, or the width of the slit (Webb et al., 1997). Pores with diameters, or slits with widths, less than 20 Angstrom units (Å), are referred to as micro-pores. Pores with diameters larger than 500 Å are referred to as macro-pores, while those with dimensions in between  $(20 \sim 500)$  $\mathring{A}$ ) are meso-pores (Simons, 1983; Webb et al., 1997). This description applies to both parent coal and char, although the configuration of the pore structure of the softening coal char after devolatilization is significant different from that of the feed coal. Two parameters of char structure, i.e., the porosity and the surface area, are usually of the most concern. Micro-pores account for the major portion (>90%) of the internal surface area and consequently provide most of the surface reaction (Dutta et al., 1977; Liu, 1999<sup>a</sup>). On the contrary, the meso-pores and macro-pores, which are important for the mass transport of gaseous phases, have a low surface area. However, they account for the major portion of total pore volume (Laurendeau, 1978).

A number of techniques are available to measure the porosity and surface area of coal and chars, including mercury intrusion porosimetry (MIP) and gas adsorption (Webb et al., 1997). In recent years, the characterization of chars extensively involves the image processing techniques (Bailey et al., 1990; Bend et al., 1992; Bailey, 1993; Menendez et al., 1993; Cloke et al., 1995<sup>a</sup>; Lester et al., 1996; Rosenberg et al., 1996; Cloke et al., 1997; Benfell et al., 1998; Gilfillan et al., 1999; Wu et al., 2000<sup>a</sup>; Benfell, 2001), mainly due to their practical applications in describing char morphological parameters. Image processing techniques can provide a number of geometric parameters of individual char particles, e.g., mean particle diameter, two dimensional macro-porosity, the particle sphericity (Benfell, 2001), etc. These parameters are crucial in the char structure classification systems to determine the structure type of individual chars.

### 2.3.2.2 Char structure classification systems

Extensive efforts have been made in the past decades to classify morphologically complicated char structures (Littlejohn, 1967; Lightman et al., 1968; Jones et al., 1985; Jones et al., 1987; Oka et al., 1987; Bailey et al., 1990; Bend et al., 1992; Alvarez et al., 1993; Menendez et al., 1993; Vleeskens et al., 1993; Cloke et al., 1994<sup>a</sup>; Rosenberg et al., 1996; Alvarez et al., 1997; Benfell et al., 1998). These classification systems largely rely on image processing techniques to obtain char morphological parameters, including the char porosity, the wall thickness, particle shape and other geometric parameters (Cloke et al., 1994<sup>a</sup>; Liu, 1999<sup>a</sup>; Wu, 2000<sup>b</sup>; Benfell, 2001). Benfell (Benfell, 2001) provided a very recent summary of different char classification systems after Cloke et al. (Cloke et al., 1994<sup>a</sup>), as shown in **Table 2.1.** These systems are based upon a combination of the structural parameters, e.g. external dimensions of particles, macro-porosity, distribution of macro-pore sizes, wall thickness and presence of anisotropy.

Char type	А	В	С	D	E	F	G	Н	Ι	J
	$\bigcirc$	0				3				
Jones et al., 1985	cenosphere	cenosphere	honeycomb		unfused	unfused	unfused	~	-	
Oka et al., 1987	thin-walled balloon	thick-walled balloon	network		unfused block	unfused block	skeleton			micro dis -rupted
Goodarzi and Vleeskens, 1988	thin-walled cenosphere	thick-walled cenosphere	cenosphere with ribs			non- reacted	fusinite			frag- ment
Bailey et al., 1990	tenui- sphere	crassi- sphere	tenui- network	meso- sphere	inertoid	solid	fusinoid	mixed porous	mixed dense	frag- ment
Menéndez et al., 1993	cenosphere (Type I)	cenosphere (Type I)	network (Type II)	network (Type II)	solid (Type III)	solid (Type III)				
Vieeskens et al , 1993	plastic/ porous	plastic/ porous	plastic/ porous	plastic/ porous	inertoid	inertoid	fusinoid			
Rosenberg et al., 1996	tenui- sphere	crassi- sphere	tenui- network	variable density type	inertoid	fusinoid/ solid	fusinoid/ solid	variable density type	variable density type	

# **Table 2.1.** Summary of various char morphology classification systems, after Benfell (Cloke et al., 1994<sup>a</sup>; Benfell, 2001).

Char groups	Group I	Group II	Group III		
	$\bigcirc$				
Char subtypes	Cenosphere	Crassisphere,	Inertoid,		
	tenuisphere,	crassinetwork,	solid,		
	tenuinetwork	mesosphere,	fusinoid		
		mixed porous,	(mixed dense)		
		(mixed dense)			
Char particle shape	Spheroidal	Spheroidal to irregular	Subspheroidal, rectangular or irregular		
Porosity	> 80%	>50%	~50%		
Pore shape	Spheroidal	Variable	Spheroidal to elongate and angular		
Wall thickness	< 5 µm	Variable	$> 5 \ \mu m$		
Dominant maceral components	Vitrinite	Vitrinite and inertinite	Inertinite		
Swelling ratio >1.3		<1.0	<0.9		

**Table 2.2**. Summary of the three-fold char classification system by Bailey and Benfell (Bailey et al., 1990; Benfell et al., 1998), after Benfell (Benfell, 2001) and Liu(Liu, 1999<sup>a</sup>).

A three-fold classification system suggested by Benfell and Bailey (Benfell et al., 1998; Benfell, 2001) based upon Bailey's twelve-fold system (Bailey et al., 1990) has demonstrated its practicability in assessment of combustion characteristics (Bailey et al., 1990; Benfell et al., 1998; Benfell et al., 2000; Benfell, 2001), and has been adopted by a number researchers (Liu, 1999a; Benfell et al., 2000; Wu et al., 2000; Wu et al., 2000<sup>a</sup>; Yu et al., 2002). The characteristics of the three groups of chars are presented in **Table 2.2**. The feasible parameters to assess char structure type are porosity, particle sphericity and wall thickness, as they can be easily quantified during the process of image analysis. However, the boundary of the porosity between different groups is not without ambiguity. For instance, the boundary values of porosity for Group I chars in the literature vary from 60% to 80% (Benfell et al., 1998; Liu, 1999<sup>a</sup>; Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>; Benfell, 2001). This is probably because the boundaries have not been quantitatively correlated to any combustion or gasification characteristic parameters. Nevertheless, the classification system provides quantitative assessment to char characteristics, therefore is very useful.

### 2.3.3 Char structure and coal properties

Previous studies show that char structure is strongly dependent on coal rank, and is certainly associated with thermoplastic properties that coal can exhibit during heating. Low rank coal, such as lignite, usually generates network-type to solid char structure. As the rank increases up to low volatile bituminous rank, there is an increase in coal aromaticity and fusibility (Bailey et al., 1990). Therefore, the proportion of network-type char decreases and the proportion of cenospheric char increases (Oka et al., 1987) (Bailey et al., 1990; Vleeskens et al., 1993; Cloke et al., 1994<sup>a</sup>; Benfell, 2001). Further increase in the coal rank results in an increase in the wall thickness of chars, and the population of thin-wall cenospheric char decreases (Alvarez et al., 1993; Alvarez et al., 1997).

Maceral composition plays a dominant role in the char morphology during devolatilization in coal combustion (Jones et al., 1985; Bailey et al., 1990; Cloke et al., 1994<sup>a;</sup> Rosenberg et al., 1996; Benfell, 2001), although vitrinite and inertinite from high rank coal above semi-anthracites may be expected to behave similarly during combustion (Jones et al., 1985; Jones et al., 1985<sup>a</sup>). Vitrinite-containing particles from bituminous coals commonly produce cenospheric chars whilst the inertinite produces a higher proportion of relatively solid chars with low porosity (Jones et al., 1985; Jones et al.,

al., 1985<sup>a</sup>; Oka et al., 1987; Bailey et al., 1990; Rosenberg et al., 1996; Gilfillan et al., 1997; Gilfillan et al., 1999; Liu, 1999<sup>a</sup>; Benfell, 2001).

The differences in the char morphology of different maceral components may be attributed to the differences in the their thermo-plasticity and the extent to which coal is devolatilized (van Krevelen et al., 1956; Van Krevelen, 1981). The thermo-plasticity of macerals as a function of coal rank has been shown in **Figure 2.10** (in section **2.2.4**). **Figure 2.13** demonstrates the volatile yields of macerals as a function of coal rank. Significant differences exist in the volatile yields among different macerals in medium to low rank coals (C<90%) (Van Krevelen, 1981; van Krevelen, 1993). The presence of inertinite in particles significantly reduces the thermo-plasticity of coal during heating (Van Krevelen, 1981) and promotes formation of thick-walled cenospheric chars (Tsai et al., 1987; Hurt et al., 1995; Hurt et al., 1995<sup>a</sup>). However, inertinite can also make major contribution to cenospheric char when suitably fusible under certain heating conditions (Bailey et al., 1990; Benfell, 2001).

At conventional heating rates, it is possible to correlate char structure to maceral composition under the assumption that porous chars are derived from liptinite and vitrinite, which develop fluidity and experience large extent of devolatilization. An empirical equation (Liu, 1999<sup>a</sup>), in Eq. 2.1, has been proposed to correlate the Group I char population to the ambient pressure and vitrinite (including liptinite) content based on the experimental results, and has been applied in predicting ash formation (Yan, 2000):

$$nGrpI(\%) = 0.6 \times Pt + 0.53 \times vitr + 37$$
(2.1)

Where *nGrpI* is the number percentage of Group I char, *Pt* is the total pyrolysis pressure (*atm*), and *vitr* is the vitrinite (including liptinite) content (%).



**Figure 2.13.** Volatile yields of maceral components as a function of coal rank (after Van Krevelen, 1981; van Krevelen, 1993).

## 2.3.4 Char structure and heating conditions

For softening coals, the formation of different char structure type is closely associated with thermoplastic behaviour, e.g., fluidity and swelling, of coal during heating. Therefore, factors that affect coal thermo-plasticity will strongly influence the char morphology, such as temperature, heating rate, ambient pressure, etc.

### 2.3.4.1 Effect of Temperature

Heat treatment temperature plays a significant part in char morphology, and has been reported in the literature (Fong et al., 1986; Bailey et al., 1990; Cai et al., 1993; Griffin et al., 1994; Rosenberg et al., 1996; Cai et al., 1998<sup>a</sup>; Alonso et al., 2001; Alonso et al., 2001<sup>b</sup>). As heat-treatment temperature increases, sub-bituminous coals produce less

amounts of high density and thick-walled chars (Bailey et al., 1990). Similar observations by Griffin et al (Griffin et al., 1994) show that the char morphology changes to structures with larger central pores and network voids with increasing temperature. A reduction in the char micro-porosity at the higher temperature was measured from the chars of the same coal prepared at 1000 °*C* and 1500 °*C* by Cai et al (Cai et al., 1998<sup>a</sup>). This is consistent with the observation of the decrease in intrinsic reactivity when increasing pyrolysis temperature, by Jenkins et al (Jenkins et al., 1973). Lewellen (Lewellen, 1975) measured the surface area of softening coal with increasing temperature, and found that a sharp decrease occurred in accessible surface area, which started at the softening points. However, porosity of non-plastic coal char increased steadily with increasing the carbonization temperature.

### 2.3.4.2 Effect of heating rate

Compared to temperature, heating rate demonstrated more significant effect on devolatilization and thermo-plasticity, as aforementioned. However, very little data are available in the literature for comparison of heating rate effect on char morphology. Limited data on heating rate effect by Cai et al (Cai et al., 1996) show that chars prepared at high heating rates contain more micro-pores and meso-pores and have greater internal surface areas, hence higher reactivity. High heating rates lead to greater anisotropy in char (Chan et al., 1994). Gale et al (Gale et al., 1993; Gale et al., 1995) combined their results with others (Zygourakis, 1993), and suggested that overall porosity and swelling ratio of char increase with heating rate up to  $10^3 K/s$ , then level off. Further increase in the heating rate above  $2 \times 10^4 K/s$  will result in a decrease in porosity and swelling, as presented in **Figure 2.14**. This is attributed to faster chemical

release rate of volatiles than relaxation time for expanding the char particle. Particle temperature gradient at very high heating rate may also take some effect.



**Figure 2.14.** Porosity and swelling ratio as a function of heating rate (after Gale et al., 1993; Gale et al., 1995).

### 2.3.4.3 Effect of ambient pressure

Effect of system pressure on char structures has attracted wide research interests in the recent years (Khan, 1985; Khan et al., 1986; Khan et al., 1988; Benfell et al., 1998; Liu et al., 1999; Wu et al., 2000<sup>a</sup>; Benfell, 2001; Wall et al., 2002). Clear evidences show that thermoplastic properties of coal cannot be predicted from the characteristics at atmospheric pressure or by standard tests (Khan et al., 1986). Effect of pressure is reflected in the reduction of tar yields and the increase in gas yields and the fluidity (see **2.2.2** and **2.2.4**). These phenomena are closely associated with coal swelling and char morphology. High swelling ratios of solid chars at elevated pressures have been observed under a variety of heating conditions (Khan et al., 1986; Khan et al., 1988; Lee et al., 1991<sup>a</sup>; Lee, 1992; Griffin et al., 1994; Benfell et al., 1998; Wu et

al., 2000<sup>a</sup>; Benfell, 2001), implying that higher porosity may result during pyrolysis at elevated pressures. The opponent factors, i.e. the decrease in the tar yield, increase in gas yields and fluidity, result in a maximum swelling ratio at an optimum pressure range, as show in **Figure 2.15** (Khan et al., 1989), depending on coal types.



Figure 2.15. Swelling ratio as a function of system pressure (after Khan et al., 1989).

Very recently, a direct measurement by Wu et al (Wu et al., 2000<sup>a</sup>) on chars collected from a pressurized drop tube furnace (PDTF) shows that both char porosity and sphericity increase with increasing the system pressure up to 1.5 *MPa* (presented in **Figure 2.16**). This is accompanied by the increased swelling ratio at the same pressure range. An increase of population of group I chars at elevated pressure has also been observed (Wu, 2000<sup>b</sup>; Benfell, 2001). An empirical correlation (similar to Eq. 2.1) between the porous char population and the ambient pressure and vitrinite concentration has been more recently provided by Benfell (Benfell, 2001).



**Figure 2.16.** Macro-porosity of DTF char as a function of ambient pressure (after Wu et al., 2000).

### 2.3.4.4 Char characteristics and gas environment

Some comparisons have been made in the literature between the char morphologies in inert gas and oxidization environments. Bailey et al (Bailey et al., 1990) found that combustion solid residue has a very similar range of particle morphologies to pyrolysis chars produced at comparable temperatures, although the proportions may vary. In combustion conditions at a burnout level of 50-60 *wt%*, the vitrinite-dominated micro-lithotypes generate crassisphere and tenuisphere chars (Rosenberg et al., 1996). Inertinites fuse more readily in combustion than in pyrolysis, producing larger quantities of tenuispheres (Bailey et al., 1990; Benfell, 2001). Char residues collected from industrial furnaces also demonstrate that inertinite may fuse more readily in boilers (Hurt et al., 1995; Hurt et al., 1995<sup>a</sup>). This may be due to the heating rate in the boiler is higher than lab scale reactors, such as DTF and WMR. Fletcher (Fletcher, 1993) suggested that changes in swelling behaviour between typical devolatilization experiments and char combustion experiments are not due to the presence of oxygen, but heating rate or post-flame gas species other than oxygen. The presence of hydrogen

during pyrolysis significantly increases tar yields and fluidity (Anthony, 1974; Suuberg, 1977), therefore may be expected to change char morphology significantly due to the strong association between char structure and the thermoplastic properties and volatile evolution. The inertinite residues are also less susceptible to a high temperature loss of reactivity than vitrinite group (Hurt et al., 1995; Hurt et al., 1995<sup>a</sup>). Overall, pyrolysis char is suitable for the study of char morphologies developed under early stage combustion conditions (Bailey et al., 1990; Benfell, 2001).

### 2.3.5 Swelling and the char structure

Strong association exists between coal swelling history during plastic stage and the ultimate char structure of softening coals (Howard, 1981; Berkowitz, 1985). The extent to which the coal swells determines not only the char particle size, but also the porosity and wall thickness. Apparently, the more the particle swells, the more porous the structure it generates. Swelling ratio is expressed as volume difference between the char and the initial coal (Berkowitz, 1985; Khan et al., 1986), or by comparing the diameter of the char particle to that of the initial particle of the feed coal ( $d/d_0$ ) (Field et al., 1967; Solomon et al., 1993). The latter one has been widely used in pf coal combustions (Lee et al., 1991a; Solomon et al., 1993; Solomon et al., 1993a; Solomon et al., 1994; Liu, 1999a; Wu et al., 2000a; Benfell, 2001; Yu et al., 2002).

**Figure 2.17** is a typical volume change of a caking coal measured by a dilatometer (Berkowitz, 1985) at slow heating rate of 1-5 °*C/min*. It demonstrates that caking coal follows quite complex swelling history, during which contraction, dilatation and resolidificaiton occur at different stage. Final swelling referred to the difference between the volume after resolidificaiton and the original one. Dilatation refers to the maximum volume to the minimum volume at contraction. The dilatation can be much

higher than swelling for caking coals that develop significant fluidity during heating. This implies that the transient physical structure change may not be reflected by the ultimate structure of the solid residue, and the maximum porosity of the coal particle during pyrolysis may be much higher than the final char at the completion of devolatilization.



**Figure 2.17.** Typical swelling curve measured by dilatometer of a caking coal (after Berkowitz, 1985).

The final swelling ratio of softening coal char is dependent on coal type, and the maceral composition is the major determining factor (Gentzis et al., 1996; Benfell, 2001). At average heating rate between  $10^2$  and  $10^4$  K/s, according to the study by Solomon et al (Solomon et al., 1993), typical swelling of Pittsburgh No. 8 coal exhibits three types: ~10% shows virtually no sign of fluidity, hence no swelling; the majority (~80%) experience swelling of about the same magnitude; the other ~10% exhibits behaviour that can be associated with a much lower viscosity than the majority. And these three types of behaviour are associated with maceral compositions, i.e. inertinite,

vitrinite and exinite, respectively (Solomon et al., 1993). Recent studies (Liu, 1999<sup>a</sup>; Benfell, 2001) show that Group I chars have larger particle size compared to solid chars. Cenospheric chars have the largest swelling during devolatilization, therefore the highest porosity. Vitrinite and liptinite macerals contribute to the fluidity during heating, therefore they are considered the major composition contributing to the swelling of coal and population of porous chars.



**Figure 2.18.** Swelling of two bituminous coal as a function of heating rate (after Khan et al., 1989).

Similar to char structure, the swelling ratio of coal is strongly influenced by heating conditions through their effects on fluidity (see 2.2.4) and devolatilization rate. Figure 2.18 presents an increase in both swelling ratio and maximum devolatilization rate when the heating rate is increased (Khan et al., 1989). The peak swelling and porosity have been observed at heating rate range of  $2-7 \times 10^4$  *K/s* by Gale et al (Gale et al., 1995; Gale et al., 1996), as shown in Figure 2.14. This heating rate range is believed the transition
value between the heating rate of drop tube furnace and that of flat-flame burner (Gale et al., 1995). However, Solomon et al (Solomon et al., 1994) predicted different heating rate range for the maximum swelling ratio, after which a sharp drop in swelling occurs, during Illinois No.6 coal pyrolysis. Khan et al (Khan et al., 1986) found that swelling may not be sensitive to heating rate at pressurized devolatilization conditions.



**Figure 2.19** Experimental data and model predictions on swelling ratio of Illinois No.6 coal against pressures (after Solomon and Fletcher (Solomon et al., 1994)).

Effect of ambient pressure on swelling of coal has been proved significant under a variety of conditions (Khan et al., 1986; Chan et al., 1994; Griffin et al., 1994; Gao et al., 1997; Liu et al., 1999; Wu et al., 2000<sup>a</sup>; Benfell, 2001). Most likely, an optimum pressure range exists for the maximum increase of swelling when system pressure increases, as shown in **Figure 2.15**. Khan and Jenkins (Khan et al., 1986) investigated swelling behaviour of 12 bituminous coals (from LVB to HVB) at elevated pressure and a particle size of  $355 \times 710 \ \mu m$ , among which 9 presented the peak swelling behaviour with increasing the system pressure. Solomon and Flectcher (Solomon et al., 1994) compared model predicted results to the experimental data (Lee et al., 1991; Lee et al.,

1991<sup>a</sup>) on swelling of the Illinois No.6 coal, and concluded that the peak is most likely to appear at 0.5 to 1.5 *MPa* at the condition studied, as shown in **Figure 2.19**. That more gaseous volatiles are trapped inside the coal particle due to the elevated external pressure is the reason for the increase of the swelling. However, some other factors are obviously doing some work, such as viscous forces, the extent of secondary reactions and surface tension, etc (Solomon et al., 1994). Very recently, Wu et al (Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>) reported increased swellings of Australian bituminous coals at elevated pressures, and attributed the formation of finer ash particles to the increased population of highly porous Group I chars.

## 2.3.6 Density separation techniques

The fact that different structures derived from in different pf coal particles is attributed to the variations in their maceral constituents (Gilfillan et al., 1999; Liu, 1999<sup>a</sup>; Benfell, 2001). In general, particles containing liptinite or vitrinite generate porous char structure, whilst those containing inertinite generate relatively dense char structures. Therefore, samples of selective maceral concentrations are very useful in investigating the char structure formation during pyrolysis. This can be achieved by selective sampling from the different coal faces (Wall et al., 1992; Benfell et al., 1998; Benfell et al., 2000; Benfell, 2001), and the correlation between the char structure and the vitrinite content has been established by Benfell et al (Benfell, 2001). Reactivity of maceral concentrations was also investigated by Cai et al (Cai et al., 1998; Cai et al., 1998<sup>a</sup>).

Density separation techniques, such as the sink-float technique and centrifugation, have been extensively employed to separate coal macerals, and provide an insight into the nature of coal and coal macerals (Dyrkacz et al., 1982; Dyrkacz et al., 1984<sup>a</sup>). Cloke et al (Cloke et al., 1997) characterized density separated coal fraction samples using FTIR

and petrographic analysis. It was concluded that Aar/Aal ratios increased for higher density samples, indicating a change in aromaticity as the density of the fraction was increased. Kawashima et al (Kawashima et al., 2000) used NMR technique to characterize the density-separated components during pyrolysis. They found that the lighter components underwent greater structural changes than the heavier components. The elimination of aliphatic side chains took place to a greater extent in lower than in higher rank coals, and the content of aliphatic moieties in each maceral group determines its reactivity. Gilfillan et al. (Gilfillan et al., 1997; Gilfillan et al., 1999) examined the structure and reactivity of density separated coal fractions of six world coals. The morphological analysis of the char clearly indicated that thin-walled chars were produced from the light density fraction, and the proportion decreased with increasing the density. The chemical structure investigations using FTIR and 13<sup>°</sup> NMR showed that aromaticity increased with the coal density, with the inertinite-rich fractions having the highest values. In the performance of the density separation process, the particle size is usually reduced to below 38 microns (Gilfillan et al., 1999). The raw coal particle sizes are even reduced to several microns to achieve effective liberation of the maceral components, and minerals are removed prior to the density separation (Dyrkacz et al., 1984<sup>a</sup>).

In investigating the heterogeneity of large pf coal particles during devolatilization process, Gibbins and his colleagues (Gibbins et al., 1999) found some synergic effect during devolatilization, and suggested that the ability of using relatively pure macerals (from hand-picking, or from micronizing, demineralization, and density separation) to represent actual pf combustion behaviour may be limited. In their study, a wide range of particle mineral content was also observed, and the minerals were generally well

dispersed and frequently associated with the inertinite maceral. By measuring the overall char intrinsic reactivity, they suggested that minerals may act as a catalyst for char oxidation, but the effect is very small. Instead, some reduction in article combustion rates during latter stage of char burnout occurred due to the increased resistance to oxygen transport and heat losses caused by relatively large quantity of mineral matter admixed with organic materials. It is therefore suggested that both inertinite content and mineral matter should be included to explain the poor burnout of chars in some cases.

## 2.3.7 Modelling effort

In terms of the nature of the phenomena described in previous modelling work, one may consider that devolatilization models, e.g. network models, deal with chemical aspects of coal pyrolysis, while the swelling and char structure models deal with physical aspects of coal pyrolysis. Although, these two aspects are closely associated with each other, in particular for softening coals, the modelling effort has been obviously separate in the past. Early studies in this field are focused on providing mechanistic interpretations of the mass transport and swelling phenomena of coal during heating (Lewellen, 1975; Sung, 1977; Oh, 1985). As abovementioned, the mode of volatile transport for plastic coal differs radically from non-plastic coals (Lewellen, 1975; Sung, 1977; Oh, 1985). Instead of using pore transport mechanism, Lewellen (Lewellen, 1975) proposed the concept of volatile transport via gas bubbles, and used this mechanism to model secondary reactions during coal pyrolysis. Based on a number of assumptions, he described the physics of bubble generation, bubble growth and destruction. During investigating the swelling of coal, Sung (Sung, 1977) employed this mechanism to interpret the swelling phenomena of coal.



**Figure 2.20.** The multi-bubble mechanism for mass transport of plastic coal during devolatilization (after Oh, 1985; Oh et al., 1989).

