PLASTICITY AND AGGLOMERATION IN COAL PYROLYSIS

by

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B.S. in Chemical Engineering
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DOCTOR OF SCIENCE

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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Submitted to the Department of Chemical Engineering at the Massachusetts Institute of Technology in February 1986, in partial fulfillment of the requirements for the degree of Doctor of Science.

ABSTRACT

Two new techniques were developed to study the plastic behavior of softening coals at severe conditions, i.e. high heating rates and high temperatures pertinent to modern coal conversion processes but previously unattainable with conventional instruments. A Pittsburgh No. 8 Seam bituminous coal was used mainly in this study.

A fast response plastometer was developed to measure the apparent viscosity of a rapidly pyrolyzing coal. The plastometer determines the torque required for constant speed rotation of a thin disk embedded in a thin layer of packed coal particles heated electrically between two parallel metal plates. Heating rates, final temperatures and sample residence times at final temperatures can be separately selected and controlled over the ranges $40 - 1000$ K/s, $600 - 1250$ K, and $0 - 40$s respectively. The instrument can be operated in hydrogen or inert gas atmospheres from vacuum to $100$ atm.

An electrical screen reactor with rapid sample quenching capability was developed to determine quantitatively the intraparticle liquid content (pyridine extract), and the growth of pyridine insolubles in the pyrolyzing coal as a function of pyrolysis temperature-time history in the same range as in the plastometer study.

The molecular weight distribution of the intraparticle liquid was also determined by Gel Permeation Chromatography as a function of pyrolysis temperature-time history.

A combination of the above three techniques allows the kinetics and mechanism of plasticity to be probed. Coal plasticity can be directly described by its viscosity change. As a Pittsburgh Seam bituminous coal is heated, the coal softens to form a solid/liquid suspension the viscosity of which decreases from more than one million poise to minimum values of order a few thousand poise. Resolidification of the intermediate liquid phase is indicated by a rapid rise in viscosity.

Initial softening of the coal is by physical melting of an estimated $25\%$ by weight of the coal. Up to $40\%$ by weight of the coal is
further converted to liquids by pyrolytic bond breaking. These liquids can condense or polymerize to give higher molecular weight liquids and solids, and crack to give gas and coke, or escape from the coal particle to give tar. The result is that the liquid weight averaged molecular weight can increase from 570 to above 800, and then decrease to around 600.

Pyrolysis of a heat-treated coal tar (similar to the intra-particle liquid in a pyrolyzing bituminous coal) exhibited a similar change in molecular weight with pyrolysis time, and a slower rate of solids growth. In the pyrolysis of a slightly caking wood, or a non-softening lignite, little or no liquids were formed. Pre-extraction of the raw bituminous coal with pyridine reduced both the plastic period and the intra-particle liquid content during pyrolysis. In vacuum or 35 atm inert gas atmosphere, the duration of plasticity is less than that under 1 atm inert gas pressure.

Experimental viscosity and intraparticle liquid formation/depletion data were described by a global model that accounts for melting, generation and depletion of the liquid, and volatiles formation. The kinetic parameters find quantitative application in modeling coal particle agglomeration and swelling behavior under rapid heating conditions. Predictions of models here developed were in qualitative accord with literature data on swelling and provide a possible explanation for coal agglomeration observed within a pulverized coal flame.

Thesis supervisors:
Professor Jack B. Howard, Department of Chemical Engineering
Dr. William A. Peters, Energy Laboratory

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CHAPTER 1. SUMMARY

1.1 BACKGROUND AND OBJECTIVES

Bituminous coals upon heating melts and decomposes to form an unstable liquid that can escape from the coal by evaporation to give tar and light oil or crack to form light gases, leaving behind a solid residue. Polymerization or cross-linking of the liquid molecules to form solids also competes with these other liquid removal processes. All the liquid is eventually depleted, leaving a porous coke residue. The kinetics of these processes are strongly temperature dependent. Figure 1 is a schematic of changes in physical structure and liquid volume fractions in coal.

The transient occurrence of the liquids, commonly referred to as the plastic phase, can strongly influence the thermal conversion and refinement of bituminous coals. Irrespective of reactive atmospheres, presence of solvents or feed size, plasticity kinetics is important for the understanding and subsequent modelling of different bituminous coal pyrolysis, gasification, combustion, carbonization and liquefaction processes. Some existing technical problems such as the serious caking difficulties encountered in fluid bed gasifiers are direct consequence of plasticity. Agglomeration of plastic particles can cause solidification of the bed, and plugged pipelines. Bubbles of volatiles can swell the plastic coal mass, in turn affecting the devolatilization rate (Oh, 1985). The yields and qualities of pyrolysis products are affected since the transport of volatiles through the viscous coal melt affords oppor-
PHYSICAL CHANGE UPON HEATING

raw coal \rightarrow S \rightarrow L \rightarrow L \rightarrow S \rightarrow char

softening  swelling

\rightarrow devolatilization \rightarrow

\rightarrow combustion \rightarrow

volume fraction

\phi_{\text{liquid}} \downarrow \phi_{\text{void}} \uparrow

\phi_{\text{solid}} \downarrow

heating time

Figure 1. Physical changes of bituminous coal upon heating
tunities for intra-particle secondary reactions (Serio, 1984). Swelling also affects the physical structure of the char, hence the burnout time and process efficiency in subsequent combustion. The development and disappearance of plasticity is closely related to formation and destruction of liquids. Study of plasticity kinetics can therefore shed light on the mechanisms of coal liquefaction. Therefore, plasticity study contributes to both basic understanding in coal science, and to improved design in several important coal conversion technologies.

Plasticity kinetics under carbonization conditions has been rather extensively studied (Loison et al., 1963, Habermehl et al., 1981). These involve low heating rate experiments to a moderate final temperature, typically at 0.05 K/s to 800 K. Very limited studies have been made to date outside this range, although rather uncertain extrapolation of these data to other conditions have been made in some modelling studies (Attar, 1978; Melia and Bowman, 1983). In modern coal conversion and combustion processes, heating rates of order $10^4$ K/s, and final temperatures to 1700 K are possible.

This thesis involves a systematic approach to the study of coal plasticity at high heating rates and temperatures pertinent to modern coal conversion processes (Fong et al., 1985). Specific thesis objectives are:

(1) Design and develop new techniques and instruments for measuring apparent viscosities and intra-particle liquid inventories of a rapidly pyrolyzing coal.
(2) Study the effects of process variables such as temperature and pressure on plasticity kinetics and investigate some qualitative aspects of the nature of plasticity and softening coal pyrolysis reactions.

(3) Develop global models of plasticity kinetics and models of agglomeration and particle swelling, and possibly other plasticity related phenomena.

1.2 EXPERIMENTAL

Two new experimental methods were developed for the present study. To measure the rapidly changing apparent viscosities of pyrolyzing coals, a fast response plastometer for high sample heating rates and holding temperatures was developed. To determine quantitatively the liquids content within pyrolyzing coal, an electrical screen pyrolyzer with rapid sample heating and quenching capability was also developed.

(a) Apparent viscosity measurement

The plastometer determines the torque required for constant speed rotation of a thin disk embedded within a thin layer of coal heated electrically between two parallel metal plates. Its geometry is similar to a rotating disk viscometer. Heating rates, final temperatures and sample residence times at final temperatures can be separately selected and controlled over the ranges 40-1000 K/s, 600-1250 K, and 0-40 s respectively. The instrument can be operated in hydrogen or inert gas atmospheres from near vacuum to 100 atm. Figure 2 is a schematic of the
Figure 2. Schematic of coal plastometer

Figure 3. Plastometer Hot Stage

Figure 4. Electrical heating circuit
plastometer system. Figure 3 shows the hot stage of the plastometer. Design specifications and performance characteristics of the instrument have been published (Fong et al., 1985).

Heating is achieved by sequentially passing two large constant pulses of D.C. electrical current of preselected duration and magnitude through the metal plates. Figure 4 is a schematic of the dual current heating circuit. Rapid changes in the torque and temperature were each recorded by a two-channel electronic recorder. By calibrating the instrument with viscous liquid standards, viscosities in absolute units are obtained from the experimental torque curves.

The coal studied was a high volatile Pittsburgh No.8 Seam bituminous coal (Table 1). Two types of temperature-time histories were employed in the study. Holding temperature runs consist of a constant heating rate to a final temperature which was then maintained constant for an extended period of time. Constant heating rate runs refer to increasing the sample temperature at a constant rate for the duration of the experiment. Several experiments with the same temperature history were made to test the reproducibility of the data (Figure 5). For comparison purpose, plasticity curves for some other materials were also obtained. These include a viscous heat treated coal tar, a low melting point pitch, a non-softening lignite, and quartz (Figures 6a and 6b).

(b) Liquids formation and depletion measurement

The electrical screen reactor (Figure 7) was developed from
COAL STUDIED

Pittsburgh No. 8 Seam
High Volatile Bituminous Coal

Proximate analysis (wt.%, dry basis)

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<th>Ash</th>
<th>VM</th>
<th>FC</th>
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<td>1.4</td>
<td>11.5</td>
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Ultimate analysis (wt.%, dry basis)

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<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Ash</th>
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<td>68.8</td>
<td>4.9</td>
<td>8.2</td>
<td>1.3</td>
<td>5.4</td>
<td>11.5</td>
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$^+$ as-received basis

Table 1. Characteristics of Coal Studied
Figure 5. Reproducibility of Plasticity Curves

Figures 6a,b. Behavior of Different Materials in the Plastometer
Figure 7. Rapid quenching screen reactor

Vertical scale is two times thermocouple reading in mV
Horizontal scale is 0 - 10 seconds
Chromel-alumel thermocouple used
Corresponding to 660 - 670 K/s heating rate,
and holding temperatures 697 - 828 K. quenching at 4500 K/s

Figure 8. Reactor temperature histories
the basic version described by Anthony et al. (1974). The following improvements were made. Larger reactor and screen size. A much larger screen to sample weight ratio was utilized to ensure a single particle coal layer during the experiments. This minimize opportunities for extra-particle secondary reactions of volatiles, and improves heat transfer to the particles. A special sample loading device was developed for uniform charging of coal onto the screen. Addition of a liquid nitrogen quenching mechanism allowed rapid cooling and precise control of the pyrolysis residence times. The electrodes holding the hot screen were spring-loaded to keep the screen flat upon heating.

About 20 mg of 75-90 μm diameter particles were spread evenly in the central region of two layers of 10.5 x 5.3 cm, 400 mesh stainless steel screen mounted between two electrode blocks. Heating was achieved by sequentially passing two constant pulses of D.C. electrical current of preselected duration and magnitude through the electrodes. The volatile products readily escaped from the screen and were quenched and diluted by the ambient reactor gas at 0.85 atm. At the end of the preset heating interval, pressurized liquid nitrogen was sprayed onto the screen by automatically opening a cooling valve, resulting in a quenching rate of 1500 K/s. In some runs cooling rates exceeding 6000 K/s were achieved using a different valve. Figure 8 shows thermocouple records of typical temperature-time histories.

Coal samples were pyrolyzed for different times. The measurements include weight loss of the sample, corresponding to the volatiles (tar, light oil and gases) yield, and the weight of extractable material in the
quenched char, determined by 2 hour Soxhlet extraction using pyridine and reflecting the intra-particle inventory of liquids at the time of quenching. The yield data are reported on a dry basis.

(c) Other techniques and experiments

Information pertinent to the reactions occurring within the liquid was obtained using Gel Permeation Chromatography (GPC) to determine the molecular weight of the extract as a function of extent of pyrolysis. A Waters Associates ALC/GPC 201 system with 500 Å and 100 Å µ-styragel columns in series was employed.

Reactions in the coal during the plastic phase were further studied using a heat-treated coal tar as a model. (This phase of the work was conducted in collaboration with Dr. Jean Louis Saint Romain). The tar was a viscous liquid initially containing 3% by weight of pyridine insolubles. Pyrolysis and plasticity measurements on this "model" system allow intra-particle phenomena such as polymerization, liquids cracking and evaporation to be studied more directly since certain complications of the initial liquid generation steps in coal itself are eliminated. Some pyrolysis and extraction experiments with wood and lignite were also performed and compared to bituminous coal data. To study the initial softening behavior of coals, some raw coal samples were pre-extracted and afterwards subjected to the plasticity and pyrolysis measurements.

A set of prompt volatiles retention experiments were performed in order to obtain additional information on secondary reactions. Coal tar
samples sealed inside stainless steel foils were pyrolyzed in the screen reactor in the usual manner. Volatiles escape was suppressed, forcing these products to remain trapped inside the foil and undergo more extensive secondary reactions.

1.3 RESULTS

(a) Plastometer results

Figures 9 and 10 present typical raw data obtained under 1 atm and 35 atm of helium respectively, at a disk rotational speed of 0.67 rpm (corresponding to an average shear rate of 1.32 s\(^{-1}\) over the area of the disk). In Figure 9 the sample was heated at 461 K/s to a final temperature of 874 K and then held at this temperature for 6.0 s. As the temperature increased, the torque decreased to a low value due to liquid formation. After a period of low viscosity, the torque value increased due to progressive resolidification of the melt. However, continued rotation of the disk broke up the coke formed, and the torque vs time signal showed a net decrease. The stages of physical change of the coal are illustrated in Figure 10. For the given shear rate, the measured torque is related to the absolute viscosity by \(1.0 \times 10^{-2} \text{ Nm} = 2.6 \times 10^4 \text{ Pa s}\), obtained by calibrating the plastometer with viscosity standards at room temperature.

Figures 11 and 12 show typical viscosity vs time curves for this coal for different constant heating rates, and different holding temperatures, all under 1 atm of helium. Measured apparent viscosities were in
Figure 9. Raw Data from Plastometer, in 1 atm of Helium

Figure 10. Raw Data from Plastometer, in 35 atm of Helium Indicating Different Stages of Plastic Behavior
Figure 11. Viscosity Curves for Constant Heating Rate Runs
Heating Rates Indicated on Curves

Figure 12. Viscosity Curves for Holding Temperature Runs
Final Temperatures Indicated on Curves
the range of a few thousand to one million poises.

Some runs were made under 0.05 torr of ambient helium atmosphere, and some under 35 atm of hydrogen or helium (Figure 13). Comparison with 1 atm data shows that the plastic period is shorter for runs in vacuum or 35 atm pressure and holding temperatures less than 900 K. In view of the heating rate effect seen in Figure 11, the difference between the 1 atm curve and the other curves in Figure 13 would be seen to be even larger if the 1 atm experiments had also been conducted at 350 K/s. Above 900 K, there is little effect of pressure on the plastic period. While the softening rate is about the same as in the 1 atm case, the resolidification rates for both the vacuum and 35 atm runs are higher for holding temperatures less than 900 K. Above 900 K, the difference is small. At about 800 °C runs under 35 atm of helium or hydrogen and 1 atm of helium all give the same plastic period, suggesting at this high temperature any effects of inert gas pressure or coal hydrogen reactions are insignificant compared to other chemical and physical phenomena. However, from the present data base, an extension of the plastic period at 550°C due to hydrogen (vs helium) at high pressures can not be ruled out. The effect of pre-extraction of the raw coal sample on its plasticity is shown in Figure 14. Also shown in Figures 6a and 6b are the different behavior of other materials in the plastometer, note especially coal tar and pitch.

(b) Screen reactor data

Figures 15a and 15b show the yields of the volatiles, pyridine extracts, and the pyridine insoluble char as a function of the heating
Figure 13. Effects of Pressure on Plastic Period

Figure 14. Effects of Extraction on Plasticity
Both Runs at 410 K/s to 900 K
Figure 15a, b Volatiles, Pyridine Extracts and Insolubles Yield for Bituminous Coal vs Pyrolysis Time

Figure 16. Pyridine Extractables Generation and Depletion at Different Temperatures
time, for two sets of experiments with rapid quenching. The correspond-
ing temperature-time histories for each set are also shown. For example,
the vertical dotted lines connect two data points from a single experi-
ment, with the temperature-time history of this experiment indicated by
the bold line. The solid curves in Figures 15a and 15b are calculated
according to a kinetic model described in the modeling section.

An initial pyridine extractables yield of about 25 % was obtained
from the raw coal. As the coal was heated, the amount of extract increas-
ed to a maximum and then decreased at a rate strongly dependent on
temperature, as indicated in Figure 16. The time interval over which the
extract concentration was high decreased rapidly with holding tempera-
ture. The first order depletion rate constants for the extracts are
indicated. The maximum amount of fluid material (extract plus volatiles)
was as high as 80 % by weight of the raw coal. However, this quantity
decreased with increasing holding temperature, or with increasing time at
a given holding temperature, primarily due to conversion of the extract-
ables to coke.

Pyrolysis in the screen reactor of a non-softening lignite
and wood were also studied. Figure 17 shows the evolution of the volta-
tiles, pyridine extracts and the pyridine insoluble char as a function of
heating time. Figure 18 is a comparison of the amount of extracts of
bituminous coal, wood and lignite, all subjected to the same temperature
-time history. Subsequent reactions of the liquid after softening of the
bituminous coal can be inferred from the pyrolysis behavior of a heat
treated coal tar. Figure 19 shows the weight loss, pyridine extracts and
Figures 17a, b Volatiles, Pyridine Extractables and Insolubles Yield
For Lignite and Wood as Function of Pyrolysis Time
Samples heated at 736 K/s to 555°C and allowed to cool by convection.

Figure 18. Pyridine Extractables for Different Materials
Figure 19. Pyrolysis of a Heat Treated Tar

Figure 20. Comparison of Pyridine Extracts for Chars from Raw Coal and Pre-extracted Coal
pyridine insoluble char as a function of temperature-time history for the tar.

The effect of pre-extracting the raw coal sample on its extract yield is shown in Figure 20, at two different temperature-time histories for the pyridine pre-extracted sample (25% of extract removed from raw coal) and the raw coal. For the pre-extracted coals the extract yield is much less.

(c) GPC Data

The molecular weight distributions of the pyridine extracts were determined for bituminous coal, coal tar, lignite and wood at different extents of pyrolysis. Figure 21 shows GPC curves (concentration vs elution volume) for different pyrolysis times. Different raw materials showed different distributions and weights reflecting structural differences in their pyridine extractables. The data were also transformed and normalized with respect to the total yield of extract (Figures 22 and 23). Changes in the moments of the distribution, such as number and weight averaged molecular weights are shown in Figures 24 and 25. For both bituminous coal and coal tar pyrolysis, the extract average molecular weights increased to a maximum and then decreased, as a result of polymerization, evaporation and cracking reactions.

(d) Other experiments
Figure 21. GPC Curves for Pyridine Extracts of Different Materials at Different Pyrolysis Times
Figures 22a,b Normalized Molecular Weight Distributions of Pyridine Extracts at Different Pyrolysis for Bituminous Coal
Heat Treated Coal Tar 828 K

Figure 23 Normalized Molecular Weight Distributions of Pyridine Extracts at Different Pyrolysis Times for Coal Tar
Figure 25 Changes in Averaged Molecular Weights during Pyrolysis of a Coal Tar

Figure 24 Changes in Extract Average Molecular Weights with Time
As mentioned above, volatiles are trapped in foils in some pyrolysis experiments, thereby promoting secondary reactions (Serio, 1984), and concomitantly, their effects on plasticity and pyrolysis. A pyridine insolubles yield exceeding 40% was obtained vs the 29% obtained in screen experiments, for the pyrolysis of coal tar at around 1000 K. This increase was observed at temperatures above 950 K.

1.4. DISCUSSION OF EXPERIMENTAL RESULTS

The plasticity and pyridine extract curves are the first such experimental data obtained under well defined rapid heating conditions. As shown in Figure 26, or by a comparison of Figures 12 and 16, the respective times for initial generation and near final depletion of extractables within the coal correspond well with the time for initiation and termination of the coal's plastic phase. This suggests that (a) plasticity results from the formation of a significant amount of liquid material from coal, and (b) the pyridine extract of the rapidly quenched coal is a reasonably accurate measure of the amount of liquid product within the pyrolyzing coal at the time of quenching.

However, the fact that even without heating, 25 wt % of the raw coal can be extracted means that "extract" and "liquids" are not identical materials. It is likely that the initial extract corresponds to some loosely bonded, low melting point material. Upon heating to a sufficiently high temperature, this material undergoes physical melting. Our observation with the plastometer that initial softening temperature $T_s$ occurs around 570 K independent of heating rate (Figure 11) supports
IN 0.1 MPa HELIUM

Comparison of Viscosity and Extract Data

Start heating at ~450Ks⁻¹

Figure 26. Comparison of Viscosity and Extract Data
the above hypothesis. If this initial amount of material is pre-extracted, and afterwards the coal is subjected to pyrolysis, the total extract formed is less and is formed at a later time (Figure 20). The pre-extracted coal is expected to soften at a later time (higher temperature), and the duration of plasticity should be shorter, as is observed in Figure 14. Other workers found the Gieseler plasticity (low heating rate type experiments) during the early softening stage to be reversible as the temperature is raised or lowered (Waters, 1962), thus supporting the picture that some part of the liquid is formed by physical melting.