A systematic multi-bubble mechanism for mass transport during the plastic coal devolatilization has been proposed in the literature (Oh, 1985; Oh et al., 1989). The physics of the mechanism is illustrated in **Figure 2.20**. Under this regime, metaplast is generated through physical melting (those pre-existing in the parent coal) and thermal decomposition. Primary gases and char are also formed simultaneously. Further decomposition of metaplast generates tar, secondary gases and chars. Bubbles are initiated from macro-pores of parent coals at the onset of the plastic stage, or through nucleation mechanism. Volatiles (i.e., tar and gases) may be transported into bubbles or to the particle surfaces through diffusion. However, time for direct diffusion of gases to particle surface is several magnitudes longer than that into the internal bubbles. Therefore, the physics of multi-bubble mechanism is summarized as the following: volatiles are carried by bubbles; the release of volatiles is through bubble movements rather than by the direct diffusion to the particle surface; the swelling of the particle is caused by bubble growth due to the generation of volatiles. Rupture of bubbles at the

particle surface is determined by force balance, for which viscous force is the major term.

Based upon the above mechanism, bubble conservation is described as Eq. 2.2:

$$\frac{dn_j}{dt} = K_{j-1}n_{j-1}n_1 - K_jn_jn_1 + \frac{1}{2}\sum_{i=2}^{N-j}P_{i,j-i}n_in_{j-i} - \sum_{i=2}^{N}P_{i,j}n_in_j - E_jn_j$$
(2.2)

Where,  $n_j$  is the number of the bubbles with size j, and N is the total number of bubbles.  $E_j$  is a bubble escape rate, and  $K_j$  and  $P_{i,j}$  are kinetic rates for bubble growth and coalescence, respectively. This equation has a similar form to that for describing colloid behaviour. Considering the uncertainty of the bubble size distribution at the onset of plastic stage, this equation is a rather complicated and un-applicable. A number of simplified cases have been thereby considered, including the extreme case that the bubbles are uniformly distributed spatially and with a uniform size (Oh, 1985).

Perhaps the most important term in describing the bubble behaviour is the bubble growth rate, which also determines the bubble escaping rate and coalescence rate. The bubble growth is caused by the generation of volatiles, which build up the internal pressure, and restrained by the external pressure, surface tension and viscous force. Therefore, the equation describing the bubble growth rate essentially describes the force balance, as shown in Eq. 2.3 (Oh, 1985):

$$\frac{P_b - P - 2\sigma/r_b}{\rho} = r_b \frac{dr}{dt} + \frac{3}{2} \left(\frac{dr}{dt}\right)^2 + \frac{4\mu}{\rho r_b} \frac{dr}{dt}$$
(2.3)

where dr/dt is the rate of bubble growth,  $r_b$  is bubble radius,  $\mu$  is the viscosity,  $P_b$  is the bubble internal pressure, P is the ambient pressure,  $\sigma$  is the surface tension, and  $\rho$  is the fluid density.

A single bubble model has been proposed by Solomon et al. (Solomon et al., 1993), incorporated with FG-DVC model (Solomon et al., 1987; Solomon et al., 1988), to predict coal swelling, for which viscosity is calculated from an empirical model by Solomon et al (Solomon et al., 1992<sup>a</sup>). More recently, a single bubble model describing transient char swelling and morphology changes has been proposed by Sheng et al (Sheng et al., 2000). The physics of single bubble models is based upon the assumption that the liquidized coal particle forms a single centric void surrounded by a porous outer shell. Volatiles are released through both bubble rupture and direct diffusion of volatiles to the particle surface. Bubble rupture occurs when the internal pressure builds up and reaches the following criterion (Solomon et al., 1993):

$$\frac{1.5r_b^3(P_b - P)}{r_p^3 - r_b^3} - P > Sw_c$$
(2.4)

where  $r_b$  and  $r_p$  are the bubble and particle radius, respectively,  $Sw_c$  is the critical wall stress,  $P_b$  is the bubble internal pressure, and P is the ambient pressure. The diffusion term of the volatile through the porous shell is expressed as (Solomon et al., 1993; Sheng et al., 2000):

$$4\pi D_{v}C_{b}/(1/r_{b}-1/r_{p})$$
(2.5)

where  $D_{\nu}$  is the diffusivity of volatiles in the porous liquid, and  $C_b$  is the molar concentration of volatiles in the bubble.  $D_L$  is used in Solomon's work (Solomon et al., 1993), and the effective diffusivity,  $D_e$ , has been used by Sheng et al (Sheng et al., 2000). Sheng et al compared their model predictions with experimental data in the literature (Gao et al., 1997).

#### 2.4 Summary and implications

From the review of the literature, the following has been concluded:

- Experimental efforts on devolatilization kinetics have been made extensively, and overall understandings of pyrolysis have been gained. The mechanisms of volatile product evolution during pyrolysis have been well established, based on which advanced network models for devolatilization have been well developed to predict yields of volatile species;
- Swelling and ultimate char structures have been studied extensively using different experimental techniques, and have been classified using different systems based on char morphological parameters;
- Limited experimental observations on the transient swelling behaviour of individual coal particle during devolatilization have been made, based on which some quantitative understanding of the coal thermoplastic behaviour have been achieved;
- Mathematical models have been developed based on bubble mechanism to predict the transient swelling behaviour of softening coals. These models provide potential capability in describing char structure evolution.

#### However:

- Full quantitative understanding of char structure evolution, i.e., the transient internal physical structure change during plastic stage, has not been achieved;
- Physical aspects, i.e., fluidity, surface tension, mass transport properties, etc, are crucial to softening coal pyrolysis, and have not been well understood;
- Further quantitative experimental observations need to be focused on the transient physical changes, in particular, bubble behaviours, during plastic stage;
- Further modelling work need to be focused on predicting transient internal char structure changes and the heterogeneity of the char structure from the standard coal properties.

## 2.5 Scope of the present work

The present work is focused on a mechanistic investigation of char structure evolution during devolatilization in an inert gas environment employing both experimental and modelling approaches, and is largely focused on heterogeneity and transient changes of char morphology. In specific, the whole project consists of three major parts:

- Experiments are conducted in the single particle reactor using density fraction coal sample to provide transient observation on the swelling and bubble behaviour of individual coal particles. The experiments provide transient mechanistic information on coal swelling and char formation;
- Analysis on the chars collected in DTF and PEFR using density fraction samples and full coal provides further insight into the char formation at high heating rates and pressures and the link between the char structure and raw coal properties;

- 3) Development of a mathematical model based upon the bubble mechanism, which simulates the transient swelling and structure evolution of single coal particles. The model provides mechanistic interpretation to the coal swelling and char structure formation during devolatilization. Char structure distribution is predicted from the density separation samples;
- 4) In combination with previous studies in this centre and from the open literature, results of DTF and PEFR chars in this study will provide validation to the mathematical model.

## **CHAPTER 3. EXPERIMENTAL**

## 3.1 Coal sample preparation

**Parent coal.** Two Australian coals are selected, and their properties are shown in **Table 3.1.** Coal A is a high volatile sub-bituminous coal with high liptinite content (24.9%). The volatile matter content of coal A is 40.2%, and the vitrinite reflectance is 0.44%. Coal B is a bituminous coal with high inertinite content (34.7%). Its volatile matter content is 29.7%, with the vitrinite reflectance of 0.73%. The coal samples are then crushed to the size range  $+63-90 \ \mu m$ .

 Table 3.1. Properties of raw coal samples.

	Proxim	Ultimate Analysis % (d.a.f.)					Maceral Analysis			Dumou			
	Air dried	Ach	VM	FC	C	п	0	N	ç	Volume		(MF)	(0/)
Coal	moisture	Asii	VIVI	гC	C	п	0	IN	3	V	L	Ι	(70)
Α	6.70	12.10	40.20	41.00	78.60	6.10	13.70	1.07	0.48	62.00	24.90	13.10	0.44
В	2.20	14.80	29.70	53.30	83.70	5.45	8.60	1.81	0.47	62.10	3.10	34.70	0.73

**Density separation.** Density-fraction samples of the above two coals are prepared using the sink-float method. The sink-float technique has been described in the literature (Van Krevelen, 1981), and has been extensively employed in recent years by coal researchers to achieve high coal maceral concentrations (Van Krevelen, 1981; Choi et al., 1987; Sugawara et al., 1994; Cloke et al., 1997; Gilfillan et al., 1999; Rubiera et al., 1999). The principle of the density-separation is based on the difference in the densities of different coal macerals. Within the same coal, the density of maceral components follows the order liptinite<virinite<inertinite, as shown in **Figure 3.1** (Van Krevelen, 1981). Density separation can also be achieved by the centrifugation method (Dyrkacz et al., 1982).



Figure 3.1. Density of coal maceral as a function of carbon content (after (Van Krevelen, 1981)).

During density separations, coal is usually crushed down to a particle size below 38  $\mu m$ in order to effectively liberate maceral components. Minerals are also chemically removed before density separation (Dyrkacz et al., 1982; Dyrkacz et al., 1984<sup>a</sup>; Gilfillan et al., 1999). Thus, very high vitrinite concentration (above 95%) can be achieved in the light density fraction, while relatively high inertinite concentration is gained in the heavy density fraction sample. To coincide with the normal pf (+45-150  $\mu m$ ) coal utilization environment, the particle size of the coals in the present study is selected in the pf size range (+63–90  $\mu m$ ), and demineralization is not performed. CsOOCH (water solution) has been used as the sink-float separation medium. Both coals are separated into five density fractions, i.e., F1.25, S1.25-F1.30, S1.30-F1.35, S1.35-F1.50 and S1.50. **Table 3.2** shows the sample mass of each density fraction gained through density separation under the present experimental conditions. It can be seen that different fractional masses are yielded for the same density cut from different coals. Majority of the mass yielded from coal A is in S1.30-F1.35 and S1.35-F1.50. However, the S1.25-F1.30 fraction of coal B accounts for 52.1% of the total mass.

	Fractional mass (wt, %)							
Coal		S1.25-	S1.30-	S1.35-				
	F1.25	F1.30	F1.35	F1.50	S1.50			
Coal A	0.6	12.9	36.5	45.7	4.4			
Coal B	2.1	52.1	17.6	19.5	8.6			

**Table 3.2**. Sample fractional mass yield from the sink-float density-separation.

Porosity and density of the raw coal samples of the density fractions of both coals have been measured using the mercury porosimetry, and the results are shown in **Table 3.3**. For both coals, there is no major difference in the porosity and average pore size among different density fractions of the raw coal samples in the same coal.

**Table 3.3.** Physical properties of raw coal samples of density fractions of coal A and B measured using a mercury porosimetry.

Sample		Coal A	L	Coal B					
~	F1.30	F1.35	F1.50	F1.25	F1.30	F1.35	F1.50	S1.50	
<b>Total Intrusion</b>									
Volume $(cm^3/g)$	0.734	0.767	0.707	0.768	0.759	0.785	0.737	0.633	
Average Pore									
Diameter (µm)	0.129	0.124	0.103	0.133	0.128	0.134	0.143	0.127	
Apparent									
Density $(g/cm^3)$	1.29	1.35	1.44	1.22	1.26	1.31	1.40	1.68	

Ultimate analysis and proximate analysis have been carried out with the density-fraction samples, and the results are presented in **Table 3.4**. With increasing the coal density, VM content (db basis) decreases significantly while a sharp increase in the ash content

(db basis) occurs. Both the carbon content and hydrogen content generally decreases with increasing the coal density, while oxygen content increases. For coal A, the carbon content decreases 5.5% (daf) while the H content decreases 0.3% (daf) from the F1.30 density fraction to the S1.50 density fraction. For coal B, the carbon content decreases from 84.4% (daf) to 81.4% (daf) while the H content decreases from 5.50% (daf) to 5.26% (daf) from the lightest density fraction to the heaviest density fraction. The petrographic analysis is carried out to determine the maceral composition of each coal sample based on the measurements of reflectogram. The maceral composition of each density-fraction coal sample is also presented in **Table 3.4**. The reflecto gram of the coal samples of density-fractions and the full coal is measured manually, and are shown in Appendix A. There exists a fluctuation of maceral composition in some of the samples with changing the coal density for coal A. However, general trend shows that the inertinite content increases while the liptinite + vitrinite content decreases as the coal density increases. The trend is more apparent for coal B, with the inertinite content of around 10% (daf) for the light density fractions while around 60% (daf) for the heavy density fraction.

Particle size distributions of raw coal samples of density fractions are measured using the Malvern Laser Sizer. The results show that particle sizes of all density fractions are distributed in a narrow and similar size range, as shown in **Figure 3.2**. This suggests that the particle size distribution of raw coal samples is independent of the coal fraction density and maceral constituents. The morphology of the raw coal samples of the density fractions under SEM is shown in **Figure 3.3**.

Coal		A	4		В						
Sample	S1.25- F1.30	S1.30- F1.35	S1.35- F1.50	S1.50	F1.25	S1.25- F1.30	S1.30- F1.35	S1.35- F1.50	S1.50		
Proximate analysis (db, %)											
Ash	4.10	10.80	25.50	45.70	0.80	2.70	7.20	26.00	45.20		
VM	38.70	40.40	38.80	27.30	41.20	37.90	33.80	28.10	21.70		
FC	57.20	48.80	35.70	27.00	58.00	59.40	59.00	45.90	33.10		
Ultimate	Ultimate Analysis (daf, %)										
С	84.30	80.80	80.20	78.80	84.38	83.23	83.85	84.90	81.41		
Н	5.88	5.70	5.68	5.50	5.49	5.72	5.40	5.00	5.26		
Ν	2.07	1.64	1.54	1.98	0.07	1.99	1.90	1.91	1.69		
0	7.15	11.42	12.13	13.10	8.67	8.63	8.44	7.80	10.78		
S	0.57	0.48	0.45	0.58	0.10	0.43	0.41	0.39	0.86		
Maceral content (MMF, %)											
v	67.8	35.4	42.6	59.0	78.8	86.6	55.4	33.4	33.8		
L	25.8	59.2	46.6	24.6	8.6	3.2	7.4	3.2	6.0		
I	6.4	5.4	10.8	16.4	12.6	10.2	37.2	63.4	60.2		

Table 3.4. Properties of density-separated coal samples.



**Figure 3.2**. Particle size distributions of the density fraction samples of both coals measured using the Malvern Sizer.



(a) Coal A



(b) Coal B

**Figure 3.3.** SEM morphology of raw coal particles of density-fraction samples of both coals; *A*—F1.25; *B*—F1.30; *C*—F1.35; *D*—F1.50; *E*—S1.50.

Size fraction samples. In addition to the density-fraction samples, size fraction samples are also prepared for both coals. Four size ranges are selected, i.e. +45-63, +63-75, +75-90 and +90  $\mu m$ , within the pf size range. Raw coal samples are analysed before pyrolysis experiments are conducted. The ultimate and proximate analysis data show

that there is no major change in proximate and ultimate composition among the different size fractions from the same coal, and is similar to that shown in **Table 3.1**. PSD of size fraction raw coal samples is measured using both Malvern Laser Sizer and SEM image analysis. The results measured using the Malvern Sizer are presented in **Figure 3.4**. Morphologies of raw coal particles are also examined under SEM, and are used in image analysis.



**Figure 3.4.** PSD (by volume) of raw coal samples of size fractions of both coals measured using the Malvern Sizer.

#### 3.2 The single particle reactor (SPR)

The purpose of the set-up of the SPR is to investigate pyrolysis behaviour of individual coal particles from density-fractions of different coals under different heating conditions. The schematic diagram of the SPR reactor is shown in **Figure 3.5**, and has been reported elsewhere (Yu et al., **2001;** Yu et al., 2002<sup>d</sup>). The reactor is operated at the atmospheric pressure. The heating rate is controlled by the level of the electrical power output, and can reach ~300 *K/s*. Coal particles of pf size are spread on a Platinum strip (the heating element) inside the glass chamber. A thermocouple is welded onto the Pt strip to measure the temperature during heating. Coal particles are heated in a

nitrogen atmosphere. With the present heating rate range, the coal particles are considered to have a uniform heating owing to the small particle size and the convective heat transfer at pyrolysis temperatures. From video images recorded, there is no apparent evidence of non-uniform heating of each single particle. A CCD video camera (PulNiX TMC-6DSP, 25 frame/s) equipped with a long distance microscopic lens is used to monitor the transient particle morphology change. In order to improve the image quality, a UV light source has also been used. The particle swelling processes are recorded on videotapes, and are transferred into the computer using a HauppaugeTV-USB (Model 706) video capture card. Images are processed on the computer using the ImageTool v2.00 software. Thus transient swelling ratios  $(d/d_0)$  and particle morphology changes are analysed.



Figure 3.5. Schematics of the single particle reactor.

## 3.3 Char preparation in DTF and PEFR

The char samples have been prepared in a drop tube furnace at the atmospheric pressure in a nitrogen gas atmosphere using density-separated samples of both coals. Two peak temperatures, i.e., 1373 *K* and 1573 *K*, are used respectively. A fluidized-bed feeder has been used to feed in coal samples. The primary flow gas carries coal particles into the furnace from the top through a water-cooled feeding probe. The coal feed rate is ~2 g/hr. Secondary gas flow enters the furnace from the top. The residence time is calculated from and controlled by the gas flow rates, and is 300~400 *ms* in the present experiments. The schematic diagram of the reactor has been described elsewhere (Yan, 2000), and is illustrated in **Figure 3.6.** Typical heating rate of pf particles in the drop tube furnace is  $1\sim5\times10^4$  K/s by calculation (Jamaluddin et al., 1986). The water-cooled sampling probe is extended into the furnace from the bottom, and chars are collected in the cyclone.



Figure 3.6. The schematic diagram of the DTF reactor, after Yan (Yan, 2000).

In order to investigate the effect of pressure on char structure and morphology during devolatilization, some char samples have also been prepared in the pressurized entrained flow reactor (PEFR), running at elevated pressure of 2.0 *MPa*. Wall temperatures are 1373 *K* and 1673 *K*, respectively. The detail of the reactor is described elsewhere by Harris et al (Harris, 2001) and Park (Park, 2002). Other experimental parameters for chars prepared in the present study are shown in *Appendix B*.

#### 3.4 Char characterization

#### 3.4.1 Determination of weight loss

Proximate analysis is carried out to determine the volatile content, fixed carbon and ash content of char samples. The weight losses ( $\Delta W$ ) and Q factors during the pyrolysis in the DTF are determined using the total ash tracer. Q factor is defined as  $Q = \Delta W/(VM_0 - R)$ , where R is the volatile matter content of the char, and  $VM_0$  is the proximate volatile content of the parent coal. The ash tracer approach has been described and employed in the literature (Badzioch et al., 1970; Jamaluddin et al., 1986; Yeasmin et al., 1998), and is detailed in *Appendix C*.

#### 3.4.2 Particle size distribution of chars

The particle size distribution of char and coal is measured using a Malvern Laser Sizer. The principle of measuring particle size using the laser diffraction method has been described elsewhere (Griffiths, 2002). The char morphology is observed under the Scanning Electronic Microscope (SEM). Char particles are spread on stubs, and coated with gold or carbon. Two or three stubs have been used for each char sample. Char particle size distribution is also measured through SEM image analysis using the ImageTools V2.00 software provided by UTHSCSA Dental Diagnostic Science (Dove et al., 2002). The variation of the char particle size measured through image analysis is dependent on the magnification. For char particles in the size range of -90+63  $\mu m$ , the errors of the results have been analysed and shown in **Figure 3.7**. Therefore, images for measuring char PSD in the present study have been taken at a magnification of  $120 \times$  in order to minimize the error to less than 1%. The final swelling ratio of the char is obtained by comparing the average char particle size to the average raw coal particle size.



**Figure 3.7.** The variation of measured char particle size through SEM image analysis as a function of the magnification.

#### 3.4.3 Pore size and porosity of individual char particles

In order to analyse char structures, cross-section samples have been prepared using resin as the binding material. Each sample is then coated with carbon, and analysed under the SEM. The porosity of individual char particles is analysed through SEM image analysis using the same ImageTools software (Dove et al., 2002). Images of cross-section samples are taken at a higher magnification of 200× in order to minimize the errors of image analysis. The char structure type (i.e., Group I, Group II or Group III) of each char particle is determined according to the three-fold char structure classification system by Bailey and Benfell (Bailey et al., 1990; Benfell et al., 1998; Benfell et al., 2000), mainly based on its porosity and internal configuration. The char structure distribution of each char sample is also obtained. It may be noted that the average porosity measured using image analysis is always lower than the true porosity due to two reasons: 1) in cross-section samples, char particles are not cut across the maximum geometric diameter; 2) micro-porosity is not able to be measured due to the resolution at the magnification of the measurement. On the contrary, for chars in pf size, the overall porosity of char samples measured using mercury intrusion porosimetry is usually larger than the true porosity, due to the difficulty in distinguishing the intra and inter particle voids.

### 3.5 Summary of this chapter

Experiments in the present study target two goals:

- i. Providing mechanistic information of swelling, bubble behaviour and morphology changes of coal particles during pyrolysis. The advantage of the single particle reactor is the transient monitoring of the swelling and bubbling behaviour of individual coal particles under controlled heating conditions. The information of the morphology and char structure is obtained through analysing the DTF and PEFR chars. The heterogeneity of char structure is revealed through density separated coal samples;
- ii. Providing experimental data for char structure model validation. Results of swelling ratio and char structure (porosity and char type distribution) of DTF chars are compared with model predictions from this study.

## CHAPTER 4. SWELLING BEHAVIOUR OF INDIVIDUAL COAL PARTICLES IN THE SINGLE PARTICLE REACTOR

## 4.1 Introduction

Direct observation of transient pyrolysis behaviour of individual coal particles during heating may provide useful information of particle swelling and morphology change, therefore can greatly enhance the knowledge of char structure formation. Single particle experiments have been extensively conducted in the past using laser heating techniques (Zlochower et al., 1990; Dodoo et al., 1991; Maswadeh et al., 1992; Zhang, 1992; Phuoc et al., 1993<sup>b</sup>; Dodoo et al., 1994; Shen et al., 1994; Thomas et al., 1994; Okazaki et al., 1996; Gao et al., 1997; Chen et al., 2001) and gas flow reactors (Boukara et al., 1992; Schroeder et al., 1992; Hackert et al., 1998; Hackert et al., 1999).

Due to its unique capability of simulating the flame heating fluxes in conventional and high intensity combustion, laser heating technique has been extensively employed in single particle experiments (Maswadeh et al., 1994; Gao et al., 1997), in particular, in investigations of combustion characteristics (Phuoc et al., 1989; Zhang, 1992; Phuoc et al., 1993; Shen et al., 1994; Thomas et al., 1994; Chen, 2002). Using a high energy Nd-Yag laser system, Phuoc et al (Phuoc et al., 1989; Phuoc et al., 1991; Phuoc et al., 1993) investigated ignitions of coal under different conditions. Two ignition mechanisms were observed: the surface ignition followed by gas-phase ignition for low rank coals while only gas-phase ignition for bituminous coal. Shen et al. (Shen et al., 1994<sup>a</sup>) investigated combustion behaviour of single pulverized coal particles, and concluded that ignition time of coal was not dependent on coal composition, but was significantly affected by

the heat influx, while the particle burning time went the opposite way. As a significant result of this study, a correlation between maximum expansion rate  $((V_{max}-V_0)/V_0)$  and the burning time was established, which demonstrated that the burning time decreased linearly with increasing the maximum expansion rate, as presented in **Figure 4.1**. This observation is consistent with the conclusion of Wu et al (Wu et al., 1999; Wu, 2000<sup>b</sup>). Chen et al (Chen et al., 2001; Chen, 2002) investigated combustion behaviour of single maceral coal particles using a laser-heating reactor, and weight loss was measured using a nano-balance system. The single maceral particles were obtained by hand pick-up under the microscope.



**Figure 4.1.** Burning time as a function of the maximum expansion rate (after Shen et al., 1994<sup>a</sup>).

Laser heating is also proved to be an effective means for coal pyrolysis studies. Using a  $CO_2$  laser heating apparatus, Gao et al (Gao et al., 1996) observed surface structure transition of coal particles, and concluded that there was an optimum range of heating rate for the increase of coal plasticity. In their further studies (Gao et al., 1997), the

#### Chapter 4. Swelling Behaviour of Individual Coal Particles in the Single Particle Reactor

swelling and fluidity of single coal particles heated with  $CO_2$  laser were evaluated using image analysis. Their investigations provided detailed and direct observations of bubble behaviour of coal particles, and linked bubble behaviour to coal plastic properties.

An in-situ observation was conducted by Hackert et al (Hackert et al., 1998; Hackert et al., 1999) on a lab-scale high-pressure drop tube furnace (KOALA-furnace) equipped with view ports and TOSCA-systems. Transient swelling index ( $v/v_0$ ) of two coals with two size fractions (+50-63  $\mu m$ , +90-105  $\mu m$ ) was measured as a function of residence time. However, no apparent bubble rupture behaviour was detected in the swelling curves. From their results, small particle sizes led to a larger maximum swelling index, while the final swelling index was not sensitive to the particle size. Schroeder and his colleagues (Schroeder et al., 1992) measured transient morphology, temperature and velocity of individual coal particles in a drop tube furnace facility (DTFF), and compared the calculated instantaneous particle burning rate ( $\mu g/s$ ) with literature data.

Captive reactors have been used in investigating devolatilization weight loss of bulk coal samples (Anthony et al., 1976; Gavalas, 1982; Mill et al., 1998; Mill, 2001) and devolatilization characteristics of large single coal particles (Saito et al., 1987) in the past studies. The morphology of residue chars from WMR reactor was also examined under SEM (Hamilton et al., 1979). Compared to gas flow reactors and laser heating system, captive reactors have lower heating rates, ~1000 K/s. However, particles can be heated under well-controlled conditions, such as heating rate, gas and pressure.

Using two different experimental techniques, Johnson et al (Johnson et al., 1988) studied the pyrolysis of single particles of several UK coals in an inert atmosphere at the heating rate of 100-1500 K/s. The onset of melting and swelling was filmed and observed. The total volatile yield and the yield of several hydrocarbon gases from the

#### Chapter 4. Swelling Behaviour of Individual Coal Particles in the Single Particle Reactor

pyrolysis of coal particles were measured. Their results showed that the heating rate had little effect on the extent of devolatilization of bituminous coal. It was also observed that the maximum rate of devolatilization and the hydrocarbon gas yield occurred at 700-1000 K, which was within the same range of temperatures for vigorous swelling.