At higher temperatures, pyrolytic bond breaking generates significant quantities of liquid which cannot be reversibly converted back to resolidified coal. The maximum yields of extractables from the coal studied approached 80% daf. In similar experiments on a lignite, which does not soften, no extract was obtained. Similarly, only a small extract yield up to 7% was observed in the pyrolysis of wood (Figure 18). The wood or lignite pyrolyzed at a much faster rate than the bituminous coal, reflecting the structural difference of the fuels. The "foil" experiments for coal tar showed more liquids are retained than in open screen pyrolysis. Figure 26 shows that at 910 K, the period of low viscosity exceeded the corresponding period of high intra-particle pyridine extractables inventory, inferred from screen heater data. This probably reflects higher mass transfer resistance for volatiles escape away from the plastometer.

Clear evidence of the resolidification reactions of softened bituminous coal at longer pyrolysis times or higher temperatures is the
increase in pyridine insolubles. Studies of the pyrolysis behavior of the heat-treated coal tar using the screen reactor showed similar evidence of the competition between coke formation via polymerization, cracking, and volatiles escape via transport away from the reacting substrate (Figure 19). However, differences in plastic behavior are expected between tar, pitch and bituminous coal (Figure 6a) since the raw tar is already a viscous liquid containing 97 % pyridine solubles, and the pitch is a solid with a low softening point at 342 K. The fluid behavior of bituminous coal requires that a minimum inventory of liquids capable of initiating and sustaining plasticity throughout a reacting, three-phase medium be available within the coal matrix. Generation of this liquid requires that at least some melting or bond breaking precede the onset of plasticity. A further complication is that heterogeneous reactions of these plasticizing agents may be more significant for the coal due to its higher mineral matter content and non-softening organic matter. This may explain the higher ultimate yields of pyridine insolubles in coal than in coal tar (56 % vs 28 %, respectively), and is consistent with the fact that the resolidification rate for the coal tar or pitch is slower than in bituminous coal (Figures 11 and 14).

The trends for extract average molecular weight evolution are strong functions of temperature-time history. In general, with increasing time at a given holding temperature, the molecular weight increases to a very well defined maximum, and then decreases (Figures 24 and 25). Figure 22a shows that besides formation of pyridine insolubles, some heavier molecular weight material are formed by polymerization. The molecular weight increase is due to polymerization reactions or release of heavier
material upon heating. Evaporation of the lighter material is also a possible cause. The decrease arises from cracking of the liquids since further generation of low molecular weight liquids by primary decomposition of the parent coal ceases under these severities. At higher holding temperatures, more severe cracking drives the molecular weight to even lower values. The maxima of these curves are thus determined by competition between evaporation, polymerization, and cracking reactions. The molecular weight distributions for the extract of coal before and after the onset of softening (0.5 and 0.8 s, respectively in Figure 22b) are identical, suggesting no chemical changes during the initial stage of plasticity. This lends strong support to the physical melting assumption. The rate of cooling in the experiments may also affect the molecular weights (Figure 24) and extract inventories. A slow cooling rate experiment allows more time for volatiles to escape, hence the molecular weights tend to be higher, and liquid yield less than those in rapid quenching experiments. Also, the heavier molecules in the liquid may have more time for realignment and cross-linking to form pyridine insolubles and hence lower extract yields are observed (compare Figures 16 and 18).

The molecular weight of the bituminous coal extract is much higher than that for the coal tar extract, or for wood and lignite extracts (Figure 24). The coal extract molecular weight declines more rapidly with continued thermal treatment than those of the coal tar extract. This probably reflects two differences expected in their thermal behavior because of differences in their structure and initial state. Cracking of the high molecular weight coal extract especially in the presence of surfaces of mineral matter, unsoftened macerals and already
available coke can give more residual coke. A larger liquid molecule also has a lower vapor pressure, and thus a slower evaporation rate, and thus has more chance to remain in the condensed phase and form pyridine insolubles. Both are consistent with the lower pyridine insolubles yield and the faster rate of weight loss observed in the coal tar pyrolysis (compare Figures 15 and 19).

Plasticity mechanisms inferred from this study suggest the following points regarding the behavior of a coal particle during heating:

(1) Initial softening at low temperature is due to physical melting.
(2) Further generation of liquids is by pyrolytic bond breaking, associated with the release of gases and tar from the coal.
(3) Liquid depletion is associated with the growth of pyridine insoluble material including solids (from plasticity curves), cracking reactions (from decreasing molecular weights), and tar evaporation.
(4) A substantial weight fraction of softening coal is transformed into intermediate liquids within the coal before these liquids are depleted by the above pathways.
(5) The structure and molecular weight of these liquids influence their evaporation behavior and reactivity in polymerization and cracking reactions. Competition among these processes in turn can determine the observed yields, quality and overall generation rate of devolatilization liquids and gases.
(6) Plasticity can be modified by changing the mass transfer resistance for liquids escape (foil experiments) or by pre-treatment of the raw
coal (pre-extraction runs).

(7) Solvent extraction of rapidly quenched char is a promising technique to determine plasticity at the higher ranges of heating rate and temperature (such as combustion conditions) where direct measurements even with the present plastometer would be difficult.

The following schematic for plasticity mechanism is proposed:

\[
\begin{align*}
\text{coal} \quad & \quad \text{bond breaking} \\
& \quad \text{melting (low T)} \\
& \quad \text{transport} \\
\overset{\text{liquid}}{\downarrow} & \quad \text{polymerization} \\
& \quad \text{heavier liquids} \\
& \quad + \\
& \quad \text{coke} \\
& \quad \text{cracking} \\
& \quad \text{gas} \\
& \quad + \\
& \quad \text{coke}
\end{align*}
\]

This picture is also consistent with the above points as well as the observed pressure effects on pyrolysis (Suuberg, 1977). High tar yields seen in vacuum pyrolysis are consistent with rapid evaporation, and the present observation of a reduced plastic period (see Figure 13 and associated discussion). Under high pressures, tar evaporation is suppressed, gas yield increases and according to the above picture, solids yields will also be higher because of augmented time for repolymerization. Hence a shorter plastic period is expected and found (Figure 13). Therefore, an optimum pressure for maximum plasticity would exist for rapid-heating, high temperature conditions. The effect of pressure on
the polymerization step is not clear. Effects of hydrogen or hydrogen donors in this reaction certainly are of practical interest. However, under the range of heating rate and reaction times studied, no difference in the plastic behavior was observed for experiments in 35 atm of hydrogen or helium at a temperature of 800°C, nor were significant differences observed in the extents of liquid generation and depletion when raw coal sample was soaked with tetralin and then pyrolyzed in the screen heater.

1.5 Modeling

(a) Plasticity kinetics

The apparent viscosity data are first fitted with the simple first order kinetic scheme of Fitzgerald (1956):

\[ \begin{align*}
 &\text{coal} &\rightarrow &\text{metaplast} &\rightarrow &\text{coke} \\
 &k_1 & &k_2 \\
\end{align*} \]

The term metaplast refers to the intraparticle liquid content M. Apparent viscosity \( \eta \) is related to the viscosity of the solids free liquid \( \eta^* \) by a concentrated suspension model (Frankel and Acrivos, 1967)

\[ \frac{\eta}{\eta^*} = \frac{9/8}{(1 - M)^{-1/3} - 1} \]  

(1)

At a late stage of resolidification, the rate of increase of log(viscosity) is approximately
\[
dln \mu / dt = k_2
\]  \hspace{1cm} (2)

Thus \( k_2 \) can be found from experimental resolidification rates. Values of \( \mu^* \) are estimated from Nazem's work (1980) on carbonaceous mesophase pitch (average value taken, 1200 poise). The parameter \( k_1 \) is then obtained by fitting data for the plastic period. Figure 27 shows calculated viscosity curves, and calculated plastic periods vs experimental values for 450 K/s holding temperature runs.

However, the Fitzgerald kinetic scheme does not fit runs at different heating rates, because physical melting of part of the coal is not taken into account.

The schematic presented in Section 4 is a starting point for a more realistic model. Both primary bond breaking and physical melting are important in coal softening. Coke formation in the primary reaction can be neglected as a first approximation since most of the organic material of the coal passes through the liquid phase, (i.e., the non-softening macerals such as fusinite and inertinite are a small fraction of the total mass) although in lower rank coals it should be considered. Polymerization in the liquid phase can result in a higher liquid viscosity, even if no solids are formed. At higher temperatures, (\( > 658^\circ\text{C} \), compare 555°C and 658°C, Figures 22a,b) cracking predominates over polymerization. For this reason, and because the detailed MWD information required for a quantitative model is not available, polymerization kinetics in the liquid phase is not modelled. Both evaporation and cracking are pathways to resolidification. High pressure or closed reactor geometry can prevent
Figures 27a, b Calculated Viscosity Curves for 450 K/s Heating Rate to Different Holding Temperatures, and Comparison with Observed Plastic Period (solid circles)
tar evaporation. Since no individual tar or gas species were collected in the present study, both evaporation and cracking are lumped into one reaction with volatiles (tar and gas that leaves the particle) and coke as products. Further reaction between intraparticle liquid and coke or mineral matter are not considered.

Here the global model assumes the coal to undergo both physical melting and pyrolytic bond breaking to form an intermediate liquid in a suspension of unreacted coal, coke and inert mineral matter. The liquid forms a volatile product which, according to the model, escapes from the coal infinitely rapidly, and leaves a solid coke. The weight ratio of coke to volatiles thus formed is assumed to be constant (= a). The initial 25 % pyridine extract from raw coal is assumed to be the maximum that can be obtained without chemical decomposition of the initial structure, and is generated by physical melting. This material is assumed to melt over a narrow range of temperatures. To account for melting, a gaussian distribution of melting points with a mean at 623 K and a standard deviation of 30 K are assumed in the calculations. These values reflect the range of the initial softening temperatures of coals (Read et al., 1985; Rees and Pierron, 1954). The rate of generation of liquids by melting alone would therefore be the product of the heating rate and this distribution function. The mineral matter (wt. fraction f$_a$ = 0.13 for the coal studied, Franklin, 1980) is assumed to be inert. The reaction scheme and corresponding rate expressions based on weight fractions of the raw coal (moisture free, mineral matter containing basis) are
\[
dC/dt = -k_1 (C - f_a) - r_m \\
dM/dt = k_1 (C - f_a) + r_m - k_2 M \\
dV/dt = k_2 M (1/1 + a) \\
dE/dt = k_2 M (a/1 + a)
\]

where \(C, M, V\) and \(E\) are the weight fractions of the unreacted coal, liquid, volatiles and coke, respectively, and \(r_m\) is the rate of physical melting.