In the present study, single particle experiments are conducted in the captive single particle reactor using density-separated pf coal samples. Such investigation has not been noted in the open literature. Some experimental results from this study have been reported elsewhere (Yu et al., 2001; Yu et al., 2002; Yu et al., 2002<sup>d</sup>). The major purpose for the investigation are: (1) to observe transient swelling behaviour of individual pf coal particles under different pyrolysis conditions; (2) to observe bubbling phenomena of pf coal particles during plastic stage, therefore to confirm the swelling mechanisms of coal particles; and (3) to compare swellings and thermoplastic behaviour of pf coal particles from different density-fraction samples of the same coal. This study extends our understanding of the heterogeneous nature of coal for char formation.

## 4.2 Experimental procedure

The experimental apparatus and sample preparation have been described in section **3.2** and reported elsewhere (Yu et al., 2001; Yu et al., 2002). The experimental procedures involve sample preparation, the calibration of heating rates and image magnification, pyrolysis experiments and image analysis.

**Calibration.** The peak temperature and the heating rate are controlled by the level of the voltage of the electrical power unit for a given dimension of the Pt strip,  $0.2 \times 7.5 \times 65$  mm in the present experiments. **Figure 4.2** shows the temperature history of the heating strip as a function of the power voltage under the present condition. As the particle size

is very small, the temperature of the particle is considered the same as the strip temperature. The heating rate is averaged between temperatures of 623 and 823 K. In the present experiment, the heating rate is in the range  $10\sim 200$  K/s. The heating rate of 10 K/s is achieved by manually controlling the power output successively.



Figure 4.2. Temperature history as a function of the power voltage.

**Table 4.1.** The magnification as a function of the work distance (lens with 2×DL tube).

Lens		3	4x lens				
Lens work							
distance (mm)	160	140	120	100	82	25	20
Magnification	131	154	177	208	246	392	438

The magnification of the lens ( $3 \times and 4 \times$ ) as a function of the work distance, as shown in **Table 4.1**, is calibrated using a reference object with the dimension of 130  $\mu m$  in diameter. The magnification is calculated by comparing the size of the image of the object on the monitor screen to the original size of the reference object. Apparently, large magnification is achieved at the expense of work distance. In the present experiments, the magnification of 246× has been used. **Pyrolysis experiments**. The chamber is closed and sealed after coal particles are dispersed on the Pt strip. The lens is focused with the UV light on, so that a clear image of the selected coal particles appears on the monitor screen. Temperature and time are also displayed on the screen. The chamber is flushed with N<sub>2</sub> gas three to four times, and pyrolysis experiments are conducted at 0.1 *MPa* pressure. The video recorder is started before the electrical power is turned on. The transient devolatilization behaviour, i.e., swelling, bubbling and morphology change, is recorded together with the temperature history. An example of the image frame during experiments is shown in **Figure 4.3**. For each density-fraction sample, the experiments have been repeated 8~10 times so that 30~40 particles are observed and recorded.



**Figure 4.3.** A video image frame recording particle pyrolysis processes during experiments on the single particle reactor.

**Image analysis.** After experiments, the recorded video images are transferred into the computer and converted to separated images (25 frames per second video image) using the video capture card (HauppaugeTV-USB Model 706) and Irfan View V3.70 software. The images are then analysed on the computer using the ImageTools software. The transient diameters of observed coal particles are measured, and swelling ratio is

#### Chapter 4. Swelling Behaviour of Individual Coal Particles in the Single Particle Reactor

determined by comparing the transient particle diameter to the original coal particle diameter. The bubbling phenomena and morphology change of different density fraction samples are also analysed and compared qualitatively. To quantitatively describe the transient morphological changes of the particles during the heating, the following parameters are measured through image analysis: (1) particle diameter; (2) elongation, which is the major axis length by the minor axis length; (3) compactness; (4) roundness, which describes the smoothness of the particle edge; and (5) sphere index, which is defined as *(perimeter/\pi-d)/d*, where *d* is the particle diameter. The particle diameter determines the swelling ratio of the particle during heating. The elongation, compactness, roundness and sphere index are parameters defining the particle shape. For instance, large elongation with high sphere index defines a particle with an elongated shape. Small elongation with small sphere index defines a particle with a spherical shape but its outer profile is round.

### 4.3 Results and discussion

#### 4.3.1 Heterogeneity of pyrolysis behaviour of coal particles

## 4.3.1.1 Comparison of swelling behaviour of density-fraction samples

Significant swelling and bubbling phenomena have been observed for both coals under the present experimental conditions. However, marked variations exist among coal particles from different density-fraction samples of the same coal. Light density samples exhibit higher swelling and more intensive bubbling compared to heavy density samples. **Figure 4.4** compares transient swelling behaviour of observed particles from three different density-fractions of coal A at the heating rate of 100 *K/s*. The particle in **Figure 4.4** (*a*) is from density-fraction F1.25 – the lightest density fraction, while the one in (b) is from medium density-fraction S1.30-F1.35, and Figure (c) from heavy density fraction S1.35-F1.50. The images in Figure (a) clearly demonstrate that the particle grows larger during the plastic stage due to the growth of the bubbles, and particle shrinks as the bubbles burst. This process occurs repeatedly before the particle resolidifies in the case of (a) and (b). At the final stage of the plastic stage, the particle looks almost transparent when the particle swells to a very large extent. This implies that the particle is highly porous at that moment, and the outer liquid shell is very thin. The author believes that this large extent of swelling of the particle without bubble rupture is attributed to high wall strength and high surface tension of the liquid shell of the particle. Solomon et al (Solomon et al., 1993) introduced the wall stress reaches its critical value, the bubble ruptures.

It is quite apparent from the picture that swelling and bubbling decrease significantly as the coal density increases. The particle in **Figure 4.4** (c) from the heavy density sample shows very little morphology changes during heating. From **Table 3.4**, the liptinite and vitrinite content decrease while ash content increases with increasing the coal density. It is therefore reasonable to consider that particles observed in (a) and (b) are most likely liptinite or vitrinite particles, while the particle (c) contains high inertinite and, or mineral matter. It has been reviewed in chapter 2 that liptinite and vitrinite macerals develop high fluidity during heating, while inertinite exhibit no fluidity at conventional heating rates. Ash grains remain solid at pyrolysis temperatures hence suppress the apparent fluidity of the whole particle. Therefore, particles from light density fractions exhibit high swelling while no apparent swelling occur with heavy density fraction particles.

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**Figure 4.4.** Transient swelling behaviour of the observed particles from different density-fraction samples of coal A at the heating rate of 100 K/s; (a) F1.25, (b) S1.30-F1.35, (c) S1.35-F1.50, scale bar—130  $\mu m$ .

Quantitative analysis of transient swelling ratios through image analysis are presented in **Figure 4.5**. A large swelling ratio is obtained for the particle from the lightest density fraction sample, and swelling decreases drastically as the coal density increases. The maximum swelling ratio for the observed particle of F1.25 fraction samples of coal A is 3.2 while final swelling ratio is around 2.0. This implies that swelling ratio measured from the DTF chars is not able to represent the transient swelling and char structure changes at the intermediate stage of the devolatilization process. Results of previous studies (Shen et al., 1994<sup>a</sup>) suggested that the particle burning time is associated with maximum expansion rate during combustion. Particles with large maximum swelling

ratios will burnout much earlier. Bubble ruptures are also clearly reflected by the sharp drops of the swelling curves of the F1.25 and F1.35 density particles.



Figure 4.5. Transient swelling ratio of the observed particles from three density-fractions of coal A at the heating rate of 100 K/s.

A decrease in the swelling with increasing the coal density has also been observed for coal B, as presented in **Figure 4.6** and **Figure 4.7**. However, particles from coal B behave quite differently from that of particles from the same density-fraction of coal A during the heating. **Figure 4.6** demonstrates transient pyrolysis behaviour of a particle from the lightest density F1.25 fraction of coal B at the heating rate of  $100 \ K/s$ . More frequent bubble ruptures, which caused particles to shrink, occur whilst both maximum and final swelling ratios of the coal particles are smaller compared to that of the particles from the same density fraction of coal A. Obviously, pyrolysis behaviour is strongly coal type dependent. The trend is more clearly demonstrated by the swelling curves of different density particles, as shown in **Figure 4.7**. The particles may shrink to a large extent that the resulted char particles are smaller than the original raw coal particles.

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The thermoplastic properties play a key role in coal particle swelling behaviour (Gao et al., 1997). The author believes that the difference in the swelling behaviour of the two examined coals is attributed to the difference in their thermoplastic properties, e.g. the fluidity and the surface tension. High fluidity and low surface tension will result in more frequent bubble ruptures as volatile gases are more difficult to be trapped inside the liquid particles, such as coal B. On the other hand, high surface tensity and high fluidity will lead to a high swelling and less frequent bubble rupture, such as coal A.



(a) F1.25

(b) S1.35–F1.50

**Figure 4.6.** Transient swelling behaviour of the observed particles of coal B during pyrolysis at the heating rate of 100 K/s.



**Figure 4.7.** Transient swelling ratio of the observed particles of coal B during pyrolysis at the heating rate of 100 K/s.

Comparing **Figure 4.7** with **Figure 4.5**, it may be noted that the difference of the swelling behaviour among the density fractions of coal B is smaller than that for coal A. This is consistent with the conclusion in the literature, as reviewed in section 2.1, that with increasing the coal rank, differences in the chemical composition among different maceral groups diminishes. It is therefore expected that they will behave similarly with high rand coal during heating. In the present study, coal A is a sub-bituminous coal with vitrinite reflectance 0.44%, while coal B is a bituminous coal with reflectance 0.77. Therefore, the differences in the swelling behaviour of different density particles of coal A are more significant than that observed for coal B. In coal B, the particles from F1.50 fraction are more likely to have some small extent of fusion and swelling, while the same density particles of coal A do not show any fusing or swelling Another phenomenon is that the medium density particles of coal A behave quite similar to that of the low density particles from coal B. It can also be seen that the time interval of the plastic stage of F1.25 fraction samples is much longer than that of F1.35 fraction, the medium density particles, **Figure 4.5** and **Figure 4.7**.

Heterogeneity of parent coal properties (Van Krevelen, 1981; Elliott, 1981<sup>a</sup>; Gavalas, 1982; Berkowitz, 1985; Bloomquist et al., 1995; Bailey, 2002) and final char characteristics (Littlejohn, 1967; Bailey et al., 1990; Smith, 1994; Benfell, 2001) have been well recognized and extensively reported in the literature. Individual coal particles of pf size behave very differently due to the heterogeneity of the raw coal properties. However, this hasn't been reported in single particle experiments in the open literature. By using the density separated coal samples in the single particle reactor, the present experiments have presented the heterogeneity of the swelling behaviour of the two examined Australian coals, which is caused by the variation in the properties among the different density fractions. The petrographic analysis shows that L+V content decreases

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while the inertinite content increases at high coal density fraction. It has been widely recognized that liptinite and vitrinite group macerals develop thermo-plasticity and swelling during heating. Liptinite contains the highest hydrogen content amongst the maceral groups, therefore develops higher fluidity and larger swelling due to the high concentration of the hydrogen donor and low cross-linking rate (Van Krevelen, 1981; Smith, 1994). This is demonstrated by the observed swelling behaviour of the coal particles of coal A. It can also be seen in **Table 3.4** that, with increasing the coal density, the volatile content decreases whilst the ash content increases for both coals. The carbon content and hydrogen content generally decrease as the fraction coal density increases. Therefore, the low-density fraction coal samples will yield more volatile upon heating, which contributes to the swelling during the pyrolysis process.

# **4.3.1.2** Heterogeneity of pyrolysis behaviour of individual particles from the same density fraction samples

In the present study, the density separation somewhat narrows the discrepancy of the pyrolysis behaviour of individual particles within one density fraction. However, the heterogeneity still exists among individual coal particles from the same density fraction, in particular for light density samples. **Figure 4.8** (a) and (b) presents transient particle swelling behaviour of individual particles from different density fraction samples of coal A. The three individual coal particles in (a) behave very differently in terms of maximum swelling ratio, final swelling ratio, and bubble rupture frequency. However, in the light density fractions, bubbling behaviour is the common feature that is distinguished from heavy density sample particles. Since particles from heavy density fraction samples generally do not fuse or swell, there appears no noticeable difference in their behaviour, as shown in (b).





**Figure 4.8.** Transient swelling ratio of the particles from density fraction F1.25 and F1.50 of coal A at the heating rate of 100 K/s.

#### 4.3.2 Transient morphology changes of particle during heating

It is also obvious from **Figure 4.4** that significant morphology changes occur for light density particles, while the morphology of heavy density particles remains almost unchanged during heating. **Figure 4.9** quantitatively shows the dramatic transient changes in morphology parameters as a function of time for the particle from the lightest density fraction sample of coal A at 100 K/s. It may be noted from **Figure 4.9** (*a*) that compactness changes in the opposite way to the elongation, while the roundness changes in the opposite way to the sphere index, in (*b*). However, this trend of the morphology changes in the captive reactor, in which the particles contact with the surface of strip, may not represent the change in the gas flow reactor or the practical
combustion situation where particles are suspended in the gas phase. A droplet of the coal liquid, which is round in the shape in the gas flow reactor, can be spread on the surface of the strip. Therefore, during the plastic stage, the elongation value can be very high while the compactness is small. At the same time moment, the sphere index is large while roundness is small. However, at the time when maximum swelling occurs, the elongation is the smallest and roundness is relatively large. This can be clearly seen from the curves in **Figure 4.9**.



(b)Roundness and shape index

**Figure 4.9.** Transient morphology changes of particle P1 from the light density fraction sample, F1.25, of coal A at the heating rate of 100 K/s; (a) Elongation and compactness; (b) Roundness and shape index.

No apparent swelling and little particle morphology change occur during the heating for heavy density particles for both coals. This is very clear by comparing **Figure 4.10** with **Figure 4.9**. All the four morphology parameters in **Figure 4.10** (*a*) and (*b*) change very little. The majority of particles from F1.50 and S1.50 density fractions of both coals do not fuse or swell, although sometimes particles from coal B tend to. For particles from heavy density fractions, the volatiles may escape through open pores or cracks through a hydrodynamic process. The observations of the particle morphology among density fractions further demonstrate the heterogeneous nature of coal.



(b)Compactness and shape index

Figure 4.10. Transient morphology changes of the particle P1 from the heavy density fraction, F1.50, of coal A at the heating rate of 100 K/s; (a) Elongation and roundness; (b) Compactness and shape index.

## 4.3.3 Particle morphology of char residues after pyrolysis

The morphology of the solid char residues after pyrolysis can be classified into five

broad groups in regards to their swellings, according to the observations by Littlejohn et

al (Littlejohn, 1967). Following this classification system, the morphology of the residue chars is described in **Table 4.2**. Obviously group A and B char particles have solid structures, and char particles of group C, D, E and F are porous.

<b>Fable 4.2.</b>	Classification	of	char	particle	morp holo gy	in	regards	to	swelling	(after
Littlejohn, 1	967).									

Classification	Description
Group A	Almost no changes on heating
Group B	Particle fuses, may become round, but does not swell
Group C	Particle swells into opaque sphere, many bubbles
Group D	Particle swells into transparent, a few bubbles
Group E	Particle has irregular shape after bubble ruptured
Group F	Particle shows more than one of the above

All the listed particle morphologies have been observed in the present single-particle experiments, although proportions of each group vary markedly with increasing the density for both coals. In the heavy density fraction samples, group A and B account for the major population, whilst in lower density fraction samples the majority of the particles fall into group C, D or E, as shown in **Figure 4.11** (*a*) and (*b*). This result qualitatively agrees with literature data (Gilfillan et al., 1999) that lower density fraction samples have a high proportion of thin-walled porous char particles. Particles that demonstrate bubble behaviour generally fall into group C, D or E. SEM analysis of the DTF char samples in the present study (as discussed in chapter 5) shows that the surfaces of char particles from low-density samples are usually closed and with flow patterns on the surface. In light density fraction samples of coal A, a higher proportion of group D have been observed, which are not apparent in coal B samples of

the same density. It is believed that this difference is caused by the different liptinite content of the tested coals. Coal A contains much higher liptinite compared to coal B, therefore presents larger swelling during pyrolysis. Char particles of group F are rare in the experiments due to the small particle size, although the phenomena are occasionally found in F1.30 and F1.35 fraction samples. This type of char is formed when the raw coal particles contains more than one type of maceral constituents, such as inertinites with vitrinites or liptinites.



**Figure 4.11.** The morphology distribution of residue chars of coal A and B after heating (at the heating rate of 100 *K/s*).





(b) Transient pyrolysis behaviour

A few experiments have been done at a slow heating rate of 10 K/s. It has been observed that particles of all density fractions exhibit very low swelling compared to that at the heating rate of 100 K/s. This is reflected in the following respects: (1) much less amount of particles swell; (2) much smaller maximum swelling ratio; (3) much less bubbling phenomena, even with low density fraction samples; and (4) smaller temperature

**Figure 4.12.** Transient pyrolysis behaviour of the observed particle from F1.25 density fraction of coal A heated at 200 K/s.

interval for swelling. A heating rate of 200 *K/s* is also used in the experiments. General trend shows that with increasing heating rate from 10 *K/s* to 200 *K/s*, swelling increases for all density samples of both coals, especially for the low-density fraction samples. Observed bubbling phenomena are more intensive at high heating rates. Some particle movements driven by volatile gas release have been observed during the heating at the heating rate 200 *K/s*. This does not occur when samples are heated at low heating rates. **Figure 4.12** shows transient swelling behaviour of a particle from F1.25 density fraction of coal A heated at 200 *K/s*. The overall swelling behaviour is similar to that shown in Figure 4.5 and Figure 4.8. The occurrence of bubble rupture is clearly presented on the curves and in the pictures.



**Figure 4.13.** Comparison of morphology of char residues of coal A after pyrolysis at different heating rates ( $\blacksquare$  – group A+B;  $\blacksquare$  – group C+D+E+F).

**Figure 4.13** compares the population of solid char residues of coal A with different morphology after pyrolysis at two different heating rates, 100 K/s and 200 K/s, based on the classification system in **Table 4.2**. A slight increase in the population of particles that become fused and develop swelling has been observed in all density fraction

samples for coal A. Similar trend exists for coal B. For all density fraction samples tested, A+B group population decreases at 200 K/s, while the population of porous chars increases. This may be attributed to the increase in both fluidity and devolatilization rate of coal at the increased heating rate.

The impact of heating rates on coal devolatilization behaviour and thermo-plastic properties has been reported in the literature (Howard, 1981; Khan et al., 1986; Khan et al., 1988; Fletcher, 1993; Smith, 1994; Gale et al., 1995; Gao et al., 1997), as reviewed in chapter 2. In general, high heating rate shifts devolatilization reactions to a higher temperature range. Hence, the devolatilization reactions occur at a high rate. Higher volatile yields and more intensive volatile release are expected, and in the meantime, secondary reactions are suppressed. Some optimum heating rate values for maximum swelling and fluidity of individual coals have been reported in the open literature(Gale et al., 1995; Gale et al., 1996). However, the value is very much dependent on coal types (coal rank, maceral constituent) and on heating environments (Khan et al., 1986). Gale et al. (Gale et al., 1995) reported decreases in swelling and porosity of bituminous coals at very high heating rates, and pointed out the transition heating rate range at  $10^3$  - $10^4$  K/s for maximum swelling ratio of Pittsburgh No.8 coal. Swelling behaviour of single particle at high heating rates ( $\sim 10^4 K/s$ ) using the laser heating has been reported in the literature (Gao et al., 1997) and gas flow reactor (Hackert et al., 1998; Hackert et al., 1999). In general, particle behaviour is rather similar to that observed in the present study. Figure 4.14 (a) shows the transient swelling during laser heating of an observed particle from Goonyella coal measured using a high-speed camera (Gao et al., 1997). Figure 14 (b) presents the measurements of the transient swelling ratios of two particles

of Ensdorf coal with different particle sizes in a gas flow reactor (Hackert et al., 1998; Hackert et al., 1999).



**Figure 4.14**. Transient swelling behaviour of coal particles at high heating rate; (*a*) Goonyella coal using laser heating (Gao et al., 1997), laser intensity =  $2.22 \ MW/m^2$ , particle size 149  $\mu m$ ; (*b*) Ensdorf coal, gas flow reactor (Hackert et al., 1998; Hackert et al., 1999), particle size in  $\mu m$  as indicated.

### 4.4 Conclusions of this chapter

- A single particle experimental set-up has been built in the present study, which allows a direct observation of transient pyrolysis behaviour of individual coal particles, and provides an effective means to enhance the knowledge of char formation;
- Results using the density fraction coal samples demonstrate that pyrolysis behaviour of individual particle in pf size from the same coal can be significantly different under the same heating conditions due to the variations in the properties of the feed coal. General trends show that swelling decreases drastically with increasing the coal fraction density;

- Apparent bubbling phenomena have been observed during heating with particles from light density fraction samples, which do not occur in the heavy density particles. The results demonstrate that bubble behaviour is responsible for particle swelling;
- The morphology of particles changes dramatically for light density particles during heating due to the development of thermo-plasticity and particle swelling;
- The maximum swelling ratio of the particles during intermediate plastic stage is much higher than the final swelling ratio. This implies that the swelling measured using DTF chars is not able to represent the transient swelling and internal structure changes during the intermediate stage of devolatilization;
- Swelling behaviour is strongly coal type dependent due to their properties, i.e. rank and maceral composition. With the two coals examined in the present study, coal A exhibits much higher swelling ratio, while more frequent bubble ruptures have been observed for coal B;
- Statistical results show that the population of porous chars decreases with increasing the coal density for both coals;
- Heating rates have apparent influence on coal swelling. At a slow heating rate of 10 *K/s*, much less swelling and bubbling is observed. At high heating rates, more particles develop fluidity and swelling.

# CHAPTER 5. THE SWELLING AND STRUCTURE OF CHARS PREPARED IN THE DROP TUBE FURNACE

## 5.1 Introduction

Drop tube furnaces have been employed extensively in the past to study coal combustion, gasification and pyrolysis behaviour (Howard, 1981; Gavalas, 1982; Boukara et al., 1992; Solomon et al., 1992; Wall et al., 1992; Bailey, 1993; Seewald et al., 1995; Gale et al., 1996; Gilfillan et al., 1997; Benfell et al., 1998; Man et al., 1998; Yeasmin et al., 1998; Liu et al., 1999; Wu et al., 1999). Compared to captive furnaces, the drop tube furnace has high heating rates and well-controlled gas environments to simulate the practical combustion and gasification processes, and is able to produce large quantities of samples required for further analysis. Pyrolysis chars from DTF are able to represent char characteristics under early stage combustion conditions (Bailey, 1993). As reviewed in chapter 2, density separation techniques have been employed extensively to study the char characteristics from maceral concentrations (Dyrkacz et al., 1982; Dyrkacz et al., 1984<sup>a</sup>; Cloke et al., 1997; Gilfillan et al., 1997; Gilfillan et al., 1999; Kawashima et al., 2000). In the present study, in order to investigate the heterogeneity of char structures, char samples are produced in a laboratory DTF reactor using density-separated coal samples, and are examined carefully. Coal samples are not subjected to demineralization. In combination with results presented in Chapter 4, experimental data of the density-fraction samples in this chapter provide systematic information of coal devolatilization and char formation, and will be used in the model validation in the subsequent chapters. In addition to the dominant role of coal macerals, the influence of ash level of coal on char formation is identified.

### 5.2 Experimental procedure

The experimental set-up of the DTF furnace and the preparation of density fraction and size fraction coal samples have been described in **Chapter 3**. The experimental procedure in this chapter involves DTF experiments, char analysis (including weight loss, particle size distribution, surface texture and char morphology, cross-section structure) and image analysis.

*Pyrolysis experiments.* Coal samples are dried at 110 °*C* in the oven before experiments. N<sub>2</sub> gas is used in pyrolysis experiments. The flow rates of the primary gas, secondary gas, quenching gas, and suction rate are carefully adjusted, shown in **Table 5.1**, to ensure that the furnace atmosphere is reduced. The residence time is calculated according to the furnace dimension and gas flow rates, and is  $300 \sim 400 \text{ } ms$  in the present experiments. Peak temperature is selected at 1573 K, but a few experiments are run at 1373 K in order to investigate temperature effect on char characters. The feeding probe, sampling probe, furnace and the cyclone are completely cleaned before each experiment run to avoid contaminations on char samples. Chars are collected in the cyclone.

**Table 5.1.** Gas flow rates used in the experiments.

Nitrogen gas	Primary gas	Secondary gas	Quenching gas
Flow rate ( <i>l/min</i> )	7.5	8.5	1.5

**Char analysis**. Ultimate and proximate analyses of char samples are carried out after char samples are collected in pyrolysis experiments. Weight losses and Q factors during pyrolysis are obtained using ash tracer by comparing the proximate analysis data of char

to that of raw coal samples, as described in Appendix C. PSD of chars is analysed using the Malvern Laser Sizer. Some of the char samples are subjected to XRD analysis to determine the extent of graphitization and mineral transformation. Char morphology and cross-section structures are analysed under the SEM. SEM images are taken at the accelerate voltage of  $5\sim15 \ Kv$ . PSD of each char sample is also measured through image analysis, as described in Section **3.4.2**. Two types of size bins are used in the PSD measurements in the present study, shown in **Table 5.2**. Size bin I is the same as that for the Malvern Sizer measurements. Size bin II is an even size bin. Swelling ratios are obtained by comparing the mean particle size of char to that of raw coal.