The model is first applied to intraparticle liquid format-
ion and depletion data from the screen reactor. At a late stage of
pyrolysis, when most of the coal has reacted \((C - f_a = 0)\) and all the
material that can physically melt has done so \((r_m = 0)\), the rate of
liquid depletion is

\[
dM/dt = -k_2 M
\]

The rate constant \(k_2\) can thus be found from a plot of \(\ln(M)\) vs time for
constant temperatures. Typical values thus obtained are shown in Figure
16. An Arrhenius plot gives an activation energy of 42.2 Kcal/mole, and
\(k_2\) is found to be

\[
k_2 = 1.9 \times 10^{10} \exp (-21200/T), \text{ s}^{-1}
\]
The rate constant $k_1$ was obtained from a best fit to the experimental data, using values of $k_2$ already found. The result was

$$k_1 = 6.6 \times 10^7 \exp \left( -14500/T \right), \text{s}^{-1} \quad (6)$$

Figure 15 gives values of pyridine insolubles and extractables (corresponding to $C + E$ and $M$, respectively) observed in the experiments and corresponding model predictions (solid lines), using an "a" value of 1.25 (obtained from long holding time data) for two sets of reaction conditions.

To calculate the apparent viscosities, Equation (1) is again used with the present scheme and rate constants in Equations (5) and (6). Figure 28 shows calculations corresponding to the experimental conditions and laboratory results presented in Figures 11 and 12. The rate constants obtained from the screen reactor describe constant heating rate plastometer runs well but underpredict viscosity for 450 K/s runs at low holding temperatures. Three possible reasons are (a) the polymerization in the liquid phase is neglected, which can affect the solids free viscosity $\mu^*$, (b) resistance to volatiles escape can exist in the plastometer, and (c) $\mu^*$ is assumed independent of temperature.

If the solids free viscosity $\mu^*$ is assumed to be proportional to a positive power of the intraparticle liquid weight average molecular weight, as in polymer melts, then from Figure 24 the lower temperature runs would have a higher viscosity than predicted since the liquid has
Figure 28 Calculated Viscosity Curves for Conditions of Figures 11 and 12, using Liquid Formation and Depletion Kinetics
higher average molecular weights. Temperature variation of \( \mu^* \) is correlated by the Andrade equation with an activation energy of 38 Kcal/mole (Bhatia et al., 1985). However, the expression is not valid over a wide range of temperatures, and the resulting fit is not improved. If the rate constant \( k_1 \) is retained (because little volatiles are formed during early softening) and \( k_2 \) allowed to vary, then \( k_2 = 8 \times 10^6 \exp(-14000/T)s^{-1} \) fits the data well (Figure 29). A lower activation energy is consistent with mass transfer resistance to volatiles escape from the plastometer. Therefore both polymerization at lower temperatures and resistance to volatiles escape cannot be ruled out.

(b) Application of plasticity data: coal particle agglomeration

The agglomeration of coal particles suspended in a gaseous medium can be expressed as,

\[
A_i + A_j \rightarrow A_{i+j}
\]

(7)

where \( A_j \) are the \( j \)-particle agglomerates with a population density \( n_j \). Assuming no agglomerates break after they are formed and no particle loss due to adherence to the reactor walls, the formation rate of \( A_j \) is:

\[
\frac{dn_j}{dt} = \frac{1}{2} \sum_{i=1}^{j-1} K_{i,j-1} n_i n_j - \sum_{i=1}^{N-j} K_{i,j} n_i n_j
\]

(8)

where \( K_{ij} \) is the overall agglomeration constant, i.e. the product
Figure 29 Calculated Viscosity Curves for Conditions of Figures 11 and 12, with $k_2$ fitted
of the collision frequency $K_c$ and the probability of forming an agglomerate per collision, $\xi$, for the agglomeration of an $A_i$ and an $A_j$ particle. For computational purposes, the largest agglomerate size is limited to $N$ single particles sticking together. Typically, $N = 10$. It is assumed that a $j$-particle agglomerate has a spherical shape and is related to the initial single particle radius by $a_j = a_0 (j)^{1/3}$. The collision constant $K_c$ of $A_i$ and $A_j$ in isotropic turbulence is (Saffman and Turner, 1956),

$$K_c = 10.4 \frac{a^3 \sqrt{\varepsilon_0}}{\nu} \quad (9)$$

where $\varepsilon_0$ is the turbulent energy dissipation rate per unit volume, and $\nu$ the kinematic viscosity of the carrier gas of particles in the agglomeration system.

If the strength of the material in the bonding neck region formed between the two particles (Figure 30) is $\sigma_m$, (assumed proportional to liquid content with constant $\sigma_0$), and if $\sigma_m$ is larger than the bending stress $\sigma_b$ (Yoshida et al, 1979) on the agglomerate pair, then successful agglomeration results. Thus,

$$\sigma_m = \sigma_0 M(t) > \sigma_b = 10.8 \frac{\mu \sqrt{\varepsilon_0}}{\nu} \frac{1}{c_1^3} \quad (10)$$

where $c_1$ is the ratio of neck radius to particle radius, which gives a critical value $c_1^* > 2.21 (\mu/\sigma_0 M)^{1/3} (\varepsilon_0/\nu)^{1/6}$ required for agglomeration. The quantity $c_1$ is assumed to be a normally distributed quantity with mean $\bar{c}_1$ and standard deviation $\delta$, since the particles in reality are
Figure 30. A Pair of Agglomerated Particles

Figures 31a,b Liquid Content and Swelling Ratio

Figures 31c,d Weight Fractions of Unagglomerated Particles at Different Intensities of Turbulence. Numbers on Curves are \( \frac{\varepsilon}{v} \), in \( s^{-2} \)
irregularly shaped. Summing over all agglomerates with $c_1$ greater than the critical value, an overall efficiency $\bar{\xi}(t)$ is obtained, which is a function of the time dependent liquid content and turbulence intensity.

\[
\bar{\xi}(t) = \frac{1}{\sqrt{2\pi}} \int_{c_1^*}^{1.0} \exp\left(-\frac{(c_1 - c_1^*)^2}{2\sigma^2}\right) dc_1
\]

Once the energy dissipation rate and the initial number density of coal particles are specified, the agglomeration equations can be solved.

To account for swelling of the particles, a single volatile bubble is assumed to grow in a viscous, spherical droplet. The viscosity of the coal melt is related to the solids fraction by the previously mentioned concentrated suspension model in Equation (1). The volatiles are assumed to be in equilibrium with, arbitrarily, 0.8 mole fraction of the liquid (see following Section (c)).

The liquid formation and depletion rate parameters derived in Section A are used. An initial particle number density of 2800/cm$^3$, and particle radii of 40 $\mu$m are assumed (corresponding to stoichiometric combustion in air of pulverized coal particles of this size). The computed liquid content and swelling ratio (radius/original radius) for heating from room temperature (a) to a final temperature of 1000 K at 10000 K/s and (b) to 1700 K at 15000 K/s are shown in Figures 31a,b. The mass fraction of single unagglomerated particles, $A_1$, for different values of $e_0/v$ in turbulent flow are plotted as functions of pyrolysis time (Figures 31c,d). As the intensity of turbulence increases, the collision frequency increases and results in more agglomeration.
At very intense levels of turbulence, the agglomeration probability per collision is low because of the high stress imposed by the fluid on potential agglomerates. Therefore little agglomeration results. Agglomeration essentially ceases when the liquid in the coal is depleted. Figures 31e,f show the generation of different size agglomerates with $\varepsilon_0/v$ at $10^6$ sec$^{-2}$. The distances between the curves indicate the mass fraction of feed coal which have agglomerated to form j-particle agglomerates.

Calculated mass fractions of agglomerates ($A_2 - A_{10}$) are plotted as a function of constant reactor temperature (Figures 31 g,h). A residence time of 0.24 second is specified. Experimentally, this would correspond to allowing the mixture of coal particles to pyrolyze, collide and agglomerate for the given temperature-time history, then quenching the mixture infinitely rapidly and collecting and counting the agglomerates.

(c) Swelling of particles

Electron micrographs of char particles fed through entrained flow reactors show existence of both cenospheres (particles with a large cavity in the center) and particles with numerous small cavities which impart a foam-like appearance to the particles. Equations for describing the two cases are given below.

(1) Swelling of a single bubble

A single volatiles-filled bubble is assumed to grow in a viscous,
Figure 31e,f Weight Fractions of Different Size Agglomerates Formed at $\dot{e}_0 / \nu = 10^6$ s$^{-2}$

Figure 31g,h Weight Fractions of Agglomeration vs Final Temperature, No. on Curves are $\dot{e}_0 / \nu$, in s$^{-2}$
spherical droplet (Figure 32a). The volatiles trapped inside the bubble are assumed to be in equilibrium with a constant mole fraction $y_i$ of the metaplast present in the coal. Expansion of the bubble is obtained by a momentum balance across the liquid layer. Defining $Q$ as the ratio of particle radius at time $t$ to the initial particle radius, the rate of change of $Q$ is given by,

$$\frac{dQ}{dt} = \frac{P_\infty \left\{ \frac{\epsilon (T/T_0)}{(1-y_i)[Q^3-(1-\epsilon)]} - 1 \right\} - \frac{2a}{R_0} \left\{ \frac{1}{[Q^3-(1-\epsilon)]^{1/3}} + \frac{1}{Q} \right\} - \frac{4\mu_1 Q^2}{Q^3-(1-\epsilon)} - \frac{1}{Q^3}}$$

where $P_\infty$, $\epsilon$, $\sigma_s$, $T$, $T_0$, and $\mu_1$ are the pressure outside the particle, initial porosity, surface tension, particle temperature, initial temperature and viscosity of the liquid/solid suspension of the softening coal, respectively. Volume shrinkage due to pyrolysis weight loss is not considered. The suspension viscosity is from Equation (1), with rate constants from Equations (5) and (6).

The surface tension effect is only significant when the ambient pressure is much less than 1 atm, or when the particle size is much less than 100 um. Results of calculations are shown in Figures 31a,b.

(b) Reacting Foam Model

The swelling of the foam layer is analogous to the processing of plastic foams. An empirical approach is attempted here to describe the swelling ratio. Consider a reacting mixture of unsoftened coal,
\[ R_0 = \text{original radius of particle} \]
\[ Q = \frac{R_2}{R_0} \]

**A. Single Bubble Swelling**

**B. Reacting Foam Model**

Figure 32. Limiting Cases of Swelling (a) Single Bubble Swelling (b) Reacting and Solidifying Foam
liquid, gas and coke, their weight fractions denoted by C,M,G,E respectively (Figure 32b). The swelling of the liquid is due to the gas generation, and is assumed to be proportional (via constant $\alpha$) to a power $\beta$ of the generation rate, $dG/dt$. The unsofterned coal (including inert mineral matter) in the suspension is assumed to have an initial density $\rho_0$. The porous coke is continuously formed from the liquid, so its porosity reflects the instantaneous porosity of the liquid. Therefore, at any time, the volumetric swelling ratio $Q(t)$ is given by

$$Q(t) = \frac{C/\rho_0 + \left[ 1 + \alpha(dG/dt)^\beta \right] M/\rho_0 + \int_0^t \left[ (dE/dt)/\rho_{M+E} \right] dt}{(1/\rho_0)}$$

(13)

The volumetric contributions of C, M and E are in the three separate terms of the numerator. The instantaneous density of the liquid is related to $\rho_0$ by $\rho_{M+E} = \rho_0 / \left[ 1 + \alpha(dG/dt)^\beta \right]$ therefore

$$Q(t) = C + \left[ 1 + \alpha(dG/dt)^\beta \right] M + \int_0^t (dE/dt)[1 + \alpha(dG/dt)^\beta] dt$$

(14)

Figure 33 shows predictions from this equation.

The two expressions above probably represent two limiting physical picture of coal swelling.

1.6 POTENTIAL APPLICATIONS

(1) The results provide an approach for describing agglomeration behavior in gasifiers and combustors.

(2) The improved physical and chemical picture of the pyrolysis of
Figure 33. Liquid Content and Swelling Ratio, Heating Rate and Final Temperature Indicated
softening coals can be used in improved description of the kinetics of coal softening, pyrolysis and liquefaction.

(3) The data showed that suitable thermal pretreatment alone can give high liquid yields, exceeding 80 % daf, and is advantageous to the production of liquids from coal.

(4) High temperature, fast response plastometer can be applied to the study of other thermoplastic materials.

1.7 CONCLUSIONS

(1) A new coal plastometer has been developed to measure the rapidly changing apparent viscosities at severe conditions, i.e. at high temperatures, pressures and heating rates pertinent to modern coal conversion processes but previously unattainable with conventional instruments.

(2) Coal plasticity can be described directly by its viscosity change. As a Pittsburgh Seam bituminous coal is heated, the coal softens to form a solid/liquid suspension the viscosity of which decreases from more than one million poise to minimum values of order a few thousand poise. Resolidification of the intermediate liquid phase is indicated by rapid rise in viscosity values.

(3) Characteristic times for softening and resolidification were obtained. The measured time interval of low viscosity varies from one
minute to less than a second, depending on the temperature-time history.

(4) Initial softening of a Pittsburgh coal is by physical melting of an estimated 25% by weight of the coal. Up to 40% by weight of the coal is further converted to liquids by pyrolytic bond breaking. These liquids can polymerize to give higher molecular weight liquids and solids, crack to give gas and coke, or escape from the coal particle to give tar. The result is that the average liquid molecular weight can increase from 570 to above 800, and then decrease to around 600.

(5) The kinetics of intraparticle coal liquid formation and depletion can be quite accurately determined in an electrical screen heater with rapid sample quenching, followed by solvent extraction of the quenched char.

(6) The new information on coal plasticity kinetics finds quantitative application in modeling coal particle agglomeration and swelling behavior under rapid heating high temperature conditions. Predictions of model here developed were in qualitative accord with literature data on swelling and provide a possible explanation for coal agglomeration observed within a pulverized coal flame.

1.8 REFERENCES FOR THIS CHAPTER

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CHAPTER 2. INTRODUCTION AND BACKGROUND

2.1 INTRODUCTION

Bituminous coals upon heating undergo a number of physical and chemical changes. Melting and pyrolytic decomposition of significant parts of the coal form an unstable liquid that can escape from the coal by evaporation to give tar and light oil or crack to form light gases, leaving behind a solid residue. Polymerization or cross-linking of the liquid molecules to form solids also competes with these other liquid removal processes. All the liquid is eventually depleted, leaving a porous coke residue. The kinetics of these processes are strongly temperature dependent, therefore their relative contributions depend on the temperature-time histories to which the coal is subjected.

From an engineering perspective, the transient occurrence of the liquids in coal, commonly referred to as plastic behavior, can strongly influence the chemistry and physics of the thermal conversion and refinement of bituminous coals. Irrespective of process temperature history, reactive atmospheres, the presence of solvents or feed size, plasticity kinetics is important for the understanding and subsequent modelling of different bituminous coal pyrolysis, gasification, combustion, carbonization and liquefaction processes. Additional heat and mass transfer phenomena, and reactions with surrounding reactive atmospheres or solvents can be suitably superimposed to describe the overall behavior in different processes.
Some existing technical problems include the serious difficulties encountered in fluid bed gasifiers are direct consequence of plasticity. Agglomeration of plastic particles can cause solidification of the bed, and plugged pipelines. Bubbles of volatiles can swell the plastic coal mass, in turn affecting the devolatilization rate. The yields and qualities of pyrolysis products are affected since the transport of volatiles through the viscous coal melt affords opportunities for intra-particle secondary reactions. Swelling also determines the density and morphology of the char, hence the burnout time and process efficiency in subsequent combustion, as well as the propensity of the char to impinge and erode heat transfer surfaces. The development and disappearance of plasticity is closely related to formation and destruction of liquids. Study of plasticity kinetics can therefore shed light on the mechanisms of coal liquefaction.

Therefore, plasticity study contributes to both basic understanding in coal science, and to improved design in several important coal conversion technologies.

Figure 2.1.1. is a schematic of changes in coal physical structure and liquid volume fractions during the onset, duration and destruction of plasticity.

Plasticity kinetics under carbonization conditions has been rather well studied (Loison et al., 1963; Habermehl et al., 1981). These studies involve low sample heating rate experiments to a moderate final
Figure 2.1.1  Physical changes of bituminous coal upon heating
temperature, typically at 0.05 K/s to 800 K. Very limited studies have been made to date outside this range, although rather uncertain extrapolation of these data to other conditions have been made in some modelling studies (Melia and Bowman, 1983; Scharff et al., 1981; Attar, 1978; James and Mills, 1976). In modern coal conversion and combustion processes, heating rates of order 10⁴ K/s or higher, and final temperatures to 2000 K are possible. This thesis addresses a systematic approach to the study of coal plasticity at high heating rates and temperatures pertinent to modern coal conversion processes.

2.2 BACKGROUND

The major reviews on coal plasticity are to be found in Loison et al. (1963) and Habermehl et al. (1981). Theories of coal plasticity are oriented towards conditions pertinent to metallurgical coke manufacture. Rather limited information exist for high heating rate, high temperature conditions. Bituminous coals heated to about 400°C or above will exhibit transient plastic properties. Coal particles will soften, swell and ultimately coalesce upon heating. Fluidity of the coal melt will increase to a maximum and then drop. Further heating causes the melt to resolidify to a solid coke. Lloyd et al. (1984) gave a summary of the different theories of coal plasticity. Earlier "bitumen" theory explains plastic development as a result of a fusible component (bitumen) which melts to provide a viscous slurry. The later "metaplast" theory is more commonly accepted (Fitzgerald, 1956; Chermin and Van Krevelen, 1957). The liquid metaplast is generated and destroyed by the following pyrolytic reactions,
The liquid metaplast concentration determines the fluidity of the melt. Kinetic constants of formation and destruction of the metaplast can be calculated from experimental fluidity data (Lloyd et al., 1980).

The onset of plasticity is generally regarded as being caused by a depolymerization reaction of some components of the coal matrix during pyrolysis producing a liquid "metaplast". This metaplast can then act as a plasticizer and cause the entire system to become fluid. At moderate pressures (around 1 atm) plasticity is normally limited to coals in the bituminous range, as anthracites and low rank coals have molecular structures that are too highly cross-linked for complete depolymerization to occur.

Resolidification or rehardening of the coal metaplast to form a coke is regarded as occurring by two processes. Parts of the metaplast evaporate from the coal surface, reducing the amount of plasticizers present in the system. In addition, the metaplast undergoes chemical reactions such as cracking, condensation and crosslinking at higher temperatures, causing it to resolidify. The phenomena of plasticity increasing with increasing pressure can be accounted for by the increased plasticizer concentration in the system caused by the lower rates of
intra–particle and external mass transfer that occur at higher pressures. Temperatures of rehardening increase with increasing heating rate of the coal sample, indicating a competition between the condensation and other reactions of the system. Evidence for participation of both mechanisms according to both theories is substantial.

Kirov and Stephens (1967) discussed the close relationship between the fluidity measured by a Gieseler plastometer and the rate of weight loss and yield of chloroform extractables for carbonized coals. The maximum of fluidity is reached about 10 - 20 °C after the maximum of the extraction curve and 20 °C before the maximum of rate of weight loss curve when these data are plotted with the final temperature of carbonization as the independent variable. Ouchi et al. (1983) discussed the relation between Gieseler fluidity and solvent extraction yield of coals. Recent studies of molecular weight distribution and yield of tar generated in flash pyrolysis of fine coal particles shed light on the metaplast transport in plastic coal (Unger and Suuberg, 1983; Oh, 1984). Their findings suggest that under rapid heating conditions, plasticity is determined by the interplay of rate processes such as thermal bond breaking, tar and reactive gas transport, and secondary repolymerization reactions. The complexity of the plasticity phenomena is well demonstrated by Figure 2.2.1. with respect to metallurgical coke formation (Klepel, 1960).

Knowledge of the viscosity of a softened coal would be useful for studying the mass transfer effects in softening coal pyrolysis. There is abundant evidence that mass transfer plays a role in determining the
Figure 6.14 Relationships between causes and experimental events for the different methods of testing of coke formation according to Klepel.  

Figure 2.2.1 Role of plasticity in coke formation according to Klepel (from Chemistry of Coal Utilization, 2nd Suppl. Vol., 1963)
yields of volatiles obtained during pyrolysis (Howard, 1981; Gavalas, 1982) with intra-particle mass transfer being rate limiting for many conditions of practical interest (Oh, 1985). Intra-particle transport of reactive gases and pyrolysis products can be achieved by diffusion in the liquid phase and by bubble transport. The liquid diffusion coefficient and melt viscosity are important in such modeling. Viscosity also influence the dynamics of bubble growth (Oh, 1985; James and Mills, 1976; Lewellen, 1975).