Size Bin I	Size Bin II
~14	~15
$14 \sim 25$	$15 \sim 30$
25~31	$30 \sim 45$
$31 \sim 37$	$45\sim 60$
$37 \sim 46$	$60 \sim 75$
$46 \sim 56$	$75 \sim 90$
$56 \sim 68$	90~105
68~83	105 ~ 120
83~101	120 ~ 135
101 ~ 123	135 ~ 150
123 ~ 150	150 ~ 165
150~183	165 ~ 180
183 ~ 223	180 ~ 195
$223\sim 272$	$195\sim 210$
$272\sim 404$	$210\sim 225$
404 ~	225 ~

Table 5.2. Two types of particle size bins used in the SEM image analysis.

*NB: numbers as in*  $\mu m$ .

Sample	Coal A					Coal B				
	F1.25	F1.30	F1.35	F1.50	S1.50	F1.25	F1.30	F1.35	F1.50	S1.50
PSD	265	165	181	211	151	172	158	141	138	164
Porosity	118	122	-	129	-	125	111	124	138	137

Table 5.3. Number of particles analysed for each char sample during image analysis.

The porosity of each individual char particle is measured through SEM image analysis. Original SEM images are in grey scale, and each SEM image contains a number of char particles. Measurements are carried out particle by particle. Certain number of char particles are analysed for each char sample, as shown in **Table 5.3**.

The image analysis for porosity measurement involves the following three steps, as illustrated in **Figure 5.1**:

- *Image separation.* Each individual char particle image (in grey scale) is separated from the whole picture, so that each char image subjected to the ImageTools measurement contains only one char particle. Figure 5.1 (A) shows single char cross section images separated from a whole SEM image.
- *Measurement of the total char particle area*. In this step, the grey scale image is converted into binary images by adjusting the threshold of the image using ImageTools, shown in Figure 5.1 (B). Then, the area of the whole char particle, A<sub>ch</sub>, is measured using the 'object analysis function' of the ImageTools.
- *Measurements of inner particle pore area, A<sub>p</sub>.* These are the black objects inside the white area, as shown in Figure 5.1 (C). The porosity is then given by A<sub>p</sub>/A<sub>ch</sub> (%). The structure type, i.e. Group I, Group II or Group III, of the measured char particle is determined according to the classification system provided in Table 2.2 (Benfell et al., 1998; Benfell et al., 2000; Benfell, 2001), mainly based on

the porosity values in the present study. Based on the above, the char type distribution of each char sample is obtained.



Figure 5.1. Image analysis procedure for porosity measurements of individual char particles using cross-section SEM images; (A) grey scale image separated from whole cross-section SEM image; (B) binary image converted from picture A; (C) colour-reversed image converted from image B.

# 5.3 Experimental results and discussion

Consistent with the results of the single particle experiments discussed in **Chapter 4**, the investigation of chars prepared from DTF pyrolysis using density separated samples demonstrates the heterogeneity of char properties, including weight losses, swelling, char morphology, char internal structure and porosity.

## 5.3.1 Results of char samples of density fraction

# 5.3.1.1 Weight losses

This section presents the results of chars from density-fractions of coal A and B, prepared in the DTF at 1573 K. Figure 5.2 shows weight losses (d.a.f.) of density-fraction samples during pyrolysis for coal A, in Figure (a), and coal B, in Figure (b). As

expected, there is a clear trend that the weight loss during pyrolysis decreases with increasing the coal density for both coals examined, although the decrease for coal A is smaller than coal B. The reason for the decreases in the weight loss for the heavy density fraction is that, with increasing the coal density, liptinite plus vitrinite content decreases while inertinite increases. Liptinites and vitrinites generate higher volatiles during pyrolysis than inertinite macerals (Van Krevelen, 1981). Coal A contains much less inertinites, 13.1%, compared to coal B, which contains 34.1% inertinite. This may provide explanation to the smaller decrease in the weight loss for heavy density samples in coal A.



**Figure 5.2.** Weight losses of density-fractions of coal A and B during pyrolysis at 1573 *K*; *(a)* coal A, *(b)* coal B.

Decreases in the Q factors for heavy density fraction samples are also observed, from **Figure 5.2,** for both coals. The value of the Q factor is mainly associated with tar generation and release (Howard, 1981). The excess volatile yields are mostly the consequence of reduced tar cracking and less carbon deposition, which are achieved by the reduction of contact between reactive tars and hot particle surfaces at high heating rates (Howard, 1981). Hodek et al (Hodek et al., 1991) found the tar yields decrease in the sequence exinite (liptinite)  $\rightarrow$  vitrinite  $\rightarrow$  inertinite. This conclusion provides supports to the observations in the present study.

#### 5.3.1.2 Char particle size distribution (PSD) and swelling



**Figure 5.3.** Particle size distributions (by volume) of DTF chars of coal A and B prepared at 1573 *K*, measured using the Malvern Laser Sizer; *(a)* Coal A, *(b)* Coal B.

Particle size distributions (PSD) of char samples of density-fractions of coal A and B measured using Malvern Laser Sizer are presented in **Figure 5.3**. As expected, there is a major shift of char particle sizes to a larger size range for light density fractions (F1.25 and F1.30) for both coals, while little shifts occur for heavy density fractions (F1.50 and S1.50).



**Figure 5.4.** A comparison of PSD (by volume) of DTF chars of light and heavy density fractions of coal A and B; *(a)* F1.30 of coal A; *(b)* F1.50 of coal A; *(c)* F1.30 of coal B; *(d)* F1.50 of coal B.

The trend is more clearly revealed in **Figure 5.4** by comparing the PSD of chars with that of raw coal samples, in *(a)* and *(c)* for F1.30, in *(b)* and *(d)* for F1.50, for both coals. Therefore, higher swelling ratios for the light density fraction samples are expected. The shift of the PSD for light density fractions of coal A is larger than that of coal B, as shown in *(a)* and *(c)*, implying a larger swelling ratio for coal A. This is probably due to a higher liptinite and volatile content in coal A. From the open literature (Howard, 1981; Oh et al., 1989; van Krevelen, 1993; Gao et al., 1997), it is generally recognized that coal particle swelling during devolatilization process is contributed by fluidity and volatile yields. High fluidity and volatile yields lead to a high swelling.

From observations in the single particle experiments conducted in this study in chapter 4, the author believes that the surface tension also plays a major role in retaining volatile gases in the liquid coal particle, which causes high swelling of chars.

Char particle size distributions (by volume) of density fractions of coal A through SEM image analysis using size bin I are shown in **Figure 5.5**. Size bin I is the same as the size bin used for the Malvern Sizer measurements. The volume distributions are converted from the number distributions. The figures present a very similar trend to that from Malvern Sizer measurements shown above. Light density fraction samples (F1.25 and F1.30) have large particle size shifts, **Figure 5.5** (*a*), and their particle sizes are distributed in a larger size range, as shown in **Figure 5.5** (*b*).



**Figure 5.5.** PSD (by volume) of the DTF char samples of coal A through SEM image analysis using size bin I as for Malvern Sizer measurements; (a) Cumulative, (b) Distribution.

**Figure 5.6** shows particle size distributions (by volume) of coal A and B using size bin II through SEM image analysis. Larger shifts of particle sizes for light density fraction samples are presented in the cumulative curves in **Figure 5.6** (*a*) and (*c*) for both coals, similar to that in *Figure 5.5* (*a*). However, size distributions in Figure (*b*) and (*d*) show

that the F1.25 and F1.30 are most likely to have bi-model or tri-model peaks. The size range of peak I, marked as 'I', is the same as the heavy density fraction samples and the raw coal particle size range. Peak II and III (marked as 'II' and 'III', respectively) are larger particle sizes contributed by those particles that experience more swelling during pyrolysis. It is logical to consider that char particles of peak II and III evolve from liptinite and vitrinite coal particles, while chars forming the peak I come from coal particles containing mainly inertinite maceral or with high ash content. However, peak II and III are not obvious in heavy density fraction samples, i.e., F1.50 and S1.50, as shown in Figure (b) and (d). For heavy density samples, their particles are distributed in peak I, which has the same size range as that of the raw coal samples. This is because the particles of high-density samples either have high inertinite content or high ash content. Inertinite maceral exhibit less swelling due to its less volatile yield and absence of fluidity. Mineral matters affect coal pyrolysis behaviour through the following aspects: (a) ash grains consume energy during heating, therefore reduce the particle heating rate; (b) ash grains reduce effective organic materials in the given particle, therefore reduce volatile yields; (c) ash grains are usually solid at pyrolysis temperatures, therefore the particle viscosity is high which restricts coal particle swelling; (d) when ash content is very high, ash grains may isolate organic materials. Therefore the pyrolysis reactions occur in isolated regions, and the whole particle does not exhibit fluidity and softening.



**Figure 5.6**. PSD (by volume) of the DTF char samples of coal A and B through SEM image analysis using size bin II; (a) Cumulative of coal A, (b) Distribution of coal A, (c) Cumulative of coal B, (d) Distribution of coal B. (I — peak I; II — peak II; III — peak III)

The decrease in the swelling of char particles with increasing the parent coal fraction density is demonstrated in **Figure 5.7** and **Figure 5.8**. Swellings in Figure 5.7 are measured using Malvern Sizer, and Figure 5.8 is obtained through SEM image analysis. It can be seen that swelling ratios from the two methods are generally consistent with each other. The swelling ratio of light density fraction chars is 25~60% higher than that of char samples from the heavy density fractions. Mean swelling ratios of coal A are a little higher than that of the same density fraction of coal B. Interestingly, from the Figure 5.8, it can be seen that the swelling ratio for F1.30 density fraction is the highest. This is more obvious for coal A, in Figure 5.8 (*a*). This observation is consistent with

the previous study by Gilfillan et al (Gilfillan et al., 1997; Gilfillan et al., 1999) using density-separated samples, for which maximum swelling occurred at F1.30 density. As high swelling of the particle will result in high porosity, it is therefore expected that porosity of char samples from light density samples will be higher than that of heavy density chars. The decrease in the swelling ratio of F1.25 chars is attributed to char fragmentation during the plastic stage owing to high fluidity and intensive volatile release.



Figure 5.7. Swelling ratios of DTF chars measured using Malvern Laser Sizer; (a) coal A, (b) coal B.



Figure 5.8. Swelling ratios of DTF chars measured through SEM image analysis; (a) coal A, (b) coal B.

#### 5.3.1.3 Char structure and porosity

The internal structures of DTF chars prepared from density-fraction samples of coal A and B are revealed by cross-section SEM images presented in Figure 5.9 and Figure 5.10. The structural characteristics of the chars are consistent with descriptions in the literature (Bailey, 1993; Wu, 2000<sup>b</sup>; Benfell, 2001). The different types of chars, e.g., cenospheric char, foam structure, tenui-network structure, solid char structure, etc, have also been observed in the present experiments. However, an important observation from this study is that drastic changes occur when the coal fraction density increases for both coals. Light density fraction samples, i.e., F1.25 and F1.30, generate very porous char particles, mostly group I chars with a cenospheric structure, as shown in (a) and (b) of Figure 5.9 and (a) in Figure 5.10. The cenospheric structure has the configuration of a single central void surrounded by a thin outer shell ( $\sim 5\mu m$ ) (Lightman et al., 1968; Bailey, 1993). The porosity of this shell is usually very low, as shown in (a) and (b) of Figure 5.9 and Figure 5.10. The shape of cenospheres is relatively round from the cross-section images. Qualitatively, it can be seen from the images (Figure 5.9 (a) and (b)) that the population of group I chars in F1.30 fraction is larger than that of F1.25 fraction. This is consistent with the above results of swelling ratios. Two somewhat conflict reasons may be attributed: (1) Low density fraction particles develop high fluidity, therefore easily to break-up during the liquid stage owing to the intensive generation of the volatiles; (2) Some of the particles in coal A may behave similarly to low rank coal particles, for which cross-linking reactions occur at low temperature, which prevent the development of fluidity and swelling. The factor I will lead to the formation of small cenospheric char particles, marked as 'SC' in Figure 5.9 (a) and (b) and Figure 5.10 (a). This is confirmed from the observations of char morphology discussed in the subsequent section. While the factor II leads to relatively solid small

chars with tenui-network structure (group II or III) in light density fractions, marked as TN' in Figure 5.9 (a).





**(b)** F1.30



(c) F1.50

**Figure 5.9.** SEM images of cross-sections of chars from density-fraction samples of coal A prepared in DTF at 1300°C; *(a)* F1.25, *(b)* S1.25—F1.30, *(c)* S1.35—F1.50;

I-group I chars, II-group II chars, III-group III chars;

SG—solid carbon particle, TN—tenui-network structure, SM—solid particle with included mineral grains, SC—small cenospheric char particle.

On the contrary, chars from high-density fraction coal samples, i.e. F1.50 and S1.50, have a very solid structure with low porosity, as shown in (c) of Figure 5.9 and (c) and (d) of Figure 5.10. Solid particles can be relatively pure carbon particles, marked as 'SG', or carbon particles with some included ash grains, marked as 'SM'. In S1.50

fraction, some excluded pure mineral grains can also be seen, marked as 'M' in **Figure 5.10** (*d*). Char sample from the medium density fraction, i.e. F1.35, contains a mixture of different types of char particles with a moderate porosity and wall thickness.



**Figure 5.10.** SEM images of cross-sections of char samples of coal B prepared in DTF at 1300°C; *(a)* F1.25, *(b)* S1.30—F1.35, *(c)* S1.35—F1.50, *(d)* S1.50;

I—group I chars, II—group II chars, III—group III chars;

SG—solid carbon particle, TN—tenui-network structure, SM—solid particle with included mineral grains, SC—small cenospheric char particle, M—excluded mineral grains.

Comparing the structure of coal A with coal B, it may be seen that coal A has a noticeable population of chars with tenui-network structure, which has a configuration of many elongated voids distributed inside the coal particle, in particular, in the medium

density and the high-density samples. The tenui-network structure has been described in the literature (Bailey et al., 1990). With the same density fractions in coal B, however, a significant amount of thick-walled cenospheric chars exists, which configures a large central void surrounded by a thick and porous outer shell, marked as 'TC' in (b) and (c) of **Figure 10**. This may be attributed to the high inertinites contents in coal B. Inertinite can contribute to the formation of thick-walled cenospheric chars at high heating rates (Benfell, 2001).

The results of the porosity for both coals measured through SEM image analysis are shown in **Figure 5.11**. A drastic decrease in the porosity as increasing the parent coal density is quantitatively presented. For coal A, the average porosity in the S1.25-F1.30 fraction is 86.8%, and 42.5% for the S1.35-F1.50 fraction. In coal B, the average porosity decreases from above 80% in the light density fractions, F1.25 and F1.30, to around 20% in the heavy fraction, S1.50. Consistent with the above observations on swelling and char structure, the porosity is also likely to have the maximum value at F1.30 density fraction for both coals, and is more noticeable in coal A.



Figure 5.11. The porosity of DTF chars of the density fraction samples of both coals, measured through image analysis (char prepared at 1573 K).

Figure 5.12 shows the char type distribution of density fractions of coal A and coal B. The figure clearly delivers the quantitative information that group I chars are mainly generated in light density fraction samples, i.e. F1.25 and F1.30, group III chars are yielded from heavy density fractions, i.e. F1.50 and S1.50, while the medium density sample contains a mixture of different types of chars. Benfell (Benfell, 2001) and Liu et al (Liu et al., 1999; Liu, 1999<sup>a</sup>) have correlated the group I char population to the vitrinite content of the parent coal using empirical correlations. **Table 5.4** compares the calculated population of the Group I chars using the empirical correlations as indicated with experimental results of density fraction samples from this study. Large discrepancies exist for medium to heavy density coal fractions with high ash levels. The correlation between the Group I char population and vitrinite (including liptinite) content (d.a.f.) from current petrographic analysis appears not straightforward from the present experiments. Two reasons may be attributed: 1) the vitrinite content by current petrographic analysis is not given on coal particle number basis. It is therefore difficult to quantify the proportions of pure vitrinite, vitrinite-dominated or inertinite-dominated particles, etc. Also, synergetic effect between coal macerals has not been clear. For instance, with an individual coal particle, how much vitrinite content will lead to the formation of Group I char. 2) It is obvious that the mineral matter in coal is doing some work, in addition to the dominant role of coal macerals. As reviewed in chapter 2, liptinite and vitrinite maceral develop high fluidity while inertinite generally exhibits no fluidity during heating. In the meantime, as aforementioned, the included ash grains also significantly influence the thermoplastic property of the coal particles during heating. At pyrolysis temperature, most of the ash grains remain solid hence decrease the apparent fluidity of the whole coal particle. Current fluidity models, Eq  $6.9 \sim 6.11$ , consider the viscosity of the coal melt as a function of the liquid fraction (metaplast content). Therefore, it is confident to conclude that ash has impact on the physical structure of the residue char. This observation supports the conclusion of Gibbins et al (Gibbins et al., 1999) that both coal maceral and ash should be considered to provide reasonable explanations to pf coal combustion behaviour. Ash content has been considered in the present char structure model, as described in chapter 7.



Figure 5.12. The char type distribution of the density fractions of coal A and B (1573 K); (a) coal A, (b) coal B.

**Table 5.4.** Comparisons of calculated Group I char populations from density fractions of coal A and B with experimental measurements.

Samples	Α					В				
	F1.25	F1.30	F1.35	F1.50	S1.50	F1.25	F1.30	F1.35	F1.50	S1.50
Calculated <sup>a</sup>	86.0	87.2	87.7	84.9	81.9	83.9	85.2	70.9	57.0	58.7
Calculated	87.6	89.0	89.6	86.3	82.8	85.1	86.6	69.9	53.6	55.6
Experiments	70.8	80.8	-	2.6	-	75.0	74.2	8.3	0.0	2.7

NB: <sup>*a*</sup>—Correlation by Liu et al (Liu, 1999<sup>a</sup>): nGrpI (%) =  $0.6 \times P + 0.53 \times Vitr + 37$ 

<sup>b</sup>—Correlation by Benfell (Benfell, 2001): nGrpI (%) =  $0.994 \times P + 0.621 \times Vitr + 29.87$ 

#### 5.3.1.4 Char morphology

The morphology of chars is examined under SEM for all the density fraction samples prepared in the DTF, and the results are presented in **Figure 5.13** (coal A) and **Figure 5.14** (coal B). Significant changes in the char morphology occur with increasing the parent coal fraction density for both coals. In general, from **Figure** (*a*) and (*b*), chars from the two light density fraction samples have larger particle size, and tend to have a round shape. Their surfaces are usually smooth with some flow patterns. Some particles have one large blow hole, which is the strong evidence of the intensive release of the volatiles during pyrolysis. This observation agrees well with other work reported in the literature (Gilfillan et al., 1999). Two possible reasons may be responsible for the formation of the flow patterns: (1) the wall between bubbles, presented as ribs in the images; (2) volatile gases travel along the particle surface due to the pressure difference within the surface layer. From the cross-section SEM images shown above, the first factor appears to be more essential. This may be confirmed by the SEM images of chars prepared by Wu et al (Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>), as show in **Figure 8.4** in chapter 8. The ribs are believed to have a low reactivity compared to the thin films.

However, char morphologies from the high-density coal samples are remarkably different, as shown in figure (*d*) and (*e*). Most of the particles have an irregular shape. No flow patterns were observed on the surface of these particles. And these char particles usually have a range of small open pores and cracks on their surfaces. Theses open pores and cracks are the paths of volatile release during pyrolysis.



**Figure 5.13**. SEM morphology of char particles of coal A prepared in DTF at 1573 K; (a) F1.25, (b) S1.25—F1.30, (c) S1.30—F1.35, (d) S1.35—F1.50, (e) S1.50.



**Figure 5.14**. SEM morphology of char particles of coal B prepared in DTF at 1573 K; (a) F1.25, (b) S1.25—F1.30, (c) S1.30—F1.35, (d) S1.35—F1.50, (e) S1.50.

**Table 5.5** lists typical char morphologies observed in the present study, group A to H, their characteristics and occurrence. This list is somewhat similar to the morphology classification system provided by Littlejohn et al (Littlejohn, 1967). However, **Table 5.5** provides more detailed information on the basis of the observations in the present

experiments. The significant differences in the morphology of char particles may be attributed to their thermoplastic properties during pyrolysis. Particles from heavy density samples do not develop fluidity during heating, they generate much less amount of volatiles, and the volatiles are released through open pores or cracks on the particle surface. These particles generate group C, D, or H chars. It can be expected that not much morphology changes will occur for these particles during pyrolysis. Some particles may develop local fluidity that, although the whole particle does not soften or swell, they have some parts of materials liquidized. These particles are most likely to generate group C or F chars. Particles that develop high fluidity during pyrolysis may have three paths: (i) The particle may break up to form several liquid drops during the plastic stage due to very high fluidity and intensive generation of volatiles. The small particles continue to undergo pyrolysis and swelling. These particles generate group Eor B chars; (ii) Particles swell to a large extent to generate cenospheric chars, and the bubble may rupture during the plastic stage. However, the holes may not be closed again due to the very intensive release of volatiles through the holes or due to a high surface tension. These particles will generate group A chars with a large blow hole at the surface. (iii) If the particle swells but the bubble does not rupture or the blow hole is closed again after the bubble rupture, then group B chars are generated. Coal particles that have a mixture of two different maceral components will generate group F chars. Group G chars evolve from coal particles with liptinite macerals. These particles obviously experienced high swelling and high conversion during pyrolysis. Overall, light density samples generate Group A, B, E or G chars, and heavy density samples yield group C, D or H chars.

Table 5.5. Typical morphology (	ology A B C D	Low densityLow densityLow densityMediumtoHigh dencesamplessampleshigh densitysample:(F1.25 and(F1.25 and(F1.25 and(F1.35, F1.50)(F1.50(F1.30)F1.30)and S1.50)S1.50)	PorousCharPorousCharSolidtionwithonewithclosedwithporeblowhole,surfaceandopeningonwithandflowpatternsonwithonsurfacepatternsonsurfaceandsurfacesurfaceonsurfaceonsurfaceonsurfacesurfaceon
f DTF char particles	E	nsity Low density samples and (F1.25, F1.30)	char Small and round racks particles the
under SEM.	F	Medium and low density samples (F1.35 and F1.30)	. Char particles with Multiple component
	G	Low density sample (F1.25 of coal A)	Char particles of high conversion
	Н	Heavy density samples (F1.50 and S1.50)	Solid char particles

As the assessment to the char morphology, two parameters, i.e., elongation and roundness, are measured through SEM image analysis, and the results are shown in **Figure 5.15** (coal A) and **Figure 5.16** (coal B). The data clearly demonstrates that more morphology changes occur in the light density fractions char samples for both coals. This implies these particles have experienced more extensive physical and chemical transformations due to more intensive pyrolysis reactions. The high-density fraction particles, however, experience much less physical changes during heating. The trends agree well with the abovementioned char structure and swelling results with respects to parent coal density.



**Figure 5.15.** Comparisons of morphological parameters of DTF chars of coal A with raw coal, analysed through SEM image analysis;  $\diamond$ --raw coal samples of density fractions,  $\times$ --DTF char samples of density fractions after pyrolysis at 1573 K; (a) elongation, (b) roundness.



Figure 5.16. Comparisons of morphology of DTF chars of coal B with raw coal samples analysed through SEM image analysis;  $\diamond$ --raw coal samples of density fractions,  $\times$ --DTF char samples of density fractions after pyrolysis at 1573 K; (a) elongation, (b) roundness.

# 5.3.2 Swelling of size fraction samples

Particle size distributions and swelling ratios of char samples from the size fractions for both coals are measured using the Malvern Laser sizer, and the results are shown in **Figure 5.17** and **Figure 5.18**. There is a trend that smaller particle size fractions tend to swell more than larger size fraction, as shown in **Figure 5.20**. This observation is consistent with the results reported in the literature (Gao et al., 1997; Hackert et al., 1999). Smaller particles are heated at a higher heating rate under the same condition, compared to larger ones. In the meantime, small particles have lower temperature gradient. Therefore, smaller particles are more readily to swell. As the particle size decreases, volatiles are easier to escape from the coal particle, which reduces the chances of secondary reactions. Therefore, there may exist an optimum particle size range for the maximum swelling. The value may be coal type dependent, and strongly affected by heating conditions, such as heating rate and system pressure. It is logical that high heating rates shift this particle size range to a smaller value.



Figure 5.17. PSD of DTF chars of size fractions of coal A and B prepared at 1573K, measured using the Malvern Laser Sizer; (a) coal A, (b) coal B.



**Figure 5.18**. Swelling ratio of DTF chars of size fractions of coal A and B measured using the Malvern Sizer.

The results of limited samples measured through SEM image analysis on swelling of coal A confirms the results from the Malvern Sizer measurements that chars of smaller size fractions have larger swelling ratio, as shown in **Figure 5.19** (*a*). On the other hand, the morphology of the chars appears not sensitive to the raw coal particle sizes, as shown in. **Figure 5.19** (*b*). There is no major difference in the morphology, such as roundness, of both chars and raw coal particles among the three measured size fractions

of coal A. However, there are considerable changes in the roundness from the raw coal to char samples for all the size fraction samples, as shown in Figure *(b)*.



Figure 5.19. Swelling ratio and roundness of DTF chars of size fractions of coal A measured through SEM image analysis; (a) swelling ratio, (b) roundness.

SEM images also show that there is no noticeable difference in both char morphology and cross-section structures among different size fraction samples. Figure 5.20 shows SEM images of the morphology, Figure (*a*), and cross-section, Figure (*b*), of DTF chars from +75-90 size fraction of coal A. The observed char morphology is covered in **Table** 5.5, such as particles with one large blow hole and flow patterns (*BH*), particles with closed surface and flow patterns (*CS*), small round particles which is possibly small cenospheric chars (*SC*), and particles with irregular shapes supposed to be solid (*SD*). Three types of chars are also apparently distributed in the cross-section image, i.e., group I, group II and group III chars, marked as I, II and III, respectively in the images.


(a) Morphology

(b) Cross-section

**Figure 5.20.** DTF Char SEM morphology and cross-section images of +75-90 size fraction of coal A; *(a)* char morphology, *(b)* cross-section; I—Group I char, II—Group II char, III—Group III char.

# 5.3.3 Effect of pyrolysis temperature on swelling of DTF chars

A few char samples have also been prepared at 1373 K to investigate the effect of pyrolysis temperature on swelling. **Table 5.6** compares the swelling results of chars prepared at different temperature as indicated, measured using the Malvern Sizer. For all the samples examined, higher pyrolysis temperature results in a larger swelling. This may be explained by the following: when coal is heated at a higher temperature, (1) the coal particles have a slightly higher heating rate; (2) devolatilization takes place at higher temperature, hence at a higher reaction rate, yielding more volatiles at a very short time. This causes higher swelling of coal particles during pyrolysis.

<b>Table 5.6.</b> A	comparison	of swellings	of DTF	chars	prepared	at	different	pyrolysis
temperatures a	s indicated, r	neasured usin	ng the Ma	alvern S	Sizer.			

Coal		1	4	В		
Pyrolysis Temperature (K)		1573	1373	1573	1373	
	F1.30	1.55	1.31	1.32	1.10	
Swelling ratio	F1.35	1.28	1.10	-	-	
	F1.50	1.34	1.10	-	-	

# 5.4 Conclusions of this chapter

- Consistent with the single particle pyrolysis results, experiments on DTF using density-separated coal samples demonstrate the heterogeneous behaviour of coal particles in pf size from the same coal under the same heating conditions. In addition to the dominant role of coal macerals, the influence of ash in coal on char structure formation is identified;
- For the both coals, the weight loss and swelling ratio of DTF chars decrease with increasing the coal fraction density. Correspondingly, the char porosity of the density fractions decreases significantly from above 80% to ~20% as the coal fraction density increases;
- Internal char structures change drastically with increasing the coal density. Light density-fraction samples, i.e. F1.25 and F1.30, generate group I chars with a high porosity and thin wall. On the contrary, heavy density-fraction coal samples, i.e. F1.50 and S1.50, yield group III chars with a solid structure and very low porosity. The char sample from the medium density fraction contains a mixture of different types of char particles with a moderate porosity and wall thickness;
- Significant distinctions in the morphology of chars among different density fractions are observed. Char particles from light density fractions are featured with a relatively round shape and a smooth surface with flow patterns, some with big blow holes. While char particles from heavy density fractions have an irregular shape with open pores and often with cracks;
- It is obvious that light density char particles have experienced intensive softening and swelling due to the development of fluidity, the bubbling

behaviour and volatile generation. With these particles, their volatile release during pyrolysis is therefore largely determined by the behaviour of bubbles. However, the particles from heavy density fraction samples are most likely to have maintained their physical structures during the course of devolatilization due to the absence of the fluidity. Therefore, these particles do not exhibit softening and swelling, and their volatiles are released through the pore openings or cracks via the hydrodynamic process;

• Results of size fraction samples reveal that particles with smaller sizes tend to have larger swellings under the same heating condition. Char samples prepared at lower pyrolysis temperature in the DTF have a smaller swelling ratio.

# CHAPTER 6. MODELLING THE CHAR STRUCTURE EVOLUTION—MODEL DEVELOPMENT

#### 6.1 Introduction

Vast experimental data in the literature, as reviewed in chapter 2, has shown that dramatic changes in the physical structure of coal particles occur during heating, which determines the mode of volatile transport during devolatilization and the structure of the char residues. There have been wide scientific and engineering interests in modelling char structure evolution in the past. To model this process, softening coals are often treated as a liquid droplet during plastic stage of the devolatilization process, while in non-softening coal, the transport of volatiles occurs within the pore structure of the particle (Suuberg, 1985<sup>b</sup>). The scope of the modelling in the present study is to deal with the char structure formation of softening coal during pyrolysis. During the plastic stage of the pyrolysis, the softening coal develops significant fluidity, and the pore structure of the feed coal is completely destroyed. Only macro-pores may survive the softening process and become bubbles (Oh, 1985). The escape of volatiles from the metaplast and out of the particle is an important process of devolatilization that needs to be understood and modelled correctly to interpret and predict the devolatilization behaviour of coals (Smith, 1994), including volatile release, coal swelling, and char formation. Diffusion mechanism through the coal melt does not explain transport behaviour of the volatiles in softened coal (Oh, 1985). Transport of volatiles to bubbles with subsequent leakage of the bubbles is therefore believed the major mode of escape of volatiles out of the softened coal particles (Gavalas, 1982), in particular for tars.

The concept of volatile transport mode through bubbles during pyrolysis was addressed by Lewellen in 1975 (Lewellen, 1975), through which the swelling behaviour of bituminous coals was interpreted (Sung, 1977). Bubble mechanism has been employed by a number of researchers after that (Sung, 1977; Oh, 1985; Oh et al., 1989; Solomon et al., 1993; Sheng et al., 2000). In their studies, the release of volatiles has been treated in different ways. Multi-bubble mechanism takes account of bubble transport (Oh et al., 1989) as the major volatile release mode by neglecting direct volatile diffusion to the particle surface, while single bubble models (Solomon et al., 1993; Sheng et al., 2000) considered both the bubble rupture and direct diffusion of volatiles out of the particle through the liquid shell. If considering the char formation as a continuous process which starts with multi-bubbles at the onset of softening and ends up with very small number of bubbles (an extreme case is the single bubble for cenospheric chars), one may say that both bubble transport and direct diffusion of volatiles should be considered to model the whole process correctly. The former mechanism may play a major role when the bubble number is large, while the latter plays an essential part in the stage that the number of bubbles is very small. Both mechanisms have been considered in the present study at different stages of the pyrolysis. To simplify the complex physical process, the author only considers the extreme case for which bubbles have a uniform size and spatial distribution.

It may be noted that, similar to previous work (Oh, 1985; Solomon et al., 1993; Sheng et al., 2000), the model developed in this study is a rather single particle model which describes the pyrolysis behaviour of a single individual particle of softening coal during heating from the standard coal properties, i.e. ultimate and proximate analysis. However, differing from the previous work, in predicting the char structure of the full

coal, the present model considers each density-fraction sample instead of the whole coal as a homogeneous material during pyrolysis, and the char structure distribution of the full coal is estimated from the mass distribution of the density fractions of a given coal. This consideration is valuable from the engineering points of view. As an advancement of previous work, the present model provides a complete description of char structure evolution process of pf coal during pyrolysis.

#### 6.2 Model development

In order to mathematically describe the char structure evolution, the devolatilization process, in terms of its physical nature, is divided into the following three stages:

- Pre-plastic stage  $(\mu > \mu_c, T < T_s)$ ;
- Plastic stage  $(\mu \le \mu_c, T_s \le T \le T_d);$
- Re-solidified stage  $(\mu > \mu_c, T > T_d)$ .

Where  $\mu$  and  $\mu_c$  are the viscosity and the critical viscosity of coal during heating, T is the particle temperature,  $T_s$  and  $T_d$  are the initial softening temperature and resolidification temperature, respectively. This division is based on the viscosity value calculated from the metaplast volume fraction in the coal particle during heating. Different values of  $\mu_c$  have been used in the literature, for instance,  $4 \times 10^4 Pa.s$  in Oh's work (Oh, 1985; Oh et al., 1989), and  $2 \times 10^5 Pa.s$  by Sheng et al (Sheng et al., 2000). There is no experimental data available in the open literature to verify the critical viscosity value for the onset and completion of the plastic stage, in particular at high heating rates.

#### 6.2.1 Pre-plastic and re-solidified stages

The pre-plastic and re-solidified stages are described as a volumetric reaction, in Eq. 6.1, during which the particle size remains constant.

$$R_{t} = \frac{d}{dt} \left( \frac{\varepsilon - \varepsilon_{0}}{1 - \varepsilon_{0}} \right) \tag{6.1}$$

where  $R_t$  is the devolatilization rate,  $\varepsilon$  is the porosity of the coal during heating, and  $\varepsilon_0$ is the porosity of the raw coal, given by experimental measurements. Therefore, during this stage, the physical structure change is simply an enlargement of its original pore structure. The release of the volatile gases out of the particle is a hydrodynamic process through the pore system.

In the present work, the devolatilization rates are predicted using the Chemical Percolation Model for Devolatilization (CPD) developed by Fletcher et al, and has been described in the open literature (Grant et al., 1988; Grant et al., 1989; Fletcher et al., 1990; Fletcher et al., 1992; Fletcher et al., 1992<sup>a;</sup> Fletcher et al., 1999). The Fortran code of the CPD model is provided on the BYU website (Fletcher et al., 1999), and is utilized directly.

Direct input data for the CPD model are coal structure parameters based on <sup>13</sup>C NMR (Nuclear Magnetic Resonance) measurements (Grant et al., 1988; Grant et al., 1989; Fletcher et al., 1999). These parameters are: the average molecular weight per side chain  $(M_{\delta})$ , the average molecular weight per aromatic cluster  $(M_{cl})$ , the ratio of bridges to total attachments  $(p_0)$ , and the total attachments per cluster  $(\sigma+1)$ . With coals not been subjected to NMR measurements, an empirical correlation has been developed by Genetti et al (Fletcher et al., 1999; Genetti, 1999) based on the data from <sup>13</sup>C NMR measurements of 30 coals. The correlation provides estimation of the above four chemical structure parameters from standard ultimate and proximate analysis data of the parent coal, which are easier to obtain. Details of the correlation and coefficients of the equation are described in *Appendix D*. The correlation is employed in the present model to estimate chemical structure parameters of the full coal and density-fractions of the coal used in this study.

# 6.2.2 Physical process and model assumptions for the plastic stage

The plastic stage is considered the key step for the evolution of char structures. The transient changes in the number of bubbles, the force balance and the mass balance, need to be formulated carefully in order to describe the pyrolysis behaviour of coal particles during the plastic stage. In the present work, a simplified mechanism of the process for volatile transport and char structure evolution is proposed based on the following assumptions:

- i. The coal particle shape is spherical during heating;
- Bubbles are spherical in their shape, and have a spatially uniform distribution within the liquid coal particle, and have a uniform size during the whole plastic stage;
- iii. Only macro-pores attribute to the initial bubble number density;
- iv. Bubble nucleation during the plastic stage is neglected. With the high heating rate and high viscosity case such as a melting coal, this is considered valid;
- v. Chemical and physical properties of the whole particle are uniform;
- vi. Diffusion of the volatiles directly out of the particle surface is negligible during the early plastic stage when the number of bubbles is large;

- vii. The whole coal particle is heated uniformly. This is valid in the present study as the particle size is relatively small (~100  $\mu m$ );
- viii. True density of the coal material remains constant during the course of heating.

On the basis of the above assumptions, the physical process of the simplified model for the char structure evolution during coal devolatilization is illustrated in Figure 6.1. A large number of bubbles with uniform size and spatial distribution exist in the liquidized coal particle at the onset of the plastic stage. The bubbles originate from the macropores that survive the softening. The initial bubble number density at the onset of the plastic stage is estimated at  $10^{13}$  per gram coal, according to Oh's calculation (Oh, 1985). Bubble growth occurs due to the generation of the volatile from decomposition of the coal matrix and the diffusion of the volatiles into bubbles. When bubbles rupture at the particle surface, the gas inventory inside bubbles is released, which is equivalent to CPD predicted volatile yield at each time step. The growth of the bubbles results in the swelling of the coal particle, in the meantime the internal physical structure of the particle changes to different extents. The direct diffusion of volatiles out of the particle surface is also considered when a cenospheric particle is formed, which has not been considered in the previous multi-bubble model (Oh et al., 1989). This mechanism has been described in the literature (Suuberg, 1985<sup>b</sup>; Solomon et al., 1993; Sheng et al., 2000). Within a liquid coal particle, the transport mechanism includes diffusion of light gases and lighter fractions of tar precursors to the surface and convective transport of bubbles (Suuberg, 1985b). The ultimate structure of the char particle depends on at which stage the coal particle is re-solidified. Thus, the dense char (Group III), foam structure (Group II or III), or cenospheric (Group I) char structure is formed, depending on the properties of the parent coal. This mechanism has been reported elsewhere (Yu et al., 2002).



Figure 6.1. The simplified mechanism of char structure evolution during coal pyrolysis.

## 6.2.3 Mathematical equations

**Bubble conservation.** As abovementioned, the bubble nucleation is not considered in the present model. Bubble size and spatial distribution are assumed uniform in the liquidized coal particle during the plastic stage. An estimate of bubble coalescence rate with a comparison to the rate of bubble ruptures has been detailed in *Appendix E*. With the uniform bubble size and coal particle size of 70  $\mu$ m, the bubble coalescence rate is 6, 8, and 10 magnitudes lower than the rate of bubble ruptures when the bubble size is 20, 2, and 0.2  $\mu$ m, respectively. Therefore, in the simplified case in the present study, the

bubble coalescence rate is negligible. As such, the variation of the number of bubbles in the particle at any time step is only caused by bubble ruptures at the particle surface, as described in Eq. 6.2:

$$dn_b/dt = -E_b n_b \tag{6.2}$$

where  $n_b$  is the number of bubbles and  $E_b$  is the bubble escape rate. The rate of the bubble escape is calculated using Eq. 6.3, following Oh's work (Oh et al., 1989):

$$E_{b} = \frac{3(R_{p} - r_{b})^{2}}{R_{p0}^{3}} dr_{b} / dt$$
(6.3)

where  $(dr_b/dt)$  is the growth rate of bubbles,  $R_p$  is the transient particle radius,  $R_{p0}$  is the original particle size of the coal, and  $r_b$  is the size of bubbles. Obviously, the bubble escape rate is associated with bubble growth rate, and is also a function of bubble size.

**Bubble growth rate**  $(dr_b/dt)$  is the result of the force balance. This involves the bubble internal pressure  $(P_b)$  due to the generation of volatiles, the surface tension ( $\sigma$ ), the ambient pressure  $(P_0)$ , and the viscous force ( $\mu$ ). In the present work, the Eq. 6.4, simplified from Eq. 2.3 (Oh et al., 1989), is employed:

$$dr_{b}/dt = \frac{r_{b}}{4\mu} (P_{b} - P_{0} - 2\sigma/r_{b})$$
(6.4)

Obviously, low viscosity and high volatile yields result in a large bubble growth rate, while high ambient pressures and surface tension restrain the growth of bubbles.

*Mass balance*. During the multi-bubble stage, the direct volatile release through diffusion out of the particle surface is neglected. As such, the mass balance considers

the generation of the volatiles within the particle, (including tar and light gas species), and the amount of volatile escaping through the bubble rupture at the particle surface at each time step. This can be expressed in Eq. 6.5:

$$\delta n_b n_m M W_v = R t W_{p0} dt \tag{6.5}$$

where  $\delta n_b$  is the number of bubbles ruptured at each time step.  $R_t$  is the devolatilization rate, and is predicted with the CPD model.  $MW_v$  is the mole molecular weight of volatiles and is given by CPD calculation,  $n_m$  is molar mass of volatiles, and  $W_{p0}$  is the total mass of the coal particle.

The mass of the volatiles inside each of the bubble may be calculated using Eq. 6.6:

$$P_b \frac{4\pi r_b^3}{3} = n_m RT \tag{6.6}$$

where  $P_b$  is the bubble internal pressure, R is the gas constant, and T is the absolute temperature.

*Calculations for the single bubble stage.* During the plastic stage, if a cenospheric char structure is formed, which is the configuration with one central single bubble surrounded by a thin porous shell (Lightman et al., 1968), a diffusion term of the volatile release is then considered, as described in Eq. 2.5 (Solomon et al., 1993; Sheng et al., 2000). The particle swelling for the single bubble case has been described in the literature (Solomon et al., 1993; Sheng et al., 2000), and some of the mathematical equations are detailed in *Appendix F* (Solomon et al., 1993). These formulations are also employed in the present work when the single bubble stage is reached. The amount

of gas remaining within the coal particle after the bubble rupture is provided in the literature by Sheng et al (Sheng et al., 2000).

Overall, the modelling of char structure evolution during the plastic stage has been considered as two successive stages, i.e. a multi-bubble stage followed the single bubble stage. During the multi-bubble stage, the volatile diffusion term is neglected. The rupture of bubbles at the particle surface is rate controlled, and volatile release is controlled by bubble rupture. The force balance is expressed through the bubble growth rate. When the cenospheric char structure is formed during the plastic stage, the bubble rupture is controlled by the wall stress, for which the criterion is described in Eq. 2.4 proposed by Solomon et al. (Solomon et al., 1993). The volatiles are released through both bubble rupture and direct volatile diffusion to the particle surface.

*Swelling ratio and porosity.* Solving the above equations 6.2 to 6.6, the new bubble size,  $r_b$ , and the new bubble number,  $n_b$ , are then obtained. The transient swelling ratio  $(R_p/R_{p0})$  can thus be calculated from Eq. 6.7:

$$R_{p}/R_{p0} = \left[ \left( n_{b} \frac{4\pi}{3} r_{b}^{3} + \frac{(1-y_{v})W_{p0}}{\rho_{o}} \right) / \frac{4\pi}{3} R_{p0}^{3} \right]^{1/3}$$
(6.7)

where  $y_v$  is the volatile yield,  $\rho_0$  is the density of coal. The porosity,  $\varepsilon$ , is calculated from Eq. 6.8:

$$\varepsilon = n_b \frac{4\pi}{3} r_b^3 / \left( n_b \frac{4\pi}{3} r_b^3 + \frac{(1 - yv)W_{p0}}{\rho_o} \right)$$
(6.8)

The char structure type is determined based on the bubble number and the porosity according to the char structure classification system established by Bailey and Benfell et al (Bailey et al., 1990; Benfell et al., 1998; Benfell, 2001), as described in **Table 2.2**.

## 6.2.4 Determination of physical properties

There is little experimental data available in the open literature on thermoplastic properties of the coal during rapid heating. Transient experimental measurements are difficult at high heating rates and under pressurized conditions, although some attempts have been made on thermoplasticity investigations (Chan et al., 1991; Gao et al., 1997). Proper correlations are therefore necessary to provide estimation of these properties in modelling work, including the viscosity, the surface tension and the diffusivity of volatiles, etc.

The viscous force is considered the dominant term in modelling the coal particle swelling behaviour. It is generally accepted that the metaplast, pre-existing in the raw coal or the intermediate liquid product during pyrolysis, is responsible for the thermoplasticity of coal (van Krevelen et al., 1956; Fitzgerald, 1957; Van Krevelen, 1981; Oh, 1985; Oh et al., 1989; Solomon et al., 1992<sup>a</sup>). Solomon et al (Solomon et al., 1992<sup>a</sup>) proposed an empirical model to calculate coal fluidity, in Eq. 6.9:

$$\mu = C \exp(E_{\mu} / RT) \exp\left[\frac{k_E \phi_s}{1 - \phi_s / \phi_c}\right]$$
(6.9)

Where C is a constant,  $E_{\mu}$  is the viscosity constant (5,000).  $k_E$  is Einstein coefficient (5.0),  $\phi_s$  is volume fraction of solid phase,  $\phi_c$  is volume fraction of solid phase at the gelpoint (0.65), R is the gas constant, and T is the absolute temperature. In the present

work, the viscosity of the coal melt is estimated from transient metaplast content using Eq. 6.10, following Oh's work (Oh, 1985).

$$\mu = \frac{1 \times 10^{-11} \exp(45,000 / RT)}{\left(\left(1 - \phi_m\right)^{-1/3} - 1.0\right)}$$
(6.10)

where  $\mu$  is the viscosity (Pa.s),  $\phi_m$  is the volume fraction of metaplast, R is the gas constant, and T is the absolute particle temperature, for which T=T when T<723 K, and T=723 K when T>723 K. The other correlation similar to Eq. 6.10 is also proposed by Oh (Oh et al., 1989), for which the viscosity constant is  $1 \times 10^{-8}$  and temperature does not use the cut-off value, shown in Eq. 6.11. In the model sensitivity analysis in the subsequent section, the above viscosity correlations, (6.10) and (6.11) are tested.

$$\mu = \frac{1 \times 10^{-8} \exp(45,000 / RT)}{\left( (1 - \phi_m)^{-1/3} - 1.0 \right)}$$
(6.11)

The surface tension of liquids decreases with increasing the temperature, and has been estimated using different correlations for different fluids (Reid et al., 1987). However, the surface tension of the liquid coal during heating is poorly understood, although some investigations have been carried out on coal-derived liquids (Hwang et al., 1982). In previous modelling work, surface tension is assumed constant, i.e. 30 dyne/cm<sup>2</sup>, during the course of plastic stage (Oh, 1985; Solomon et al., 1993; Sheng et al., 2000). In the present work, the surface tension is estimated using the following correlation, combining the correlation in the literature (Reid et al., 1987) and metaplast content following Oh's concept (Oh, 1985), in Eq. 6.12:

$$\sigma = \sigma_0 P_0^{s_p} \left( 1 - (T/Tc) \right)^{(11/9)} (1 - \phi_m)^n$$
(6.12)

where  $\sigma$  is the surface tension,  $\sigma_0$  is surface tension coefficient,  $P_0$  is the ambient pressure,  $s_p$  is a coefficient (2/3), T is the absolute temperature,  $T_c$  is the critical temperature and  $\phi_n$  is volume fraction of metaplast, and n is the coefficient. It can be seen that  $\sigma$  is a function of both temperature and pressure for a given coal. It is obvious that a high surface tension reduces bubble growth rate, in the meantime, prevents bubble ruptures. This enables the liquid coal to keep more gases trapped in bubbles, therefore results in a larger swelling ratio and a larger number of bubbles remaining in the char. From Eq. 6.12, surface tension increases with increasing the ambient pressure. This may partly explain that the elevated system pressure increases the coal swelling, and favours the formation of foam char structure, as reported in the literature (Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>) and observed in the present study.

The diffusivity of volatiles in the coal melt is a crucial term in the latter plastic stage when the number of bubbles is very small. In the single bubble case when a cenospheric structure is generated, volatiles diffuse to the particle surface through the porous liquid shell and are released as devolatilization products. The effective diffusivity of the volatiles through the porous liquid shell is estimated from the diffusivity of volatiles in the gas and liquid phase using Rayleigh's model (Gupta et al., 1997):

$$D_{e}/D_{L} = \frac{(2+R_{d})/(1-R_{d}) - 2\varepsilon_{shl}}{(2+R_{d})/(1-R_{d}) + \varepsilon_{shl}}$$
(6.13)

Where  $D_e$  is the effective diffusivity,  $R_d = D_g/D_L$ ,  $D_g$  is the volatile diffusivity in gas phase,  $D_L$  is the volatile diffusivity in liquid phase and  $\varepsilon_{shl}$  is the porosity of the outer liquid shell. Calculations of  $D_g$  and  $D_L$  are provided in the literature (Oh, 1985; Reid et al., 1987).

#### 6.3 Sensitivity study

#### 6.3.1 General information

**Figure 6.2** shows the schematics of the flow diagram of the computer program for the char structure model calculations compiled using Fortran. The char structure model includes four sub-modules, i.e. the pre-softening sub-module, the multi-bubble sub-module, the single bubble sub-module and the re-solidification sub-module.

**Figure 6.3** (*a*)-(*e*) present the results of transient devolatilization behaviour as a function of particle temperature as predicted in the present study for coal B. The coefficients and input parameters for this calculation are shown in **Table 6.1**. Figure (*a*) and (*b*) are results of transient volatile yields and molecular weight of tars calculated by CPD model. Details of the information of coefficients and parameters for the CPD calculation are shown in *Appendix G*. It has been noticed in the literature (Mill et al., 1998) that CPD Model over predicts the gas yields at high temperature range (above *1100K*), hence over predictions of the total weight losses. However in the temperature range (plastic stage) of the present interests in this study, the results are reasonably well. Figure (*c*) and (*d*) present the estimations of the viscosity, metaplast fraction and diffusivity of volatiles through porous liquid shell is virtually determined by the diffusivity of volatiles in the liquid phase. Figure (*e*) shows results of transient swelling ratio and porosity of the simulated coal particle during heating.





**Figure 6.3** Devolatilization behaviour of coal B predicted using the present model; *(a)* Yields of volatiles; *(b)* Molecular weight of tars; *(c)* Viscosity and metaplast contents; *(d)* Diffusivity of volatiles; *(e)* Transient swelling ratio and porosity.

Viscosity model ( $\mu$ , Pa.s) <sup><i>a</i>,c</sup>	Eq. (6.10)
Diffusivity $(m^2/s)^{a,b,d}$	Eq. (6.13)
Initial number density (per gram coal) <sup>a</sup>	$1.87 \times 10^{13}$
Surface tension $(N/m)^{a,b,d}$	Eq. (6.12)

 Table 6.1. Correlations and coefficients used in the calculation.

Macro-pore volume of parent coal $(cm^3/g)^a$	0.04
Critical viscosity for onset of plastic stage $(Pa.s)^a$	4×10 <sup>4</sup>
Critical wall stress for bubble rupture ( <i>atm</i> ) <sup>c</sup>	1.0
Peak temperature ( <i>K</i> )	1,573
Ambient pressure (MPa)	0.1
Heating rate (K/s)	16,000
Parent coal properties	Table 3.1
Apparent density $(kg/m^3)$	1,400
Diameter of the raw coal particle (µm)	70

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NB: Sources of correlations and coefficients: **a**—Oh et al (Oh, 1985); **b**—Reid et al (Reid et al., 1987); **c**—Solomon et al (Solomon et al., 1993); otherwise or **d** from this study.