Rheological measurements on coal are almost exclusively made under coking conditions, i.e. low heating rates and up to moderately high temperatures. Detailed techniques of measurements are discussed in Kirov and Stephens (1967) and ASTM D2639-74 (1974). The Gieseler plastometer is widely used. A finely powered coal is compacted into a cylindrical crucible containing a bladed stirrer. A constant torque is applied to the stirrer as the coal is heated at 3K/min. The angular velocity (100 dial divisions/min) is recorded in units of dial divisions per minute (ddpm). Most plastic coals have a distinct softening stage followed by a resolidification stage. At 3K/min heating rate, the transient plasticity occurs between 400°C - 500°C. Figure 2.2.2. shows a Gieseler plastometer and a plasticity curve. The stirring arm subjects the softened coal to a spatially complex flow field, and the measurement is over a widely varying range of shear rates. Other limitations of the Gieseler plastometer are discussed by Kirov and Stephens (1967). The coal melt actually consists of a liquid phase of chemically reacting polymeric substance in which is suspended a mixture of gases and solids (including coal mineral matter and possibly non-softening coal macerals). It is obvious such a
Figure 2.2.2 Plasticity data from Gieseler Plastometer

(From Chemistry of Coal Utilization, 2nd Suppl. Vol.)
melt cannot be Newtonian. Waters (1962) found coal to have pseudoplastic behavior in the early softening stages. Fitzgerald (1957) fitted data to a visco-elastic model. Hence a constant-torque plastometer is not suitable for making apparent viscosity measurements. Other plastometers such as the Brabender plastograph, the Sapozhnikov plastometer and the concentric cylinder viscometer (Stephens, 1963) are all designed for making measurements under coke-oven conditions. Davies et al (1983) have reported viscosity measurements with a capillary viscometer. Besides low heating rate and moderate final temperatures, these plastometers also operate at shear rates much lower than those experienced in fluidized beds. For higher heating rates (up to 100 K/min), a shock dilatometer can give qualitative data on plastic behavior as inferred from swelling behavior. Khan and Jenkins (1984) have used a high pressure microdilatometer to measure plastic properties at heating rates of 65 K/min. Thus, previous studies did not meet the need for measuring the rapidly changing viscosity of coal under high temperature, high heating rate and different reactive gaseous atmospheres.

Swelling, agglomeration and caking of coal particles is a direct consequence of the plastic properties of coal. To avoid these problems, there are two approaches. The first is to decrease the softening properties of coals, which can be achieved by pre-oxidation, partial pyrolysis and pretreating the coal with chemicals. Many chemical decaking treatments have been discussed in the literature (Habermehl, 1981). The second approach involves the selection of suitable process conditions. The extent of agglomeration depends on the duration of the plastic period, surface tension and the actual viscosity of the particles, and
the flow field of the continuous medium. Experimental studies of agglomeration have been described by McCarthy (1980) and Tyler (1979, 1980). A study of free thermal agglomeration of two coal particles heated at \( 3 - 7 \) K/min was made by Klose (1983). Scharff et al (1981) have modelled agglomeration in gasifiers. Viscosity data in modeling are usually assumed or extrapolated from data under coking conditions.

Swelling of packed, powered coal particles heated in small diameter tubes have been studied in dilatometers up to \( 65 \) K/min (Khan and Jenkins, 1984). Swelling of individual coal particles at high heating rates have been studied by Hamilton (1980), Culross (1984), Matsunaga et al.(1978) and more recently by Lowenthal (1985). Models of swelling have been proposed by Melia and Bowman (1983), Lewellen (1975) and Oh (1985).

The plastic behavior of coal has other important consequences in coal conversion processes. One example is its effect on liquefaction kinetics. High fluidity is desirable for high reactivity in short contact time liquefaction (Whitehurst, 1980) A close relationship between liquefaction and plasticity has been observed (Gorin, 1981; Wilhelm and Hedden, 1983). Neavel (1982) discussed plasticity mechanism from a coal liquefaction viewpoint. Okutani et al.(1984) studied viscosity changes in coal/oil pastes during hydrogenation and found that the existence of a maximum in the slurry viscosity was due to extractive distegration of the coal by the vehicle oil.

A brief summary of the different factors affecting coal plasticity will be given below. Most of the observations are from experimental
results from Gieseler plastometers operating under carbonization (coking) conditions.

Coal type - plasticity is normally observed in bituminous coals. Coals with 25 - 30 % volatile matter exhibits maximum fluidity. Fluidity is also evident in coals with carbon content (daf) in the range 81 - 92 %, with maximum fluidity at 89%. Vitrinite is the main petrographic component that contributes to fluidity (Van Krevelen, 1961).

Heating rate - an increase in the heating rate shifts the Gieseler softening and resolidification points to higher temperatures, broadens the plastic region and increases the fluidity (Loison, 1963). Swelling is found to increase with heating rate at the low heating rates (to 10 K/s). Swelling may actually decrease at high heating rates or high temperatures (Pohl et al., 1978).

Particle size - very fine grinding of coal reduces its plastic properties. Swelling of particles decreases with particle size.

Pressure - the effects of pressure have only been studied rather recently. In inert gases, the maximum fluidity increases with pressure to some limit and then levels off. In hydrogen, the increase is almost linear in the range 0 - 450 psig. (Lancet and Sim, 1981; Kaiho and Toda, 1979) When heated under pressure, the caking of the particles is promoted and
Chemical pretreatment and additives — pre-oxidation of a bituminous coal will destroy its caking properties. Ignasiak et al. (1974) found that the destruction of plasticity is due to hydroxyl groups undergoing condensation reactions during pyrolysis. Alkali salts reduce coal plasticity by promoting crosslinking reactions in the coal (Crewe et al, 1975). A large number of additives are capable of changing the plastic behavior. Additives affect the plasticity by chemical reaction between coal and additives, catalysis, interaction of the additive with the surface of the plastic coal or by changing the thermal conductivity of the plastic mass (Habermehl et al., 1981).

2.3 *THESIS OBJECTIVES*

The thesis objectives include the following:

(1) Conceptualize, design and develop new techniques and instruments for measuring apparent viscosities and intra-particle liquid quantities of a rapidly pyrolyzing coal.

(2) Study the effects of process variables such as temperature and pressure on plasticity kinetics and investigate some qualitative aspects of the nature of plasticity and softening coal pyrolysis.
(3) Develop global models of plasticity kinetics and models of agglomeration and particle swelling, and possibly other plasticity related phenomena.
CHAPTER 3. EXPERIMENTAL TECHNIQUE AND APPARATUS

3.1 INTRODUCTION

The non-existence of experimental methods for studying the rheological properties of softened coal under rapid heating conditions have already been discussed. In modern coal conversion processes, heating rates of 15000 K/s or more can occur. Final temperatures can exceed 1100°C and shear rates can be high (estimated to 1000 s⁻¹). Requirements for a new coal plastometer therefore require an ability to operate at high temperatures (to 1100°C) and heating rates to 1000 K/s. Ability to monitor the rapidly changing viscosity is important in order to follow the short duration of plastic phase at high temperatures.

Observation of the deformation and swelling behavior during heating reflects only indirectly the plastic behavior. A direct method would be to determine the resistance to shear of the coal, or to determine the amount of liquid present in the coal during pyrolysis.

Two new experimental methods were developed for the present study. To measure the apparent viscosities of pyrolyzing coals, a fast response plastometer for sample heating rates and holding temperatures of 40-1000 K/s and 600-1250 K, in vacuum or in an ambient gas atmosphere up to 100 atm was designed and constructed. To determine quantitatively the liquids content in the pyrolyzing coal, an electrical screen pyrolyzer with rapid sample heating and quenching capability (up to 1000 K/s, and 6000 K/s respectively) was also designed and constructed. From the
pyrolyzer data, devolatilization and liquid formation/destruction reactions were studied and compared to the plastometer data. A second larger pyrolyzer with gas and tar collection capability, higher heating rates, and allowance for photographic recording of experiments was developed later. Sample loading techniques and devices for both plastometer and pyrolyzer were also developed and tested.

Reactions in the transient liquid phase were studied in terms of molecular weight evolution by Gel Permeation Chromatography, and solids growth by solvent extractions. Pyrolysis experiments of a model coal liquid system (a heat treated coal tar), and other solid phase fuels (wood and lignite) were also performed and compared to that of a plastic coal. Some additional experiments (foil experiments, pre-treatment experiments, etc) were also performed. Table 3.1.1. is a summary of experiments performed.

3.2 APPARENT VISCOSITY MEASUREMENT

A fast response, rapid-heating high temperature plastometer has been developed for apparent viscosity measurement. The instrument determines the torque required for constant speed rotation of a thin disk embedded within a thin layer of coal heated between two parallel metal plates. Heating rates, final temperatures and sample residence times at final temperatures can be separately selected and controlled over the ranges 40-1000 K/s, 600-1250 K, and 0-40 s. The instrument can be operated in hydrogen or inert gas atmospheres from near vacuum to 100 atm.
Table 3.1.1. Summary of Experiments

<table>
<thead>
<tr>
<th>EXPERIMENTS</th>
<th>ABBREVIATION</th>
<th>PARAMETERS STUDIED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastometer</td>
<td>PO</td>
<td>prototype development and testing</td>
</tr>
<tr>
<td></td>
<td>PT</td>
<td>heating rate and holding temperature</td>
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<td>pressure effects</td>
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<tr>
<td></td>
<td>SE</td>
<td>pre-extraction effect on liquid amount</td>
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<td></td>
<td>SF</td>
<td>foil experiments: mass transfer and secondary reactions</td>
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<td></td>
<td>GM</td>
<td>miscellaneous: MWD in wood, lignite</td>
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</table>
Apparatus description

Figure 3.2.1. presents a schematic of the coal plastometer. The unit is enclosed in a high pressure vessel (316 stainless steel rated for 205 atm) that can be evacuated to 5 Pa or charged with hydrogen or inert gas. One end of the torque transducer shaft is joined to the shaft of the shearing disk, while the other end is coupled to a 12V DC gear-motor (Barber CYQM 23410-61-5, 1.70Nm) driven by a speed controller (Minarik LV 1207). The torque transducer is a non-contact strain gauge type torquemeter (S. Himmelstein MCRT 3L-08T and System 6 readout, 0.1% accuracy). The response time of the transducer is less than 10 ms.

The details of the coal shearing device are illustrated in Figure 3.2.2. The shearing chamber is a 38.1 mm x 10.2 mm x 0.76 mm slot formed by upper and lower bounding plates. It supports a 0.50 mm thick, 3.75 mm radius axially symmetric shearing disk. These parts are machined from a nickel superalloy (Rene 41) selected for its high temperature strength and resistance to alkali and hydrogen corrosion. The disk and flat plate design was chosen for convenience of instrument construction and duration, and ease of data inversion to yield apparent viscosity information. The demanding experimental conditions of interest for coal, including shearing of refractory solid particles and operation at high temperature and high heating rates also favored this design. Desire for spatially uniform sample heating and minimization of secondary reactions in the coal layer suggested use of as thin a sample layer as possible consistent with machining tolerances and accommodation of representative
**Figure 3.2.1** Schematic of coal plastometer

- Independent variables:
  - Holding temperature and heating rate
  - Shear rate
  - Total pressure and reactive gases
  - Torque and temperature reading

- Raw data

- Schematic components:
  - Heating circuit
  - Motor speed control
  - Hydrogen, helium, etc.
  - Fast response recorder
  - Transducer
  - Motor
  - T.C.
Details of shearing chamber: (1) aluminum electrodes; (2) stainless steel clamp; (3) thermocouple (0.012 mm thickness); (4) shearing disk; (5) sample (coal); (6) nickel super-alloy plate; (7) high temp. ceramic

Figure 3.2.2  Details of plastometer hot stage
size coal particles. The shearing disk was thus positioned to establish a symmetrical 0.13 mm thick layer of coal between each of its faces and the corresponding bounding plate of the chamber, as shown in Figure 3.2.2.