**Table 6.2.** Some results of the model prediction for coal B.

Softening temperature (K)	937.9
Re-solidification temperature ( <i>K</i> )	1114
Temperature interval of the plastic stage $(K)$	176.1
Final / initial number of bubbles	0.25
Macro-porosity (%)	98.8
Maximum swelling ratio $(d_{max}/d_0)$	3.80
Final swelling ratio $(d/d_0)$	3.63

The value of the swelling ratio in **Figure 6.3** and **Table 6.2** is consistent with the results reported in Oh's work (Oh, 1985). However, it is higher compared to the experimental data of the swelling and char structure of the full coal data of size fractions provided in chapter 5 for coal B, although the model has used the properties of the full coal as the model input data. Therefore, the model input data need to be carefully adjusted

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accordingly. In this typical case, the model considers the whole coal as a homogeneous material, therefore can only give one type of char structure rather than the heterogeneous behaviour of the full coal. In the practical situation, the chemical composition varies significantly from particle to particle for pf coal, resulting in significant variations in the swelling and char chemistry of individual coal particles. However, in the subsequent sections, it will be demonstrated that the present model is very useful when combined with other measures such as density-separation technique.

The sensitivity study of the model involves three groups of parameters: (i) model assumed parameters and correlations, such as the initial bubble number density, viscosity models and surface tension, etc; (ii) parent coal properties, such as ultimate and proximate analysis data, coal density, particle size, etc; (iii) heating conditions, such as heating rate and ambient pressure. The sensitivity of the model to the parent coal properties and effect of heating conditions will be demonstrated in the subsequent chapter using density-fraction samples. In this section, group (i) parameters and particle size will be discussed. For the purpose of comparison, the following calculations are conducted mainly using coal B data.

# 6.3.2 Sensitivity study of initial bubble density, viscosity model, and surface tension

*Initial bubble number density* is a critical parameter for the multi-bubble model, and is difficult to handle. In Oh's work (Oh, 1985), it has been estimated at  $1.87 \times 10^{13}$  per gram coal based on the assumption that only macro-pores survive the softening to form bubbles. It is not possible to validate this value experimentally, and it is not clear to what extent the value is dependent on raw coal properties, such as rank and maceral compositions, etc. Although the macro-porosity of the parent coal decreases with increasing the coal rank, the change is not obvious among the density fractions of the

same coal, as shown in **Table 3.3**. The input value of the initial bubble density does not result in any change in the CPD model predicted volatile yields, but influence the char structure model predicted results. **Table 6.3** and **Figure 6.4** present the results predicted using the char structure model when the value of the initial bubble number density is changed between  $1.87 \times 10^{12} \sim 6.87 \times 10^{13}$  per gram coal while keeping the other parameters the same.

Initial bubble number density (as per gram coal)	1.87×10 <sup>12</sup>	6.87×10 <sup>12</sup>	1.87×10 <sup>13</sup>	6.87×10 <sup>13</sup>	
Maximum swelling ratio $(d_{max}/d_0)$	2.95	3.35	3.80	4.32	
Final Swelling ratio $(d/d_0)$	1.39	2.80	3.63	4.29	
Char porosity (%)	80	97.5	98.8	99.3	
Initial bubble size $(\mu m)$	0.24	0.16	0.11	.07	
Final bubble number	5743	182784	1171397	5439159	
Final / initial bubble number (%)	1.2	12.3	25.1	37	

 Table 6.3. Model predicted results as a function of initial bubble number density.



Figure 6.4. Model predicted char structure parameters as a function of initial bubble number density.

It is apparent that the predicted results of char structure parameters during the multibubble stage are sensitive to the initial bubble number density, in particular when bubble number density is smaller than  $10^{12}$  per gram coal when critical viscosity value is  $4.0 \times 10^4$  *Pa.s.* Final swelling ratio is more sensitive to the initial bubble number density than the maximum swelling ratio. When initial bubble number density is smaller than  $10^{11}$  per gram coal, the calculation will reach the single bubble stage. Then it is difficult to refer the final results to the initial bubble density. On the other hand, large initial bubble number (above  $1.87 \times 10^{13}$  per gram coal) density leads to over predictions of the swelling and porosity. Therefore, in the present study, the initial bubble number density is chosen at  $1.87 \sim 6.87 \times 10^{12}$  g<sup>-1</sup> coal with critical value at  $4.0 \times 10^4$  *Pa.s.*, and  $3.87 \sim 6.87 \times 10^{11}$  g<sup>-1</sup> coal with critical value at  $1.0 \times 10^4$  *Pa.s.* With this value, the final results are not strongly dependent on the initial bubble number density while the model does not over-predict the swelling and porosity. However, this remains the critical issue in future work of modelling the char structure formation.

**Viscosity** ( $\mu$ ) of the coal melt during the plastic stage is the determining term in modelling the char structure evolution. The sensitivity analysis for viscosity term is essentially to test viscosity models listed in section 6.3. When Eq. 6.10 is used, the minimum viscosity value during plastic stage is around 10<sup>3</sup> *Pa.s.*, which is comparable to reported value in Oh's work (Oh, 1985) and other literature. When Eq. (6.9) or (6.11) is used, the minimum viscosity is 3 magnitudes lower than the above value, which results in: (i) very high bubble escape rate, hence only cenospheric char structure is obtained even initial bubble number density is larger than 10<sup>13</sup>; (ii) very large diffusivity (2 magnitudes higher) of volatiles, hence very small even negative mass increment of

volatiles in the bubble during single bubble stage. Therefore, in the present study, Eq. 6.10 is used in the following model calculations.

**Surface tension** ( $\sigma$ ) is a crucial term in the force balance, which determines bubble growth rate and the rupture of bubbles at the particle surface. In the present study, instead of using a constant value (0.03 *N/m*), Eq. (6.12) has been used to provide estimation of the surface tension of the coal melt during the whole course of plastic stage. **Figure 6.5** shows calculated results of the surface tension of the coal melt of coal B during the plastic stage.



**Figure 6.5**. Calculated results of the surface tension of the coal melt during plastic stage.

**Table 6.4** compares the present model predicted results of char structure parameters using the two different surface tension correlations. It can be seen that the results are similar in this specific calculation. However, as Eq. 6.12 has included effects of temperature and pressure, therefore provides better capacity to the model when modelling char structure formation under different heating conditions, such as heating rate and pressures. This will be further discussed in the subsequent sections.

**Table 6.4.** Model calculated results of char structure parameters using different surface tension models (full coal B, initial bubble number density,  $1.87 \times 10^{12}$  g<sup>-1</sup> coal, critical viscosity value,  $4.0 \times 10^4$  *Pa.s*, other parameters as shown in **Table 6.1**).

Surface tension model (N/m)	Eq 6.12	0.03
Maximum swelling ratio $(d_{max}/d_0)$	2.95	2.95
Final Swelling ratio $(d/d_0)$	1.39	1.48
Char porosity (%)	80	83.5
Final bubble number	5743	7493
Final / initial bubble number (%)	1.2	1.6

**Critical viscosity value** ( $\mu_c$ ) is crucial in modelling char formation and swelling, as it determines the onset of plastic stage, hence the starting point of coal swelling and bubbling. It is also a difficult issue to handle, and different values have been proposed in the literature (Oh, 1985; Solomon et al., 1993; Sheng et al., 2000) to fit different model parameters. In Oh's work,  $\mu_c$  is  $4 \times 10^4$  *Pa.s* (Oh, 1985), while  $2 \times 10^5$  *Pa.s* has been used by Sheng et al (Sheng et al., 2000). A gel point (at which the viscosity is infinite) at the liquid fraction of 0.35 is used in Solomon's work (Solomon et al., 1993). The liquid volume fraction at the onset of softening is therefore higher than 35 %. Experimental data is still required to verify the critical value for the onset of the plastic stage. In model calculations, it is apparent that a larger value of  $\mu_c$  leads to lower starting point of softening and larger temperature interval of plastic stage. In the present study, the viscosity value is estimated from metaplast fraction calculated using CPD model. When using Eq.(6.10),  $4.0 \times 10^4$  *Pa.s* corresponds to 3% (*v*) metaplast at temperature 723 *K*, and  $1.0 \times 10^4$  *Pa.s* corresponds to 10% (*v*) metaplast content.

**Critical wall stress**  $(Sw_c)$  is a very important term in single bubble model, which determines to what extent the coal particle swells during this stage, hence virtually the

maximum swelling ratio and bubble rupture frequency. In Solomon's work (Solomon et al., 1993), the critical wall stress is assumed 1.0 *atm*. When bubble wall stress calculated using Eq. 2.4 (left side) reaches this value, then the bubble ruptures, and releases the volatiles inside the bubble. The calculation approach of the remained mass of volatiles after bubble rupture has been described in the literature by Sheng et al (Sheng et al., 2000). In the present study, the critical wall stress,  $Sw_c$ , has been set as  $P^{2/3}$ , where P is the ambient pressure. Although the inclusion of pressure has no theoretical basis, it is crucial in modelling the char formation under pressurized conditions. The verification of this correlation may be solved in future work of the char structure models. When coal is heated at the pressure of 0.1 *MPa*, the value of  $Sw_c$  is virtually the same as Solomon's (Solomon et al., 1993).

# 6.3.3 Parameters and correlations used in the present char structure model

Viscosity model $(\mu, Pa.s)^a$	Eq. (6.10)
Diffusivity $(m^2/s)^{a,b,d}$	Eq. (6.13)
Initial number density (per gram coal) <sup>a</sup>	4.87×10 <sup>12</sup>
Surface tension $(N/m)^{a,b,d}$	Eq. (6.12)
Macro-pore volume of parent coal $(m^3/kg)^a$	4.0×10 <sup>-5</sup>
Critical viscosity value $(Pa.s)^a$	1×10 <sup>4</sup>
Critical wall stress for bubble rupture (atm)	$P^{2/3}$

**Table 6.5.** Parameters and correlations used for the present modelling work.

NB: Sources of correlations and coefficients: **a**—Oh et al (Oh, 1985); **b**—Reid et al (Reid et al., 1987); **c**—Solomon et al (Solomon et al., 1993); otherwise or **d** from this study.

On the basis of the above sensitivity study, **Table 6.5** shows the parameters and correlations selected for the calculations of the present char structure model. Other parameters and coal properties are also determined accordingly. Coal properties are shown in Table 3.1~Table 3.3.

# 6.3.4 Effect of raw coal particle size

**Table 6.6.** Effect of particle size on char formation predicted by the present char structure model, with input data in **Table 6.1** and **Table 6.5** (coal properties in Table 3.1).

Raw coal particle size (µm)	70	100	150	
Maximum swelling ratio $(d_{max}/d_0)$	2.95	3.32	3.8	
Final Swelling ratio $(d/d_0)$	1.39	2.7	3.58	
Char porosity (%)	80	97.2	98.6	
Final bubble number	5743	151206	1076485	
Final / initial bubble number (%)	1.2	11	23	

**Table 6.6** shows the model predicted results of the effect of raw coal particle size for coal B under the following heating conditions: the heating rate of  $1.6 \times 10^4$  K/s, peak temperature at 1573 K and the ambient pressure of 0.1 MPa. The results of the swelling and the porosity suggest that the model calculations are sensitive to the particle size. The model predicts an increase of swelling with increasing the particle size. In the meantime, the bubble number and the ratio of the final to the initial bubble number decrease apparently when particle size decreases. This implies that smaller particles tend to generate cenospheric char, while foam structures tend to evolve in larger particles, probably because small particles have higher surface/volume ratio to allow the escape of bubbles during the plastic stage. This trend qualitatively agrees with the

observations in the literature (Sung, 1977). However, different results are observed from DTF chars prepared in this study, as discussed in chapter 5. It appears that this is a complicated issue, associated with both coal type and heating conditions under which char is produced.

#### 6.4 Conclusions of this chapter

- A mathematical model for swelling and char structure formation of single coal particle during devolatilization has been developed based on a simplified multibubble mechanism. As an advancement of previous work, the present model provides a complete description of char structure evolution process of pf coal during pyrolysis;
- In the model development, the devolatilization process is divided into three stages, i.e., pre-plastic stage, plastic stage and resolidified stage, based on the viscosity value. The three stages are described respectively, and the plastic stage is considered the key step for char structure formation;
- The char formation during plastic stage has been considered as two successive steps, i.e. a multi-bubble stage followed by the single bubble stage. During the multi-bubble stage, the rupture of bubbles is a rate-controlled process, while the volatile release is determined by the bubble rupture rate. When the cenospheric char structure is formed, the single bubble model applies for which the bubble rupture is controlled by the wall stress, and the volatiles are released by both bubble rupture and direct volatile diffusion to the particle surface through the porous liquid shell;

- The devolatilization rate is predicted using CPD model, and the NMR chemical structure parameters are estimated from proximate and ultimate data of the parent coal by employing an empirical correlation from literature;
- Some correlations have been employed to provide reasonable estimation of thermo-plastic properties, including the viscosity, surface tension and diffusivity, of the coal during heating;
- Sensitivity study of the model has been carried out with the model assumed parameters and correlations. This includes the initial bubble number density, viscosity models, the surface tension and the coal particle size. Based on the sensitivity study, parameters for the present modelling work have been determined;
- The present model provides simulations of the transient coal swelling and the char structure evolution of pf coal of bituminous coal during pyrolysis from the standard raw coal properties, therefore improves current understanding of char formation mechanism.

# CHAPTER 7. MODELLING THE CHAR STRUCTURE EVOLUTION—THE MODEL VALIDATION

#### 7.1 Introduction

The model developed in the present study can provide transient simulation of swelling and char structure evolution process of individual coal particle during heating. Therefore the best way to validate the model prediction is to use transient swelling and char morphology data from direct experimental observations. However, it is not applicable to compare the present model calculations with individual swelling curves from experimental measurements using the single particle reactor from this study and in the open literature due to two reasons: (1) the proximate and elemental compositions of the observed individual coal particles reported are unknown, and there is no technique available to allow direct measurements of the chemical composition of individual single particles so far; (2) there are significant variations in the swelling behaviour of individual particles of pf size under the same heating condition, even the particles are from the same coal density cut in this study. From engineering points of view, it may be a comprehensive way by employing data of density-fraction samples to provide reasonable estimation to the char structure distribution and swelling of a given coal from the present model calculations. In this section, model predicted results of densityfraction samples of coal B are compared with experimental data obtained from analysis of DTF chars. Model prediction on the effect of heating conditions on devolatilization and char structure of the full coal is also discussed.

# 7.2 Comparison of model prediction with experimental data of DTF chars



# 7.2.1 Model predicted results

**Figure 7.1.** Transient devolatilization behaviour of density-fraction samples of coal B predicted in the present study, (a) Volatile yields (db); (b) Tar yields (db); (c) Gas yields (db); (d) Metaplast contents; (e) Viscosity; (f) Swelling ratio  $(d/d_0)$ . (Heating rate of 16,000 K/s, peak temperature of 1573 K and pressure at 0.1 MPa).

Parent coal properties of density-fraction samples of coal B used for the following calculations have been shown in Table 3.3 and Table 3.4, and model input parameters are shown in **Table 6.5**. Heating conditions used for this calculation are: heating rate of 16,000 K/s; ambient pressure of 0.1 MPa, peak temperature of 1573 K and particle size of 70  $\mu m$ . Predicted results of devolatilization behaviour are presented in **Table 7.1** and Figure 7.1 (a)  $\sim$  (g). Figure (a) and (b) demonstrate that the CPD predicted yields (d.b.) of volatiles and tars decrease with increasing the parent coal density, in particular the yield of tars. The decrease in the volatile yields is consistent with the trend from the proximate analysis data in **Table 3.3**. However, the yield of gases increases at heavy density samples, as shown in Figure (c). An important fact from the prediction in Figure (d) is that the metaplast content in the coal particle during heating decreases significantly for heavy density-fraction samples. This causes significant decreases in the coal fluidity during pyrolysis heating, as presented in Figure (e). The predicted values of the minimum viscosity of the two heavy density fraction samples, F1.50 and S1.50, are  $1.05 \times 10^4$  and  $1.68 \times 10^4$  Pa.s, respectively, as shown in **Table 7.1**. When using  $1.0 \times 10^4$ *Pa.s* as the critical value of softening point, F1.50 and S1.50 density fractions virtually exhibit no softening and no swelling. This viscosity cut-off is corresponding to around 10% metaplast content. Meanwhile, the light density fractions, i.e. F1.25 and F1.30, and the medium density fraction sample, F1.35, develop significant fluidity and swelling, as presented in Figure (e) and (f). It can be seen from Figure (f) that F1.25 fraction particle exhibits intensive swelling and contraction due to the bubbling behaviour. With increasing the coal density, particle softens at higher temperature, and exhibits less bubbling and lower swelling, although the predicted maximum swelling ratios are similar. These results also demonstrate that the present char structure model calculation is sensitive to the parent coal properties. When other parameters remain the same, the coal swelling and char structure are virtually determined by the properties of the parent coal, and change significantly with changing the coal properties.

**Table 7.1**. Predicted coal swelling and char structure of density-fraction samples of coal B using the present model under the conditions as indicated (heating rate, 16,000 K/s; ambient pressure, 0.1 *MPa*; peak temperature, 1573 K; particle size,  $70\mu m$ )

Density fraction	F1.25	F1.30	F1.35	F1.50	S 1.50
Final bubble number	1	1	1260	-	-
Char type (Groups)	Ι	Ι	II	III	III
Softening temperature, T <sub>s</sub> (K)	917.8	947.1	980.3	-	-
Plastic temperature interval, $T_d$ - $T_s$ (K)	173.0	137.9	102.7	-	-
Final swelling ratio $(d/d_{\theta})$	1.66	1.42	1.24	1.00	1.00
Maximum swelling ratio $(d_{max}/d_0)$	2.54	2.54	2.53	1.00	1.00
Porosity of char (%)	89.90	82.70	69.10	40.06	31.92
Minimum viscosity $(10^3, Pa.s)$	1.82	2.41	4.20	10.51	16.97

More specifically, **Table 7.1** shows that the present model has predicted the occurrence of the cenospheric char structure for the two lightest density fractions, i.e. F1.25 and F1.30, the foam char structure for F1.35 density fraction, and dense char structure for the two heavy density samples, F1.50 and S1.50. Correspondingly, Group I char evolves for F1.25 and F1.30, Group II char is predicted for F1.35, and Group III char is obtained from F1.50 and S1.50. With increasing the coal density, the model predicted minimum viscosity increases from  $1.8 \times 10^3$  *Pa.s* for F1.25 density fraction to  $1.7 \times 10^4$  *Pa.s* for S1.50 sample. The final swelling ratio decreases from 1.66 for the lightest density sample to 1.00 for the two heaviest density fractions, while the char porosity decreases from 89.9% to 32%. The results agree well with experimental observations as discussed

in chapter 5 and reported elsewhere (Yu et al., 2002; Yu et al., 2002<sup>c</sup>). The predicted softening temperature increases with increasing the coal fraction density, while an apparent decrease in the temperature intervals of the plastic stage occurs as the coal fraction density increases. Obviously, the present model has predicted the heterogeneity of coal swelling behaviour and different types of char structures using the data of density samples of the same coal under the same heating conditions.

# 7.2.2 Comparisons of model prediction with experimental data

Figure 7.2 (a)  $\sim$  (d) compares present model predicted results with experimental data of DTF char samples prepared using density fractions of coal B at temperature 1573 K and pressure 0.1 MPa. Figure (a) shows the decrease in the weight losses of both prediction and experimental data with increasing the coal fraction density. However, smaller decrease in the weight losses have been predicted than experimental results probably due to the over-prediction of gas yields by CPD model at high temperatures, in particular for heavy density samples. Figure (b) compares model predicted results of swelling ratio with experimental data measured using the Malvern sizer and through SEM image analysis of the DTF chars. Apparent decreases in the swelling ratios with increasing the coal density occur for both prediction and experimental measurements. However, the model has predicted much higher swelling ratio, 1.66, than the measured results, 1.44, for F1.25 density-fraction. During experiments, when the lightest density fraction sample, F1.25, is devolatilized at high heating rates ( $\sim 10^4$  K/s), such as in the gas flow reactors, some of the particles may break up during the plastic stage due to the high fluidity and high devolatilization rates. Although the fragmented liquid particles continue to swell, the final swelling ratio of the chars may be much smaller than particles that do not experience fragmentations. This mechanism has not been included

in the present char structure model. But it may be considered in future work by establishment of a criterion similar to that proposed for the bubble rupture in the single bubble model (Solomon et al., 1993) for liquid particle fragmentations.

Figure (c) demonstrates well agreements between the model-calculated char porosity and experimental results from DTF chars measured through image analysis. Both the predicted porosity and measured data decrease remarkably as the coal fraction density increases, corresponding to the decreases in the swelling ratios. The char porosity is the major parameter of its structure. Therefore, the decrease in the char porosity virtually leads to changes in the char structure type, according to the char structure classification system given in **Table 2.2**. Specifically, Group I chars have a porosity above 80%, Group II chars have a porosity of 50~80%, while Group III chars have a porosity below 50%. On this basis, the present model gives the char structure type of different density fraction samples, shown in Table 7.1, by considering each density sample as a homogeneous material. In combination with the mass yields of the density separation shown in **Table 3.2**, the char structure distribution of the full coal B is obtained. Figure (d) compares model predicted char type distribution with measured results. It can be seen the calculated results agree reasonably well with the experimental measurements on DTF chars. However, there are still discrepancies between the two results. For instance, the model predicted Group I char population is 12.2% higher than the measured result. This may be partly because the large density bins have been used in density-separations in the present work. Therefore, it is not possible for the model to carry out calculations with resolutions high enough to compare with experimental measurements. To provide a finer resolution of the model calculations, two approaches may be considered in further study: (1) Narrow the density bins for the density separation during coal sample preparations; (2) Utilize coal reflectograms by establishing correlations between the reflectance of the parent coal and its chemical composition or chemical structure parameters. An ongoing project in the CCSD (Tang et al., 2002) is targeting the development of correlations between coal reflectograms and raw coal properties and char characteristics. Technically, the reproducibility of both approaches is still an issue. However, these treatments will greatly enhance the present char structure model.



Figure 7.2. Comparison of present model predicted results with experimental data of DTF chars of density-separated samples of coal B. (a)—Weight loss; (b)—Swelling ratio of the density fractions; (c)—Porosity of the density fractions; (d)—Char type distribution of the whole coal.
Overall, the present char structure model predicts the experimental trends of coal pyrolysis behaviour, including swelling, porosity and char structure distribution under the present conditions. An important feature of the present work is, in combination with density-separation techniques, to provide mechanistic information of heterogeneity of swelling behaviour and char structure type distribution of a given coal under different heating conditions. This is an important advancement over previous modelling work.

## 7.3 Model prediction on effect of heating conditions

As reviewed in the previous chapters, coal devolatilization behaviour, e.g. devolatilization rate, swelling and char structure, are strongly influenced by the conditions under which coal is heated. During this complex process, chemical reactions and physical alterations interact with each other, resulting in significant changes in volatile yields, thermo-plastic properties and char formation. In the present study, the change in volatile (tar and gas) yield is predicted with changing heating conditions using the CPD model. Similar prediction can be provided using FG-DVC model. As a comparison, *Appendix H* presents the predicted results of volatile yields of coal B under different heating conditions calculated using FG-DVC model. Metaplast contents are also predicted using CPD model, from which viscosity is calculated under different heating conditions. The surface tension term is a function of temperature and pressure. As such, it is expected that the present model may provide simulations of char structure evolution with changing the heating conditions. In this section, effects of heating rates and pressures on coal swelling and char structure of coal B during pyrolysis are investigated using the present model. Parameters used for the following calculations are shown in Table 3.1 (coal properties) and **Table 6.5**, and heating conditions are as indicated.

## 7.3.1 Effect of heating rates

Figure 7.3 (a)~(g) and Table 7.2 present the model predictions of the transient devolatilization behaviour and char structure as a function of heating rates in a limited heating rate range (at the peak temperature of 1573 K and the pressure of 0.1 MPa). Figures (a)  $\sim$  (d) are CPD predicted transient yields of tar, gas and total volatiles, and the average tar molecular weight. Consistent with the literature data, apparent increases in tar yields occur at higher heating rates, as shown in Figure (a). The increase in the total volatile yield due to the increased tar yields is offset by the decrease in the gas yields with increasing the heating rates, as shown in Figure (b) and (c). Figure (d) shows the increase in the average molecular weight of tars with increasing the heating rate. This agrees with the increase of the tar yields. Apparent decrease of the metaplast content and a shift of metaplast generations to a higher temperature range with increasing heating rates have been predicted, as shown in Figure (e). This leads to a slight increase of the viscosity at the same temperature and a shift of the peak to a higher temperature range. This is shown in Figure (f). As viscosity is the dominant term in modelling the coal swelling and char structure formation, the change of viscosity with changing heating conditions is important in the subsequent model calculations. Figure (g) presents the model predicted transient swelling of the coal particle as a function of heating rates. It is obvious that the present model predicts the increase of swelling with increasing the heating rate. The coal particle exhibits significant contraction and bubbling at 8,000 K/sheating rate, but very little contraction at heating rates above  $4 \times 10^4$  K/s. The predicted result of the increase of the coal swelling with increasing the heating rate qualitatively agrees with some literature data, as reviewed in chapter 2. However, the present model has not predicted the optimum heating rate range for the maximum swelling as suggested by some previous work in the literature (Gale et al., 1995). This means the application of the model to a wide range of heating rates is still a matter to be solved.





**Figure 7.3.** Transient devolatilization behaviour of full coal B as a function of pyrolysis heating rate predicted in the present study; (a) taryields; (b) gas yields; (c) total volatile yields; (d) average tar molecular weight; (e) metaplast content; (f) viscosity; (g) swelling ratios. (Heating rates as indicated,  $\times 10^3$  K/s.)

**Table 7.2** shows more clearly the model predicted coal swelling and char structure as a function of the heating rate. At the relatively slow heating rate, i.e. 8,000 *K/s*, the coal tends to form cenospheric char structure. As the heating rate increases to above 16,000 *K/s*, more bubbles are remained in the char, and foam structures are predicted. Consistent with literature reports, the softening temperature,  $T_s$ , increases at higher heating rates, from 910 *K* at the heating rate of 8,000 *K/s* to around 1000 *K* at of 10<sup>5</sup> *K/s*. Also, the temperature interval of the plastic stage increases with increasing the heating rate. Significant increase in the final swelling ratio has been predicted at higher heating rates while the maximum swelling ratio is not sensitive to the heating rate. This virtually suggests that less particle contraction occurs at higher heating rate due to the decrease in the predicted metaplast content. This leads to a smaller bubble rupture rate during the plastic stage. Because of the high swelling ratio at higher heating rate, the char porosity also increases significantly, from 67% at 8,000 *K/s* to 97% for 10<sup>5</sup> *K/s*.

Heating rate (10 <sup>3</sup> , <i>K/s</i> )	8	16	40	100
Final /initial bubble number (%)	0.0	1.2	16.6	37.7
Char structu re	С	F	F	F
Ts (K)	910.3	937.9	968.8	999.0
$T_{d} T_{s}(K)$	161.7	176.1	200.2	210.0
Final swelling ratio (d/d0)	1.18	1.39	2.63	2.92
Maximum swelling ratio $(d_{max}/d_{\theta})$	2.95	2.95	2.94	2.93
Porosity (%)	67.20	80.12	97.05	97.80
Minimum viscosity (10 <sup>3</sup> , <i>Pa.s</i> )	4.55	4.99	5.10	5.43

**Table 7.2.** Model predicted results of coal swelling and char structure under different heating rates as indicated.

*NB: C*—*cenospheric char structure, F*—*foam char structure.* 

Overall, although the magnitude of the increase in the swelling, porosity and other parameters with increasing the heating rate still needs to be validated using experimental data from the same coal in future work, the present model prediction provides very useful mechanistic information on char formation of softening coals with changing the heating rate. The present model predicts the increase of swelling and char porosity with increasing the heating rate. There is also a trend that cenospheric char structures tend to be generated at slow heating rates. The results show that the present model prediction is sensitive to the heating rate. The model predicted trends are considered reasonable in a limited heating rate range ( $\sim 10^4 K/s$ ). Very slow heating rate (< 100 K/s) allows time for bubble nucleation and direct diffusions of volatiles out of the particle, even during the multi-bubble stage. These are the limits of the present model, and needs to be considered in future work. It is not clear, however, to what extent the bubble nucleation will take effect in the char structure formation during plastic stage. In

fact, in the single particle experiments, the occurrence of high swelling and possible cenospheric chars has been observed, as shown in chapter 4. On the other hand, high heating rate shift devolatilization reactions to a high temperature range, resulting in a high devolatilization rate. This may increase the possibility of particle fragmentation during plastic stage. At extremely high heating rates (>10<sup>5</sup> K/s), the rheological behaviour may play an important role to cause decrease of swelling (Waters, 1962; Khan et al., 1985<sup>b</sup>; Khan et al., 1989; Gale et al., 1995; Gale et al., 1996). This mechanism has not been included in the present model. However, the calculated results do demonstrate that metaplast content decreases while the minimum viscosity value slightly increases at high heating rates, which may restrain the swelling of the particle. The analysis on PEFR char samples in **Chapter 8** shows that the number of bubbles of PEFR chars is much higher than that of DTF chars. Apart from the major role of pressure (discussed in subsequent chapter), the higher heating rate in entrained flow reactor than in DTF reactor may be one of the reasons responsible for formation of foam structure in this case. Therefore, in future work, the model may be improved by considering bubble nucleation rate and size distribution for low heating rates, and by consideration of rheological properties of coal when heated at extremely high heating rates.

## 7.3.2 Effect of ambient pressure

Effect of pressure on devolatilization behaviour has become an interesting topic in the recent years, as reviewed in **Chapter 2**. However, the nature of coal pyrolysis process under elevated pressure is still not well understood. Chapter 8 presents characteristics of chars collected under pressurized conditions. This section discusses model predicted results of the pressure effect on coal swelling and char structure for coal B at the heating

rate of  $1.6 \times 10^4$  K/s using the present char structure model in combination with CPD model. Figure 7.4 (a)~(h) and Table 7.3 present model calculated devolatilization behaviour as a function of the ambient pressure. Figure (a) shows that the CPD predicted yields of tars decrease considerably as the pressure increases. With the present predicted results, the ultimate tar yield decreases from 26% at pressure 0.1 *MPa* to ~16% at pressure 5.0 *MPa*. In the meantime, the gas yields increase with increasing the system pressure, as shown in Figure (b). The total yields of volatiles and the average tar molecular weight decrease apparently at higher pressures as shown in Figure (c) and (d). These results qualitatively agree with conclusions in the open literature, as reviewed in chapter 2.

Figure (e) shows the metaplast content increases considerably with increasing the ambient pressure. Correspondingly, a slight decrease in viscosity during the plastic stage has been predicted, as presented in Figure (f). This result suggests that the pressure may play an important role in coal thermo-plastic behaviour during heating. The model prediction for transient swelling of the coal particle as a function of pressure is presented in Figure (g). The results show that the coal swelling increases at a low pressure range from 0.1 MPa up to 1.0 MPa. Above 1.5 MPa, the swelling decreases as the pressure increases, under the present calculation conditions. The trend is more clearly revealed in Table 7.3. This suggests that the effect of pressure on coal swelling is complex. An optimum pressure value exists for the maximum coal swelling. This conclusion is consistent with previous work in the open literature (Khan et al., 1989; Lee et al., 1991<sup>a</sup>; Solomon et al., 1994; Wu, 2000<sup>b</sup>). In the meantime, Figure (g) also suggests that much less particle contractions take place at elevated pressures. However, this phenomenon needs to be confirmed with experimental observations in future work.

A pressurized single particle reactor has been built in an ongoing project conducted by this research team, and the experiments will be focused on pf coal particle swelling behaviour and char formation under elevated pressures up to 10 *MPa*.





Figure 7.4. Transient devolatilization behaviour of coal B as a function of ambient pressure predicted in the present study; (a) tar yields; (b) gas yields; (c) total volatile yields; (d) average tar molecular weight; (e) metaplast content; (f) viscosity; (g) transient swelling. (Heating rate,  $1.6 \times 10^4$  K/s; peak temperature, 1573 K, particle size, 70  $\mu$ m.)

**Table 7.3** presents the calculated results of swelling and char structures under different pressures using the present model. As expected, significant increases in the final bubble number in the char occur as the pressure increases. The results suggest that high pressure favours the formation of foam structure. This is consistent with previous observations in the literature by Wu et al (Wu et al.,  $2000^{a}$ ; Wu,  $2000^{b}$ ), and is also confirmed in observations on PEFR chars presented in chapter 8. While final char swelling ratio peaks at 1.0 MPa, the maximum swelling ratio decrease monotonically as the pressure increases. The predicted char porosity change correspondingly to that of final char swelling ratio reaches the maximum. The pressure range for the maximum char swelling ratio and porosity in the present calculation is similar to that reported in the previous work (Lee et al.,  $1991^{a}$ ) (Wu,  $2000^{b}$ ). It can also be seen from the results listed in the table that minimum viscosity decreases noticeably as the pressure increases. The

5.0 *MPa*. There is a corresponding increase in the temperature interval for the plastic stage as the pressure increases. According to the present model calculations, the char structure is sensitive to the change of the ambient pressure. Therefore it is confident that the present char structure model can provide reasonable prediction to the coal swelling and char formation with changing the ambient pressure, and provide mechanistic insight into the char structure evolution under pressurized conditions.

**Table 7.3.** Model predicted results of coal swelling and char structure as a function of the ambient pressure (heating rate,  $1.6 \times 10^4$  *K/s*; peak temperature, 1573 *K*)

Pressure <i>(MPa)</i>	0.1	0.5	1.0	1.5	2.0	5.0
Final / initial bubble number (%)	1.2	28.3	54.4	67.4	74.8	89.1
$T_{s}(K)$	937.9	926.7	922.9	919.2	915.4	880.9
$T_d - T_s(K)$	176.1	187.3	191.1	194.8	198.6	233.1
Final swelling ratio $(d/d_0)$	1.39	2.80	2.88	2.69	2.51	1.92
Maximum swelling ratio $(d_{max}/d_{\theta})$	2.95	2.94	2.88	2.69	2.51	1.92
Porosity (%)	80.1	97.4	97.5	96.9	96.2	91.4
Minimum viscosity (10 <sup>3</sup> , Pa.s)	4.77	3.99	3.76	3.60	3.47	2.94

## 7.4 Discussion

The present model predicts experimental trends on swelling and porosity of DTF chars from density fraction samples under the present conditions, and provides reasonable estimation of the char structure type distribution of the full coal. Also, the model provides valuable mechanistic information on coal swelling and char formation under different heating conditions, such as heating rates and ambient pressures. The model predicted results of coal swelling with changing the heating conditions are consistent with previous data in the open literature, in particular with results for pressures.

Compared to experimental results, the present model over predicts the swelling ratio and char porosity at some points, in particular for the lightest density fraction sample, F1.25. The predicted trends of coal swelling ratio agrees with literature data only in a limited heating rate range. The model does not predict the occurrence of the optimum heating rate range for the maximum coal swelling as reported in the literature reviewed in chapter 2. The discrepancy between the model prediction and experimental data may be attributed to the following reasons:

- (i) The severe uncertainties of physical properties of coal at high temperatures cause the discrepancy between the model calculations and experimental data. In particular, there is very little experimental data on the viscosity and surface tension during plastic stage, and their changes under different heating conditions and with different coals. As the viscosity and surface tension are critical terms in modelling the char structure formation, they need to be understood in future study. Development of experimental techniques to allow direct investigations of viscosity and surface tension at high temperature, high heating rate and high pressure are essential;
- (ii) Two critical values, i.e., the  $\mu_c$  and  $Sw_c$ , are extremely important in the model calculations. The former term,  $\mu_c$ , determines virtually the softening point and the temperature interval of the plastic stage, hence determines how long time the coal particles undergo swelling. The latter term virtually determines to what extent the particle swells during the single bubble stage, hence, the maximum swelling and the final swelling ratio. However, the two values need to be verified using experimental

data. And obviously, the values may change with changing parent coal properties, i.e. coal rank and maceral compositions, and heating conditions, such as heating rate and pressure;

- (iii) Initial bubble number density is a very sensitive and critical parameter for the model prediction. Although this value can be theoretically estimated, the question still remains for future work: how to determine the value reasonably for a specific case? Whether the value changes with different types of coal? And does the value change for different maceral components or different density fraction particles?
- (iv) The physical nature of pyrolysis process under elevated pressures is not well understood. Further experimental investigations are essential to provide quantitative information of this process;
- (v) The present model does not include the mechanism of particle breaking-up during the plastic state, therefore, is not able to predict the char fragmentation and the occurrence of blow holes;

Overall, the present model has predicted the heterogeneity of coal swelling and char structure from standard coal properties, and provides useful mechanistic information of char formation.

## 7.5 Conclusions of this chapter

• The comparisons of the model prediction to the experimental data of DTF chars of coal B prepared in the present study show that the present model predicts experimental trends in the swelling and char structure characteristics. The present model prediction provides useful mechanistic information of coal devolatilization behaviour and a detailed insight of the char formation under different heating conditions;

- From standard parent coal properties of density-fraction samples, the present model predicts the heterogeneity of char structures from the same coal. For low density-fraction, F1.25 and F1.30, the model has predicted high swelling and porosity, and the formation of cenospheric char structure (Group I char). The decreases in swelling and porosity and the change in the char structure type towards dense structures (Group III char) for heavy density fraction samples, F1.50 and S1.50, have also been predicted using the present model. Other thermo-plastic properties are also predicted as a function of the coal fraction density. The model prediction is consistent with experimental measurements;
- In combination with the data of density-separated coal samples, the present model provides estimation of char structure distribution of the full coal;
- The present model predicted results at different heating rates and pressures demonstrate that heating conditions play an important role in coal devolatilization behaviour, including volatile yields, thermo-plastic properties, swelling, and char structure characteristics. The prediction is consistent with previous work reported in the literature;
- With increasing the heating rate, the model predicts the increase in the swelling and porosity, softening temperature and temperature interval of the plastic stage. The results suggest that cenospheric chars tend to form at relatively slow heating rate, while foam structure tends to evolve at high heating rates;

• Significant change in coal swelling and char structure occurs under different ambient pressures. As the ambient pressure increases, the porosity and final bubble number in the char increase remarkably. However, the final swelling ratio of char increases at first in the low-pressure range up to 1.5 *MPa*, and decrease when the pressure increases further. The model predicted pressure range for the maximum swelling is consistent with literature data.

## CHAPTER 8. EFFECT OF PRESSURE ON CHAR STRUCTURE FORMATION

## 8.1 Introduction

Wide research interest on the effect of ambient pressures on char formation has been driven by the development of new efficient power generation technologies, such as pressurized fluidized bed combustion (PFBC) and integrated gasification combined cycle (IGCC), over the last decades (Takematsu et al., 1991; Harris et al., 1995; Wang et al., 1998; Liu, 1999<sup>a</sup>; Wu, 2000<sup>b</sup>; Benfell, 2001). These technologies provide several advantages over the conventional coal firing processes, including an increase in coal throughput, a reduction in pollutant emission and an enhancement in the intensity of reactions. Recent previous work on coal pyrolysis (Lee et al., 1991; Lee, 1992; Cai et al., 1993; Griffin et al., 1994; Cai et al., 1996; Benfell et al., 1998; Mill et al., 1998; Megaritis et al., 1999; Mill, 2001), coal swelling and char structure (Khan et al., 1986; Khan et al., 1988; Lee et al., 1991<sup>a</sup>; Benfell et al., 1998; Wu, 2000<sup>b</sup>; Benfell, 2001; Matsuoka et al., 2002) and char reactivity (Lee, 1992; Cai et al., 1996; Benfell et al., 2000; Liu et al., 2000; Roberts, 2000; Gadiou et al., 2002), have revealed that: the operating pressure has a marked impact on coal swelling during devolatilization; char reactivity is enhanced at high pressure; and the operating pressure significantly influence the ash formation mechanism through its effect on the structure of chars formed during the devolatilization. Effect of pressure on ash formation and coal reactions has been recently reviewed by Wall et al (Wall et al., 2002; Wall et al., 2002a).

Influence of the ambient pressure on char structure has been investigated very recently using Australian bituminous coals (Liu, 1999<sup>a</sup>; Wu, 2000<sup>b</sup>) and maceral concentration coal samples (Benfell, 2001), as shown in **Figure 8.1** and **Figure 8.2**. Clear trends show that, as the pressure increases, the overall proportion of Group I chars increases while that of Group II and III chars decreases. For instance, in Figure 8.2, when pressure increases from 0.5 *MPa* to 1.5 *MPa*, the Group I chars increase from 38% to 72% for the sample containing high inertinite maceral. Chars with different structures tend to behave differently during the subsequent char combustion or gasification. Group I chars, due to the high porosity, are more easily fragmented, leading to the formation of finer ash particles. Therefore, the change in the population of the Group I chars has a significant influence on the final ash chemistry (Wu, 2000<sup>b</sup>).



**Figure 8.1.** Char characteristic of an Australian bituminous coal generated at different pressures (after Wu, 2000<sup>b</sup>).

More recently, Gadiou et al (Gadiou et al., 2002) investigated the influence of pressure on the structure and reactivity of millimetre sized single coal particles using a laser heating reactor, and concluded that their results are consistent with the results of Wu et al., 2000<sup>a</sup>) in terms of swelling.



**Figure 8.2.** Percentages of Group I, II and III chars for inertinite-concentration coal sample as a function of the system pressure (prepared at 1573 K in a PDTF) (after Benfell, 2001).



**Figure 8.3.** Proposed mechanism of the evolution of a highly porous foam char structure under pressurized conditions during pf coal devolatilization (after Wu, 2000<sup>b</sup>).

Wu et al (Wu, 2000<sup>b</sup>) concluded that highly porous foam char structure tend to be generated during pyrolysis under elevated pressures compared to the atmospheric

pressure, and qualitatively proposed a mechanism of the evolution of the foam structure through bubble generation, as shown in **Figure 8.3**. This mechanism has been proposed on the basis of their experimental investigations on characteristics of chars prepared in a pressurized drop tube furnace (PDTF). However, this process has not been quantitatively modelled in their study. Their experimental results suggest that the population of chars with a foam structure appears to dominate the char sample, and the typical char morphology under SEM is shown in **Figure 8.4**.



**Figure 8.4.** SEM image of a typical char particle which has a foam internal structure, prepared in PDTF furnace (after Wu, 2000<sup>b</sup>).

In this chapter, char samples collected in the pressurized entrained flow reactor (PEFR) at an elevated pressure have been examined under SEM. All the SEM images are taken using the same acceleration voltage, 15 kV. The operation conditions of pyrolysis experiments on the PEFR have been shown in **Table 8.1** and *Appendix B*, and the experimental apparatus is described elsewhere (Park, 2002). The wall temperature is selected at 1373 K and 1673 K, respectively. The ambient pressure is 2.0 *MPa*, and 2.5~5% oxygen is used during experiments. The characterization of char samples has

been described in chapter 3. The characteristics of PEFR chars is compared with DTF chars prepared at the atmospheric pressure from this study and PDTF chars prepared at the pressure of 0.5~1.5 *MPa* reported in previous studies through CCSD projects (Liu, 1999a; Benfell et al., 2000; Wu, 2000<sup>b</sup>; Benfell, 2001). **Table 8.2** compares the experimental conditions of PEFR and DTF for char preparations in this study with PDTF reactor reported in the previous work (Wu et al., 2000). Apart from the difference in the system pressure, the heating rate in PEFR is estimated higher than in the drop tube furnace. The residence time in the PEFR is much longer than in DTF reactor. Some model predicted results at elevated pressures are presented. The mechanism of char formation at pressure is also discussed.

Table 8.1. Operation conditions for PEFR char preparations in this study.

Coal	System	Wall	Oxygen	Coal Feed	Stoichio-	Residence
	Pressure	Temperature	%	Rate (kg/hr)	metry	Time $(s)$
	(MPa)	( <i>K</i> )				
В	2.0	1373	5	2.5	104	4.7
	2.0	1673	5	2.5	154	2.3
Α	2.0	1373	2.5	2.1	93	2.8

**Table 8.2.** Comparison of experimental conditions of the three reactors for char sample preparation.

Coal	System	Wall	Gas flow	Heating	Residence
	Pressure	Temperature		rate	Time $(s)$
	(MPa)	<i>(K)</i>		(K/s)	
DTF	0.1	1573	N <sub>2</sub>	$10^{3} \sim 10^{4}$	0.3 ~ 0.5
PEFR	2.0	1373, 1673	2.5~5%	>104	2.3 ~ 4.5
			$O_2$		
PDTF (Wu,	0.5~1.5	1573	N <sub>2</sub>	$10^{3} \sim 10^{4}$	~0.5
2000 <sup>b</sup> )					

## 8.2 PEFR char properties

**Table 8.3.** Properties of PEFR chars of coal B prepared at different wall temperatures at the elevated pressure of 2.0 *MPa*.

Coal	Wall Temper- ature	Oxygen %	Proximate analysis (%, ad basis)			Ultimate analysis (%, daf)				Conver- sion (%, daf)		
	( <b>K</b> )		Moist	Ash	VM	FC	С	Η	N	S	0	
В	1373	5	5.8	17.4	2.5	74.3	94.7	0.62	1.75	1	1.9	49.5
В	1673	5	3.4	21.8	1.5	73.3	96.8	0.26	1.23	0.63	1.1	60.8



**Figure 8.5.** PSD (by volume) of PEFR chars prepared at the wall temperature of 1373 *K* and pressure of 2.0 *MPa*; (*a*) coal A, measured through SEM image analysis, (*b*) coal B, measured using the Malvern Sizer.

**Table 8.3** shows properties of PEFR char samples of coal B prepared at different wall temperatures and under the pressure of 2.0 *MPa*. It can be seen that the conversion rate is 11% higher when wall temperature increases from 1373 *K* to 1673 *K*. The particle size of the feed coal is +45-150  $\mu m$ , and the mean particle size of coal B is 111.14  $\mu m$ . The particle size distribution (by volume) of chars of coal A and coal B at the wall

temperature of 1373 K and pressure of 2.0 MPa is shown in **Figure 8.5** (a) and (b). It is apparent that the PEFR char particles are mainly distributed above 150  $\mu m$ . The mean particle size of chars from coal A is 192.3  $\mu m$ , and is 223.94  $\mu m$  for coal B.

## 8.3 SEM morphology and structures of PEFR chars



**Figure 8.6**. SEM images of PEFR chars morphology of coal A and coal B prepared at wall temperature 1373 K and pressure 2.0 MPa; (a) low magnification, coal A, (b) high magnification, coal A, (c) low magnification, coal B, (d) high magnification, coal B.

Figure 8.6 shows SEM images of the morphology of PEFR chars from coal A and coal B prepared at the wall temperature of 1373 K and pressure of 2.0 *MPa*. Pictures in Figure (a) for coal A, and (c) for coal B, present char morphologies at a low

magnification under SEM. The particles have a closed and smooth surface and rounded contour, and the shape is very irregular with many projections and noses. This is very different from the DTF char. The irregular shape and the formation of the projections and noses may be attributed to the following reasons: (1) The extremely high heating rate and larger particle size cause significant temperature differences not only between the surface and the interior of the particle, but also among the different locations at the surface due to the irregular shape of the feed coal particles; (2) Particles of larger sizes have higher chances of containing different maceral constituents in one particle. Therefore, the decomposition and thermo-plastic properties of different parts in the same particle may be different; (3) coagulations of liquidized coal particles at high coal feed rate can lead to the irregular and large char particles observed under SEM. This may occur at high coal feed rate.

The smooth and closed surface is more clearly demonstrated at high magnification under SEM, as shown in Figure (b) for coal A and (d) for coal B. The surface texture has some obvious similarity to that of the PDTF chars reported in the literature (Wu,  $2000^{\text{b}}$ ), shown in **Figure 8.4.** This is more apparent for coal B, probably because coal B has the similar rank to the coal used in Wu's work. The images suggest that typical PEFR chars have a honeycomb-like cellular configuration as the internal structure. It may be noticed that the outer shell is very thin. Some open holes at the particle surface in Figure (b) are believed due to the sample collection and transport. Crucial information shown in these pictures is that the bubble number in char particles from high pressure is large. This observation supports the model predicted trends of pressure effect on the char structure that both the porosity and bubble number increases with increasing the ambient pressure, as shown in **Table 7.3**. Bubble sizes are not

significantly different in the whole particle, implies that the present model assumption of uniform bubble size is applicable. The highly smooth surface is considered as the strong evidence of low viscosity at the elevated pressure. The char morphology also suggests that particle contraction is small during the plastic stage. This is also consistent with the present model prediction, as presented in section **7.3.2**.



(b) Coal B

**Figure 8.7.** Cross-section SEM images of PEFR char samples prepared at the wall temperature of 1373 *K* and the pressure of 2.0 *MPa*; (*a*) coal A, (*b*) coal B.

Cross-section images observed under SEM, in **Figure 8.7**, show that chars prepared at elevated pressure are highly porous, for both coals. Consistent with observations from previous work (Wu et al., 2000<sup>a</sup>; Wu, 2000<sup>b</sup>) and model prediction from this study, the

foam structure is the typical structure of high-pressure chars, as can be seen from the images. This is also coincident with the above observations on the surface morphology. The wall thickness is very small for most of the particles. Some cenospheric chars can be seen, but the population is much smaller than DTF chars of the same coal. Most importantly, solid char particles (with dense structures) are very rare, which means the population of group III chars is very small.



**Figure 8.8.** Macro-porosity and char type distribution of coal A and B measured through image analysis, sample prepared at the wall temperature of 1373 K and the pressure of 2.0 *MPa*; (*a*) porosity of coal A, (*b*) char type distribution of coal A, (*c*) porosity of coal B, (*d*) char type distribution of coal B.

Figure 8.8 quantitatively shows the high porosity of the most PEFR char particles, in (a) and (c), and group I chars dominates the PEFR char samples for both coals, in (b)

and *(d)*. It is clear that, compared with DTF chars of the same coal, PEFR char samples have significantly higher population of group I chars, much lower population of group III chars, for both coals. Also, the average porosity of group II chars is above 70%. The results imply that coal develops higher fluidity when high ambient pressure is applied. More particles that do not develop fluidity at the atmospheric pressure will undergo softening and swelling at elevated pressures. The results provide solid support to the model predicted results of porosity and char structure with changing the pressure.



(a) Morphology

(b) Cross-section

**Figure 8.9.** Morphology and cross-section image of chars of coal A prepared in ordinary drop tube furnace (1573 K, N<sub>2</sub> gas, 0.1 MPa, feed coal particle size, +90-105  $\mu$ m); (a) char morphology, (b) cross-sections.

As a comparison, **Figure 8.9** and **Figure 8.10** show the morphology and cross-section images of char samples from coal A and B prepared in ordinary DTF at 1373 *K* and under the atmospheric pressure, with the raw coal particle size of +90-105  $\mu m$ . Apparent distinctions in both morphology and cross-section structure exist between PEFR chars and DTF chars for both coals. Blow holes and cracks observed in the DTF char morphology do not appear in PEFR chars. Wall thickness is obviously larger for DTF chars, as can be seen in cross-section images. Tenui-network structure, which frequently

appears in DTF char of coal A, is not typical configuration for PEFR chars from the same coal.





(b) Cross-section

**Figure 8.10.** Morphology and cross-section image of chars of coal B prepared in ordinary drop tube furnace (1573 K, N<sub>2</sub> gas, 0.1 *MPa*, feed coal particle size, +90-105 $\mu$ m); (a) char morphology, (b) cross-sections.