The thermal lag of this arrangement is due primarily to the coal and can be estimated by treating the two layers of sample as a single, 0.26 mm thick slab. Then, assuming a low value of coal thermal diffusivity of $1.5 \times 10^{-7}$ m$^2$s$^{-1}$, the temperature drop from the surface to the center plane of the coal layer at heating rates of 100 K/s and 1000 K/s would be 5 and 50 K respectively. This is a conservative estimate since thermal diffusivities of coals increase rapidly with temperature above 773 K, to values of $5 \times 10^{-6}$ m$^2$s$^{-1}$ at 1123 K. Heat conduction across the metal disk is much faster since the metal has a thermal diffusivity of about $5 \times 10^{-6}$ m$^2$s$^{-1}$. For the 0.50 mm thick disk, the thermal conduction time through the disk would be an order of magnitude smaller than through the coal layer. Measurement of temperature is by a 0.012 mm thin-foil thermocouple (Omega C02-K) attached to the outside surface of the upper metal plate of the shearing chamber. Its stated response time to a stepwise temperature change is 2 - 5 ms. Rapid changes in the torque and temperature are recorded by a two-channel electronic recorder (Bascom-Turner 4120) capable of acquiring data at 1000 data points/s.

The coal sample is heated by two independent DC circuits as shown in Figure 3.2.3. Power is supplied from a set of parallel connected 12 V lead acid batteries. During an experiment, two essentially constant pulses of current are sequentially obtained from these two circuits and
Electrical circuits for independent control of sample heating rate, final temperature and heating time.

Figure 3.2.3  Electrical circuits for sample heating
delivered through the metal plates for heating up and holding the sample temperature, respectively. Two carbon rheostats (Biddle #410040 and #410010) are used to adjust the magnitude of these current pulses, which can exceed 500 A. Timing of the current pulses is by two solid state digital relays adjustable from 0.00 to 99.99 s in 0.01 s increments (Agastat DSB XX0125). These timers in turn activate heavy duty DC contactors (Stancor 124-909) which activate or deactivate the heating and holding temperature circuits.

The device in Figure 3.2.4. was developed to permit reproducible loading of the coal particles into the shearing chamber and alignment of the rotating disk with the axis of the transducer shaft.

**Procedure**

Approximately 190 mg (± 2% by wt. max. error) of ground coal are used in each experiment. Using the loading device (Figure 3.2.4.), the coal is uniformly placed between the lower and upper bounding metal plates M₁ and M₂ while holding the disk in proper position. This operation is achieved by first holding M₁ down (on clamp I) with displacement blocks D. Some coal is poured into the channel, i.e., the half-slot of M₁, and spread into a uniform layer of prescribed thickness by sliding a grooved smoothing block S along the shoulders of D. The rotating disk K is then lowered onto this layer of coal, aligned, and secured. More coal is poured over K and a second, more shallow smoothing block S' is slid along the shoulders of D, leaving a uniform layer of coal of a preset thickness covering the disk. The displacement blocks D are then removed,
Device for uniform loading of coal in shearing chamber:
C - centering rod; D - displacement blocks; I, I' - stainless steel/ceramic clamps;
K - rotating disk; M, M - lower and upper heating plates; S, S' - sliding blocks;
T - teflon bushing; P - coupling.

Figure 3.2.4   Device for loading coal into shearing chamber
and $M_2$ is rotated into alignment with $M_1$ and lowered carefully on $M_1$. In order to achieve good contacting between the two plates, the surface of $M_1$ must be cleaned of any coal remaining from the loading operation. The metal plates, disk and coal assembly are then secured between two C-shaped metal/ceramic pieces $I$ and $I'$. These two pieces are tightened against each other with their ceramic faces pressing on the outer surfaces of $M_1$ and $M_2$. This procedure prevents dislocation of the disk and the metal plates.

The assembled and loaded shearing chamber is then placed between the two electrodes in the plastometer. The couplings to the transducer are tightened and the thin-foil thermocouple is then attached to the outer face of $M_2$. To protect the transducer against overload during startup the shearing disk is rotated manually one or two turns until a steady torque in a measurable range ($4 - 5 \, \text{Nm}$) is attained. The cover of the pressure vessel is then lowered and the vessel is evacuated to approximately 5 Pa and flushed twice with helium at 0.1 MPa. The test gas (helium or hydrogen) is then admitted until the desired pressure is reached. The drive motor is started 0.5 s before the heating relays are activated. The torque vs time, and temperature vs time profiles throughout the entire run are measured, both at an acquisition speed of 200 points/s, on an electronic recorder and also digitized and stored for subsequent data processing. For experiments under vacuum the plastometer unit is enclosed in a pyrex chamber to allow direct observations of the hot stage during operation.
Typical results

Two types of temperature-time histories were employed in the study. **Holding temperature runs** consist of a constant heating rate to a final temperature which was then maintained constant for an extended period of time. **Constant heating-rate runs** refer to increasing the sample temperature at a constant rate for the duration of the experiment.

Experiments to date have employed a Pittsburgh Seam bituminous coal of 39% volatile matter and 63 - 75 μm particle diameter, vacuum dried at 383 K for 4 hours. The coal, which was from the same mine as the samples used previously in this laboratory by Suuberg (1977), Franklin (1980) and Anthony (1974), was freshly ground under nitrogen. Table 3.2.1. is a summary of proximate and ultimate analysis of the coal. Figures 3.2.5. and 3.2.6. present typical holding temperature run data obtained under 0.1 and 3.5 MPa of helium, respectively, at a disk rotational speed of 0.67 rpm (corresponding to an average shear rate of 1.32 s⁻¹). In the former run the coal was heated at 461 K/s to a final temperature of 874 K and then held at this temperature for 6.0 s. As the temperature increases, the torque decreased to a low value due to liquid formation. Following a period of low viscosity, the viscosity of the molten coal rises rather rapidly due to progressive resolidification of the melt. However, continued rotation of the disk eventually breaks up the resultant coke, and the torque vs time curve fluctuates but maintains an overall decrease. The stages of physical change of the coal are indicated in Figure 3.2.6. For present purposes the plastic period is arbitrarily defined as the interval during which the torque is less than
COAL STUDIED

Pittsburgh No. 8 Seam
High Volatile Bituminous Coal

Proximate analysis (wt.%, dry basis)

<table>
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<th>Moisture</th>
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<td>1.4</td>
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Ultimate analysis (wt.%, dry basis)

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<th>C</th>
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<th>O</th>
<th>N</th>
<th>S</th>
<th>Ash</th>
</tr>
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<tr>
<td>68.8</td>
<td>4.9</td>
<td>8.2</td>
<td>1.3</td>
<td>5.4</td>
<td>11.5</td>
</tr>
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+ as-received basis

Table 3.2.1 Characteristics of Coal Studied
Figure 3.2.5 Raw data from plastometer, in 1 atm of helium
Figure 3.2.6 Raw data from plastometer, in 35 atm of helium indicating different stages of plastic behavior
1.4 x 10^{-2} \text{ Nm} which correspond to a viscosity of $3.6 \times 10^4 \text{ Pa s}$.

The geometry of the shearing chamber can be approximated as two sets of parallel disks. The standard equation for a concentric rotating disk viscometer can then be employed to relate the observed torque $\tau$ to the apparent Newtonian viscosity $\eta$, for two sets of disks,

$$\eta = \frac{\tau / \pi R^3}{\dot{\gamma}_R} \quad (3.2.1)$$

where $\dot{\gamma}_R = \omega R/H$ is the shear rate at a disk radius of $R$, $\omega$ is the disk angular velocity, and $H$ is the distance between the parallel faces of the moving and fixed disks. A calibration factor $b$ is introduced to account for the deviation of the actual instrument geometry from two parallel disks. Thus

$$b = \frac{\eta_{\text{obs}}}{\eta_a} \quad (3.2.2)$$

where $\eta_{\text{obs}}$ is the viscosity calculated from the experimental values of torque using Equation (1), and $\eta_a$ is the true viscosity. The quantity $b$ is found using liquids of known viscosity (Cannon Instrument R450000) gives $b = 1.20$ at a shear rate $\dot{\gamma}_R = 1.98 \text{ s}^{-1}$. That $b$ exceeds unity is reasonable since the drag force experienced by the disk exceeds that expected from two sets of parallel disks due to the larger surface area of the bounding metal plates. At a shaft speed of 0.67 rpm (or $\dot{\gamma}_R = 1.98 \text{ s}^{-1}$), this calibration factor implies that an observed torque of $1.0 \times 10^{-2} \text{ Nm}$ is equivalent to a true apparent viscosity of $2.6 \times 10^4 \text{ Pa s}$.
For comparison purposes, plasticity curves for some other materials were also obtained. These included a heat treated coal tar, (which is a viscous liquid at room temperature), and a low melting point pitch,(Figure 3.2.8) and a non-softening Montana lignite, and quartz (Figure 3.2.7.). These materials show expected behavior in the plasticometer. The pitch softens very rapidly upon heating, then it starts to resolidify due to coke formation. The coal tar shows a constantly increasing viscosity due to coke formation, its increase being temperature dependent. Quartz particles do not soften and they offer high resistance to the rotating disk. The initial drop is probably due to a slight expansion of the shearing chamber. Montana lignite shows a decreasing torque value although it does not soften. The decrease is probably due to volume decrease upon pyrolysis. Several experiments with the same temperature-time histories were performed to test the reproducibility of the data (Figure 3.2.9.). The viscosity curves are quite reproduceable, especially the softening portion of the curves. The minima of the curves do show fluctuations, probably due to existence of some single non-softening macerals. The pitch softens rapidly due to its low melting point. Coal tar shows a slower resolidification to form a weak coke.

Since plasticity arises from the formation of liquid within the coal continuum, valuable complementary information can be obtained by determining the amount of liquid in a rapidly pyrolyzing coal particle. A technique for the quantitative study of intra-particle liquids formation and depletion reactions was therefore developed as described below.
Figure 3.2.7  Behavior of quartz and lignite in plastometer
Figure 3.2.8  Behavior of pitch, coal tar and bituminous coal in plastometer
Figure 3.2.9 Reproducibility of plasticity runs

Bituminous coal
Three runs all at
664 K/s to 1030K

Apparent viscosity $10^4$ Pa s
3.3 LIQUIDS FORMATION AND DEPLETION MEASUREMENT

Coal samples were pyrolyzed for different residence times using an electrical screen reactor and the liquid left in the solid residue after rapidly quenching the sample was determined by solvent extraction of the residue. The coal used was same as that studied in the plastometer.