Quantitative comparisons in **Table 8.4** demonstrate that group I char population of coal A at high pressure is ~25% higher than DTF chars, and around 30% higher for coal B, while group III char population at elevated pressure is very small, 9.1% for coal A and 8% for coal B, respectively. This further suggests a large number of particles that generate dense chars (Group III chars) under DTF conditions will develop significant fluidity and swelling, and become porous chars at elevated pressures. In the meantime, some particles evolving group II chars in the DTF may develop even higher porosity and contribute to the population of the group I chars. The results agree qualitatively with the experimental data of previous work (Wu, 2000<sup>b</sup>; Benfell, 2001), as shown in **Figure 8.1** and **Figure 8.2**. The average macro-porosity measured through image analysis for PEFR char sample of coal A is 24% higher than that of the DTF char

sample of the same coal, and around 18% higher for coal B. Therefore, high swelling ratio is also expected for PEFR chars.

**Table 8.4.** Comparisons of average char porosity and char type distribution of PEFR char and DTF char from coal A and B measured through image analysis (PEFR char sample prepared at the wall temperature of 1373 K and pressure of 2.0 *MPa*).

Coal	1	4	В		
Char	PEFR char	PEFR char DTF char <sup>a</sup> P		DTF char <sup>b</sup>	
Group I char (%)	50.0	24.6	73.1	41.97	
Group II char (%)	40.9	42.0	19.2	24.01	
Group III char (%)	9.1	33.4	7.7	34.02	
Average porosity (%)	77.41	52.83	80.46	61.9	

*NB:* **a**--data of size fraction +75-90  $\mu$ m; **b**--data of density fraction samples.



**Figure 8.11.** Morphology of PEFR chars of coal B prepared at wall temperature of 1673 *K*, pressure of 2.0 *MPa*. (Left—low magnification; right—high magnification)

**Figure 8.11** presents the morphology of PEFR chars prepared at a higher wall temperature, 1673 *K*, at the same pressure, 2.0 *MPa*. From **Table 8.3**, it can be seen that

the conversion rate of this sample is around 11% higher than that of the chars collected at 1373 *K*. The pictures show that the thin carbon films have been partly gasified at high temperature. However, the honeycomb-like cellular structures are more clearly revealed. Some researchers suggest that the gasification reactivity of the ribs is lower than the thin film (Matsuoka et al., 2002).

## 8.4 Discussion—char formation at pressure

From the above results, it is apparent that the pressure plays a significant part in char formation. It has been concluded in the literature, as reviewed in chapter 2, that high pressure increases the resistance to the volatile escape, and promote secondary reactions. Model predicted results show that liquid fraction increases at high pressures, as discussed in chapter 7. The liquid may further promote the destructions of coal macromolecular structure during devolatilization. With the increase of the liquid fraction, the apparent fluidity of the whole material increases. On one hand, at high pressure, the increases in fluidity and higher yields of light gases due to secondary reactions increase the bubble growth rate, therefore enhance the particle swelling. On the other hand, the high external pressure reduces the bubble growth rate, hence reduces particle swelling. This results in an optimum pressure range for a maximum char swelling, and the trend has quantitatively predicted by the present char structure model, as shown in Figure 8.12 (a) for coal B. Correspondingly, the change in the char porosity follows the same trend as the swelling ratio with increasing the ambient pressure, as shown in Table 7.3. Figure 8.12 (a) also compares the model predicted swelling ratios with experimental data at two pressures, 0.1 MPa and 2.0 MPa. The predicted swelling ratios of chars are higher than the experimental results. At 0.1 MPa, the predicted swelling ratio is 1.39, while experimental result is 1.27. At 2.0 MPa, the model predicts 2.51 of the swelling ratio, while the experimental result is 2.01. However, the trend agrees reasonably well. In the meantime, high pressure reduces bubble rupture rate, therefore the number of bubbles in the resulting char residues at high pressure increases significantly, as predicted in **Figure 8.12** (*b*). This explains why high pressure favours the formation of foam char structures and the decrease of the population of cenospheric chars, as observed in the present experiments.



**Figure 8.12.** Swelling ratio and final bubble number of char as a function of ambient pressure at the heating rate of  $1.6 \times 10^4$  K/s and peak temperature of 1573 K; (a) swelling ratio of char (prediction and experimental data), (b) final/initial bubble number (predicted).

Characteristics of PEFR chars collected in this study and PDTF chars in the literature (Wu, 2000<sup>b</sup>) suggest that coalescence of bubbles may not play significant roles in char structure formation due to the high viscosity of the coal melt during pf coal pyrolysis in gas flow reactors where heating rate is very high ( $\sim 10^4 K/s$ ). Otherwise the number of bubbles in the high-pressure chars would not be significantly different from that of ordinary DTF chars. This supports the model assumptions made in the present work.

Even though, it is worth considering the bubble coalescence rate during plastic stage in future work of modelling the char formation at slow heating rates.



(a) PEFR char

(b) DTF char

**Figure 8.13.** Comparison of surface textures of the PEFR char with the DTF char prepared in this study (coal B); (a) PEFR char particle, (b) DTF char particle. (SEM images are taken at 15 kV)

**Figure 8.13** compares the typical surface texture of PEFR char with DTF chars with porous structure of coal B. Comparing the two pictures with **Figure 8.4** from Wu's work, it may be noted that the bubble size of the PEFR chars, in **Figure 8.13** (*a*), is smaller than that of the DTF chars, in **Figure 8.13** (*b*), while that of PDTF chars (in **Figure 8.4**) is closer to PEFR chars. Only the DTF char has a large blow-hole (which is believed the strong evidence of the volatile release) at the surface, while the PEFR char and PDTF char have a closed and smooth surface. Regular cellular structure and ribs are seen for PEFR and PDTF chars instead of irregular flow patterns with the DTF chars. Comparisons of the char morphology further suggest that elevated pressures promote coal fluidity and suppress the volatiles release.

## 8.5 Conclusions of this chapter

- PEFR chars prepared at the elevated pressure of 2.0 *MPa* have the characteristics similar to that of PDTF chars prepared at the pressure of 0.5~1.5 reported in the literature, but very different from that of DTF chars of the same coal prepared under the atmospheric pressure from the present study. It is apparent that the ambient pressure plays a significant role in char formation;
- Compared to DTF chars, PEFR chars have a closed surface with smooth surface textures and contour and smaller bubble sizes. The average porosity of PEFR chars from coal A is 25% higher, and is 20% higher for Coal B than the DTF chars. The regular honeycomb-like cellular internal structure is clearly observed under SEM;
- Qualitatively, from the char morphology, it has been observed that PEFR chars have a large number of bubbles compared to DTF chars and PDTF chars. Model predicted results consistently suggest that the bubble number increases significantly as the ambient pressure increases;
- Consistent with the literature report, experimental results of PEFR chars and the present model prediction demonstrate that the high pressure favours the formation of foam char structures with high porosity (>70%), and leads to the decrease in the populations of both cenospheric chars and dense chars (Group III char). An optimum pressure range exists for the maximum swelling ratio of chars.

# CHAPTER 9. CONCLUSIONS AND RECOMMENDATIONS

## 9.1 Conclusions

- A systematic investigation on the char structure evolution process of bituminous coal has been carried out using both experimental and modelling measures. Experiments conducted on SPR (single particle reactor) and DTF (drop tube furnace) provide mechanistic information of swelling, bubble behaviour and morphology changes of coal particles during pyrolysis and experimental data for char structure model validation, while the modelling study provides detailed insight of the char formation mechanism;
- Transient observations using SPR reveal that pyrolysis behaviour of particles in pf size from the same coal can be significantly different under the same heating condition. General trends show that swelling decreases drastically with increasing the coal fraction density. Apparent bubbling phenomena have been observed during the heating of particles from light density fraction samples, which do not occur for heavy density particles. The results demonstrate that bubble behaviour is responsible for the swelling of coal particles. The morphology of coal particles changes dramatically during heating owing to the development of thermo-plasticity and particle swelling. The maximum swelling ratio of particles during the intermediate plastic stage is much higher than the final swelling ratio, which implies that the swelling ratio measured using DTF chars cannot represent the transient internal structure changes during the intermediate stage of devolatilization process. Statistical results show that the

population of porous chars decreases with increasing the coal fraction density for both coals. Heating rates have apparent influence on coal swelling. At the low heating rate of 10 K/s, much less swelling and bubbling are observed. At high heating rates, more particles develop fluidity and swelling. Observations in the present study are consistent with the literature data;

Experiments on the DTF using density-separated samples consistently • demonstrate the heterogeneous behaviour of coal particles in pf size from the same coal under the same heating condition. The weight losses and swelling ratio of DTF chars decrease with increasing the coal fraction density. Correspondingly, the char porosity of the density fractions decreases sharply as the coal fraction density increases. Internal char structures change drastically with increasing the coal density. Group I chars are mainly generated from light density-fractions, i.e. F1.25 and F1.30. On the contrary, heavy density-fraction samples, i.e. F1.50 and S1.50, yield group III chars with a solid char structure. The char sample from the medium density fraction contains a mixture of different types of chars with a moderate porosity and wall thickness. In combination with SPR observations, it is apparent that char particles from light density fractions have experienced intensive softening and swelling due to the development of fluidity, bubbling behaviour and intensive volatile generation. With these particles, the volatile release during pyrolysis is largely determined by the behaviour of bubbles. However, particles from the heavy density fraction samples are most likely to have maintained their physical structures during the course of devolatilization due to the absence of the fluidity. Therefore, these particles do not exhibit softening and swelling, and their volatiles are released through the pore openings and cracks;

- The heterogeneity of coal devolatilization behaviour and char structure is attributed to the variations of the parent coal properties. In addition to the dominant role of coal macerals, the influence of ash level of coal on char formation is confidently identified. This study extends current understanding of heterogeneous nature of coal for char formation;
- Results of size fraction samples reveal that smaller size fractions tend to have larger swellings. Char samples prepared at lower pyrolysis temperature in the DTF have a smaller swelling ratio. These observations are consistent with literature data and model prediction from this study;
- A mathematical model for coal swelling and char structure formation of single coal particles during devolatilization has been developed based on a simplified multi-bubble mechanism. The char formation during the plastic stage has been considered as two successive steps: a multi-bubble stage followed by a single bubble stage. During the multi-bubble stage, the rupture of bubbles is a rate-controlled process, while the volatile release is determined by the bubble model applies. During single bubble stage, the bubble rupture is controlled by the wall stress, and the volatiles are released through both bubble rupture and direct volatile diffusion to the particle surface through the porous liquid shell. The sensitivity study of the model is carried out with the model assumed parameters and correlations, coal properties and heating conditions. Based on the sensitivity study, parameters for the present modelling work have been determined. The

present model provides simulation of transient coal swelling and char structure evolution of plastic coals during devolatilization under different heating conditions from the standard raw coal properties, and provides useful mechanistic information of coal devolatilization behaviour and a detailed insight of the char formation under different heating conditions;

- Model prediction has been compared with the experimental data of DTF chars of density fraction samples prepared in the present study. The results show that the present model predicts the experimental trends of the swelling and char structure characteristics. From standard parent coal properties of density-fraction samples, the present model predicts the heterogeneity of char structures from the same coal. For low density-fraction, F1.25 and F1.30, the model has predicted high swelling and porosity and the formation of cenospheric char structure (Group I char). The decreases in swelling and porosity and the change in the char structure type towards dense structures for heavy density fraction samples (F1.50 and S1.50) have been predicted. The char structure distribution of the full coal has also been determined, and the predicted results agree with the experimental measurements;
- The present model predictions at different heating rates and pressures demonstrate that heating conditions play an important role in coal devolatilization behaviour, including volatile yields, thermo-plastic properties, swelling and char structure characteristics. The predicted trends are consistent with previous work reported in the literature. With increasing the heating rate, the model predicts the increases in the swelling and porosity and temperature interval of the plastic stage. The results suggest that cenospheric chars tend to

form at relatively slow heating rates, while foam structure tends to evolve at high heating rates. As the ambient pressure increases, the porosity and final number of bubbles in the char increase remarkably. However, the final swelling ratio of char increases at the low-pressure range up to 1.5 *MPa*, and decreases when pressure increases further. The predicted pressure range for the maximum swelling is consistent with literature data;

• PEFR chars prepared at the high pressure of 2.0 *MPa* have the characters (including the morphology and internal structures) similar to that of PDTF chars (prepared at elevated pressures of 0.5~1.5 MPa) reported in the literature, but very different from that of DTF chars of the same coal prepared under the atmospheric pressure from the present study. The results of PEFR chars and the present model prediction suggest that high pressures favour the formation of foam char structures with high porosity, and lead to the decrease in the populations of both cenospheric chars and dense chars (group III char).

## 9.2 Recommendations for future work

Recommendations for future work as an extension of the present study are made for experiments and the char structure model respectively.

## **Experiments:**

• Density separation is an effective approach to investigate the char formation. In the present study, demineralization has not been performed, and the density bins are too large to allow a fine resolution of the model prediction. Therefore, in future experiments, smaller density bins may be used. In the meantime,
demineralization should also be performed before density separation. The characteristics of chars with and without demineralization should be compared. As such, effects of both minerals and macerals on char formation may be clarified. And the char structure data will be able to provide better validation to the present model prediction;

- o Both experimental observations and model prediction have shown some interesting results for char formation under elevated pressures. Some of the model predicted phenomena, such as swelling ratio, particle contraction, softening temperatures and bubble number, etc, need quantitative experimental data to validate. The pressurized single particle reactor (already built through this project), which allows direct observations of individual coal particles at high pressures, will provide the first hand information for char formation under pressurized conditions. Equally important, further analysis of char samples from the PEFR reactor is crucial to investigate the effect of pressures on the char formation and to provide validation to the model prediction;
- Extension of single particle experiments to high heating rates equivalent to practical pf coal conversion process is essential to the investigation of the heating rate effect on char formation.

#### Char structure model:

• The present model is developed based on a highly simplified physical process. Although the model has predicted the experimental trends on coal swelling and char structure under the present conditions and provided very useful mechanistic information for char formation, some critical issues are still remained to be improved in future work, such as further consideration of nucleation and coalescence rate of bubbles during the plastic stage, validation of thermo-plastic properties, initial bubble number density and critical value for viscosity and wall stress, etc;

- To allow finer resolution of the present model calculations for char structure distributions, the alternative engineering approach instead of using smaller density bins during density separation is the establishment of correlation between coal reflectogram and parent coal properties or chemical structure parameters. From engineering points of view, this approach will be an enhancement to the present char structure model;
- Inclusion of the fragmentation mechanism of char particles during plastic stage is crucial to allow application of the present model to a wider range of heating conditions, in particular heating rates.

### **APPENDICES**

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### Appendix A. Reflectograms of density-separated raw coal samples of coal A and B (in oil)





*NB*: The petrographic analysis reported a slight contamination of the light density fraction of coal A.

Coal	System	Wall	Oxy gen	Coal Feed	Total Gas	Residence
	Pressure	Temperature	%	Rate (kg/hr)	Flow	Time (s)
	(atm)	(°C)				
В	20	1100	5	2.5	23.9	4.7
	20	1400	5	2.5	49.7	2.3
Α	20	1100	2.5	2.11	50.0	2.83

# Appendix B. Experimental conditions of the PEFR for chars prepared in the present study

## Appendix C. Determination of the weight loss and the *Q*-factor during coal devolatilization in DTF (Badzioch et al., 1970) using ash tracer

1. Volatile matter of char. The volatile matter, R, of the char expressed as a percentage of the weight of the weight of the original dry-ash-free coal is calculated from:

$$R = (\frac{100A_0}{100 - A_0})(\frac{VM'}{A'})$$
 A-1

where  $A_0$  and A' are the proximate ash content, on dry basis, of the original coal and the char respectively and VM' is the proximate volatile matter of the char on dry basis.

2. Change in Volatile Matter. The change in volatile matter  $\Delta V$ , as a percentage of the original dry, ash-free coal, is calculated from:

$$\Delta V = VM_0 - R \tag{A-2}$$

where  $VM_0$  is the proximate volatile matter of the original dry-ash-free coal.

3. Weight loss. Ideally the weight loss,  $\Delta W$ , should be determined directly by weighing the feed coal and the char produced. However this was not possible because the decomposing particles become sticky and tend to adhere to the walls of the collector, so that they cannot be recovered quantitatively. The weight loss has been calculated indirectly using the ash associated with coal as a tracer. Thus the yield of char expressed as a percentage of original dry-ash-free coal is given by:

$$Y = (\frac{100 A_0}{100 - A_0})(\frac{100 - A'}{A'})$$
 A-3

where  $A_0$  and A are the proximate ash content, on dry basis, of the original coal and the char respectively. Hence the weight loss,  $\Delta W$ , expressed as a percentage of original dry-ash-free coal is:

$$\Delta W = 100 - Y$$
 A-4

The indirect determination of the weight loss is of poor reproducibility. When the ash content is low a wide scatter of results arises from even small analytical errors in the determination of ash. This is particularly serious when the amount of decomposition is small so that the concomitant change in the ash content may be too small to be detected. The scatter resulting from analytical errors becomes less important when the ash content is high. There another source of scatter which arrises because the ash particles are

predominantly discrete from coal and tent to segregate on handling—e.g., in the vibrating feeder. Thus, a series of samples collected after passing through the furnace inevitably have a more widely scattered ash content than repeat samples of the original coal. The tendency to ash segregation occasionally leads to freak results.

4. **Q-factor**. *Q* is defined the ratio of weight loss to change in proximate volatile matter, i.e.:

$$Q = \Delta W / (VM_0 - R)$$
 A-5

There is a tendency that Q reaches the highest for the intermediate rank coals, which are in the bituminous range where the yield of tar also exhibits a maximum. This is because the excess volatile yields are mostly the consequence of reduced tar cracking and less carbon deposition, which are achieved by the reduction of contact between reactive tars and hot particle surface (Howard, 1981). An important fact should be noted that Hodek et al (Hodek et al., 1991) found the tar yield decreased in the sequence exinite vitrinite—inertinite. It may also be noted that a R-factor defined by Kimber and Gray (Kimber et al., 1967) as the ratio of  $\Delta W/VM_0$ .

## Appendix D. The correlation of 13<sup>C</sup> NMR data to coal properties by Genetti et al (Fletcher et al., 1999; Genetti, 1999)

Direct input data for the CPD model are: the average molecular weight per side chain  $(M_{\delta})$ , the average molecular weight per aromatic cluster  $(M_{cl})$ , the ratio to bridges to total attachments  $(p_0)$  and the total attachments per cluster  $(\sigma+1)$ . With coal that have not been subjected to NMR measurements, an empirical correlation has been developed by Genetti et al (Fletcher et al., 1999; Genetti, 1999) based on  $13^{C}$  NMR data from 30 coals. The correlation provides estimation of the above four structure parameters from standard ultimate and approximate analysis data of the parent coal.

The equation to calculate  $M_{\delta}$ ,  $M_{cb}$ ,  $p_0$  and  $\sigma + 1$  is given by:

$$Y = c1 + c2 \times C + c3 \times C^{2} + c4 \times H + c5 \times H^{2} + c6 \times O + c7 \times O^{2} + c8 \times VM + c9 \times VM^{2}$$

Where, *Y* is  $M_{\delta}$ ,  $M_{cb}$ ,  $p_0$ , or  $\sigma + 1$ , respectively;

*C* = Weight Percent Carbon (*daf*)

H = Weight Percent Hydrogen (*daf*)

N = Weight Percent Nitrogen (*daf*)

O = Weight Percent Oxygen (*daf*)

VM = ASTM Volatile Matter (*daf*)

Coefficients are shown in the following table:

	Μ <sub>δ</sub>	мw	P <sub>0</sub>	σ+1
c1	421.957	1301.41	0.489809	-52.1054
c2	-8.64692	16.3879	-0.00982	1.63872
c3	0.046389	-0.18749	0.000133	-0.01075
c4	-8.47272	-454.773	0.155483	-1.23688
c5	1.18173	51.7109	-0.02439	0.093194
c6	1.15366	-10.072	0.007052	-0.16567
c7	-0.0434	0.076083	0.000219	0.004096
c8	0.556772	1.36022	-0.01105	0.009261
c9	-0.00655	-0.03136	0.000101	-8.3E-05

CPD model calculations also require values for  $c_0$ , the fraction of stable bridges. The correlation for  $c_0$  that seems to work best is as follows:

For %C > 85.9% (daf), c0 = 0.1183×%C - 10.16, with a maximum value of 0.36. For %O > 12.5% (daf), c0 = 0.014×%O - 0.175, with a maximum value of 0.15.

Otherwise,  $c_0 = 0.0$ 

## Appendix E. A comparison of the rate of bubble coalescence to that of bubble ruptures with uniform bubble size

Bubble escape rate is expressed as (Oh, 1985):

$$E_{b} = \frac{3(R_{p} - r_{b})^{2}}{R_{p0}^{3}} dr_{b} / dt$$
 E-1

where  $r_b$  is bubble radius,  $R_p$  is the particle radius,  $dr_b/dt$  is bubble growth rate. Rate of bubble coalescence is(Oh, 1985):

$$P_{i,i} = \rho_0 4\pi (r_{b,i} + r_{b,j})^2 (dr_{b,i}/dt + dr_{b,j}/dt)$$
 E-2

where  $\rho_0$  is coal density. When bubble size is uniform, the coalescence rate is expressed as:

$$P_{i,i} = 32\pi\rho_0 r_b^{2} dr_b / dt$$
 E-3

Compare E-3 to E-1, it is then obtained:

$$\frac{P_{ij}}{E_b} = \frac{32\pi\rho_0 r_b^2 R_{p0}^3}{3(R_p - r_b)^2}$$
E-4

Equation E-4 gives an estimate to the comparison of bubble coalescence rate to the bubble rupture rate, as show in Table E.1.

Table E.1. Comparison of bubble coalescence rate to bubble rupture rate

$\rho_0(g/cm^3)$	r <sub>b</sub> (µm)	$R_p(\mu m)$	$P_{i,j}/E_b$
1.4	0.2	70	1.32E-10
1.4	2	70	1.39E-08
1.4	20	70	2.57E-06

It can be seen from the table that, when particle size is 70  $\mu$ m with uniform bubble size, the coalescence rate is 6, 8 and 10 magnitudes lower than that of bubble rupture rate when bubble size is 20, 2 and 0.2  $\mu$ m, respectively. Therefore, in the simplified case in the present study, the bubble coalescence rate is negligible.

## Appendix F. Mathematical equations of the single bubble model (Solomon et al., 1993)

The velocity of the outer wall of the coal particle is given by:

$$\frac{dr_p}{dt} = \frac{r_b^3 r_p \Delta P_t}{4\mu (r_p^3 - r_b^3)} + \frac{r_p}{3(r_p^3 - r_b^3)} \frac{d(r^3)}{dt}$$
**F-1**

for which the viscosity is predicted using the viscosity model proposed by Solomon et al (Solomon et al., 1992<sup>a</sup>). Of the total evolved volatile gas, the captured gas can be calculated by:

$$\frac{dn_c}{dt} = n_g r_b^2 / (r_b^2 + r_p^2)$$
 F-2

The amount of gas diffuses out in the same period is:

$$\frac{dn_d}{dt} = \frac{4\pi D_l C_b}{(1/r_b - 1/r_p)}$$
 F-3

where  $D_l$  is the volatile diffusivity of the volatile in the liquid phase. An effective diffusivity,  $D_e$ , is used by Sheng et al (Sheng et al., 2000). The total gas inside the cenosphere is the sum of E-2 and E-2:

$$\frac{dn_g}{dt} = \frac{dn_c}{dt} - \frac{dn_d}{dt}$$
 F-4

The excess of internal over the ambient pressure is then:

$$\Delta P_g = \frac{3n_g RT}{4\pi r_b^3}$$
 F-5

The amount of trapped ambient gas is given be:

$$\frac{dn_{a}}{dt} = \frac{4\pi D_{a}}{(1/r_{b} - 1/r_{p})} \left[ \frac{P_{0}}{RT} - \frac{3n_{a}}{4\pi r_{b}^{3}} \right]$$
 F- 6

The total pressure differential is calculated by:

$$\Delta P = \frac{3(n_g + n_a)RT}{4\pi r_b^3} - \sigma \left(\frac{1}{r_b} + \frac{1}{r_p}\right) - P_0$$
 F-7

The criterion for bubble rupture during the pressure difference is given by:

$$\frac{1.5r_b^3(P_b - P)}{r_p^3 - r_b^3} - P > S_w$$
 F-8

Parameters of the model, e.g.  $D_{i}$ ,  $D_{a'}$ ,  $\sigma$ ,  $S_c$ , are also listed in the literature (Solomon et al., 1993).

Similar mathematical equations for single bubble model have been provided by Sheng et al (Sheng et al., 2000) more recently to simulate coal particle swelling and morphology change during devolatilization process.

Appendix G.	Coefficients	and some	input	data for	r CPD	model	used in	the	present
	study								

Coefficients or variables	Values
ab	2.602e15
eb	55400
ebsig	1800
ac=rho	0.9
ec	0
ag	3.e15
eg	69000
egsig	8100
acr (pre-exponential factor for crosslinking rate)	3.e15
ecr (Activation energy for crosslinking rate)	65000
dt (s),print increment,max dt (s)	1.e-4,1,1.e-3
timax (maximum residence time (s) for calculations)	60.e-1
nmax (maximum number of mers for tar molecular wt)	20



## Appendix H. Devolatilization behaviour of coal B as a function of heating rate and pressure predicted using FG-DVC model

**Figure H.1.** Effect of heating rates on devolatilization behaviour of coal B predicted using FG-DVC model, at the pressure of 0.1 *MPa* and the temperature of 1573 *K*.



**Figure H.2.** Effect of pressure on devolatilization behaviour of coal B predicted using FG-DVC model, at the heating rate of  $1.6 \times 10^4$  K/s and temperature of 1573 K.

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