Apparatus

The reactor (Figure 3.3.1.) was developed from the basic version of the one described by Anthony et al. (1974). Some important differences include a larger reactor volume and screen size. A much larger screen to sample weight ratio was employed to ensure a single particle coal layer during the experiments. This minimizes the possibility of extra-particle secondary reactions, and improves heat transfer to the particles. A special sample loading device was developed for uniform loading onto the screen. Addition of a liquid nitrogen quenching mechanism allowed precise control of the pyrolysis residence times. The electrodes holding the hot screen were spring-loaded to keep the screen flat upon heating. A more powerful 12 volt DC heating circuit with improved control electronics was installed. The reactor is designed for pyrolysis measurements at atmospheric pressure and also under vacuum. The reactor vessel is a cylindrical pyrex pipe 23 cm in diameter and 23 cm long. The top and bottom of the reactor are two 3/8 inch thick stainless steel plates, which are sealed to the reactor with O-rings. The bottom plate is equipped with electrical leads, thermocouple feed and gas inlet/oulet ports, and a liquid nitrogen
RAPID QUENCHING SCREEN REACTOR

Figure 3.3.1 Rapid quenching screen reactor

Pittsburgh seam bituminous coal
75 - 90 μm
in 1 atm helium
valve. About 15-20 mg of 75-90 um diameter particles were spread evenly in the central region of two layers of 10.5 x 5.3 cm, 400 mesh stainless steel screen mounted between two electrode blocks. The reactor is then closed and evacuated to 1 mm Hg, flushed two times with helium, and then helium is admitted to 0.85 atm absolute pressure. Heating was achieved by sequentially passing two constant pulses of electrical current of preselected duration and magnitude through the electrodes. The volatile products readily escaped from the screen and were quenched and diluted by the cold ambient gas at 0.85 atm. At the end of the preset heating interval, pressurized liquid nitrogen was sprayed onto the screen by automatically opening a cooling valve, resulting in a quenching rate of 1500 K/s. Other runs featured cooling rates exceeding 6000 K/s using a different valve, or less than 200 K/s when the screen was allowed to cool by natural convection. Figure 3.3.2. shows some temperature-time histories from thermocouple readings acquired at 200 data points/s.

The weight loss of the sample was determined by weighing the loaded screen before and after the experiment. This corresponded to the volatiles (tar, light oil and gases) yield. The extract yield was determined by 2 hour Soxhlet extraction of the char left on the screen using pyridine at its boiling point (116°C), drying the extracted char and screen in a vacuum oven at 110°C for four hours and reweighing. This quantity reflects the intra-particle inventory of liquids at the time of quenching. All yield data reported are based on a dry basis. Figure 3.3.3. shows the volatile yield, extract and pyridine insoluble plotted as a function of the heating time, for two different temperature histories.
**Screen reactor temperature history**

Figure 3.3.2 Screen reactor temperature histories

Vertical scale is two times thermocouple reading in mV
Horizontal scale is 0 - 10 seconds
Chromel-alumel thermocouple used
Corresponding to 660 - 670 K/s heating rate,
and holding temperatures 697 - 828 K, quenching at 4500 K/s
Wt. loss, pyridine extract & insol.

Figure 3.3.3  Weight loss, pyridine extract and insolubles yield of bituminous coal at different pyrolysis times
At the later stage of this thesis work, another new reactor was developed with the experience from the previous screen reactor. This reactor is a 1' x 1' x 2' plexiglass box with a hot stage in the center, surrounded by tar collection and liquid nitrogen quenching mechanisms (Figure 3.3.4.). New features include (1) plexiglass walls for photographic recording of experiment, (2) real-time collection of tar and light oil, (3) overall mass balance by collecting gas products is possible, (4) more powerful heating circuit for higher heating rates, (5) horizontal liquid nitrogen jet for sample quenching but preventing sample loss from the screen.

3.4 OTHER TECHNIQUES AND EXPERIMENTS

Better understanding of the reactions occurring within the coal can shed light on the fundamental mechanisms of coal plasticity. An important measurement is the molecular weight distribution of the extract as a function of the extent of pyrolysis. This was obtained by Gel Permeation Chromatography (GPC). A Waters Associates ALC/GPC 201 system with 500 Å and 100 Å µ-styrigel columns in series was employed. Figure 3.4.1. is a schematic of the GPC system. The basic system consists of a U6K injector, and M-45 pump and a model 440 UV detector. A Bascom Turner 4120T electronic recorder was used to digitize and store the detector output signals. Subsequent data manipulation to convert to molecular weight distributions were made on an IBM PC, and average molecular weights were calculated. The columns were calibrated with different size fractions of coal and wood tars. A linear calibration line
Figure 3.3.4  New box screen reactor
Figure 3.4.1  Schematic of Gel Permeation Chromatography system
was obtained (Oh, 1985; Boroson, 1985):

\[
\log MW = 4.086 - 0.0965V
\]

where \( V \) is the elution volume in ml. Pyridine is used as the carrier solvent for the molecular weight determination. The 500 Å column has an exclusion limit of 10,000 which is well above the values reported for coal tars in the literature (150 - 3000). The actual separation is done in the second column, which has the separation range of 2000 - 100 MW.

Reactions in the coal during the plastic phase were further studied employing a heat-treated coal tar as a model. This is a viscous liquid with initially 3 % weight fraction of pyridine insolubles. Phenomena such as volatiles escape, polymerization and cracking of the metaplast (an equivalent name for the liquid) in coal can be more readily studied from pyrolysis and plasticity measurement on this simpler system, since the initial liquid generation or softening step need not be considered, as compared to that of the bituminous coal. Some pyrolysis and extraction experiments for wood and lignite were performed and compared to bituminous coal data. To study the initial softening behavior of coals, some raw coal samples were pre-extracted and afterwards their plastic and pyrolysis behavior determined.

Mass transfer effects and secondary reactions were briefly investigated with a set of "foil" experiments. Sealed stainless steel foils (0.001 inch thickness) with samples inside were pyrolyzed in the screen reactor. The evaporation of material was suppressed, and volatiles
were trapped inside the foils and allowed to undergo secondary reactions. These experiments offer an approach for determining the relative contribution of evaporation, polymerization and cracking in softening coal pyrolysis.
CHAPTER 4. RESULTS OF EXPERIMENTS

Experimental results from different reactors are presented mainly in this section, although some preliminary data have also been presented in Chapter 3. Plastometer, screen heater results, pyrolysis of other materials and GPC data are presented in order.

4.1 PLASTOMETER RESULTS

Viscosity curves for the Pittsburgh Seam No. 8 coal as a function of heating time for different constant heating rate experiments, and different holding temperature experiments (Figure 4.1.1.) under 1 atm of helium are shown in Figures 4.1.2. and 4.1.3. For runs at different heating rates, the initial softening temperature, $T_s$, determined as the temperature when the initial drop of the torque is observed, was rather insensitive to the heating rate. Apparent viscosities measured were in the range of a few thousand to one million poises. The viscosity values are obtained from raw data (Figure 4.1.4.), which is torque vs time signal by calibration with viscosity standards, giving $1.0 \times 10^{-2} \text{ Nm} = 2.6 \times 10^4 \text{ Pa s}$.

Figure 4.1.5. is a plot of the plastic period (time when viscosity is less than $3.6 \times 10^5$ poise) against holding temperature for runs with 450 K/s heating rate. Figure 4.1.6. is the rate of increase/decrease of torque at the point in time when the torque = 2.0 oz-in. Since softening occurs mostly during the heating period, for the same heating
Temperature-time history

Holding temperature run

Constant heating-rate run

Figure 4.1.1  Temperature histories of plastometer runs
Figure 4.1.2  Viscosity curves for constant heating rate runs
Start heating at constant rates

Figure 4.1.3  Viscosity curves for holding temperature runs
Figure 4.1.4 Raw data for holding temperature runs
 Runs in 1 atm helium, Pittsburgh No. 8 coal

Figure 4.1.5 Plastic period for runs at 450 K/s to different holding temperatures
Figure 4.1.6  Rates of softening and resolidification for 450 K/s runs
rate, the softening rate is almost constant. The resolidification rate, however, increases rapidly with holding temperature and reaches an asymptotic value above 700 °C. The plastic period and the rate of softening at \( J = 2.0 \text{ Oz-in} \) are presented in Figures 4.1.7. and 4.1.8. respectively, for a series of constant heating rate runs.

Some runs were made under 0.05 torr of ambient helium atmosphere, and some under 35 atm of hydrogen or helium (Figure 4.1.9). Comparison with 1 atm data shows that the plastic period is shorter for runs in vacuum or 35 atm pressure and holding temperatures less than 650°C. Above 650°C, there is no clear effect of inert gas or hydrogen pressure on the plastic period, as shown in Figure 4.1.9. While the softening rate is about the same as in the 1 atm case, the resolidification rates for both the vacuum and 35 atm runs are higher for holding temperatures less than 600°C (Figure 4.1.10.). Above 600°C, their difference is small. Runs under 35 atm of helium or hydrogen give virtually the same plastic behavior, implying no major effect of hydrogen under these conditions.

The effect of pre-extraction of the raw coal sample on its plasticity is shown in Figure 4.1.11. Also shown in Figures 3.2.7. and 3.2.8. are the different behavior of other materials in the plastometer, note especially coal tar and pitch.

The apparent viscosities measured reflect the resistance to shear of a complex, reacting suspension of partially reacted coal, mineral matter and coke in a polymerizing and cracking viscous liquid. Description of the rheological properties of this system in fundamental terms is
Figure 4.1.7 Plastic period at different heating rates

![Plastic period graph]

- ATM HELIUM
- CONSTANT RATE OF HEATING
- FIGURES 840, 860°C ARE HOLDING TEMPERATURES REACHED

Figure 4.1.8 Softening rate at different heating rates

![Softening rate graph]
* Time interval when viscosity is less than $3.6 \times 10^4$ Pa s

Figure 4.1.9  Effects of pressure on plastic period
Figure 4.1.10  Resolidification rates at different ambient pressures
Figure 4.1.11  Effects of extraction on plasticity
difficult. However, one can relate the relative viscosity of this suspension to the solids volume fraction, and hence to the liquids formation and depletion kinetics in the coal. The existence of bubbles in the melt has to be taken into account when such a correlation is made. Therefore, the interpretation of these plasticity curves is more difficult than those for less complex, non-reacting liquid/solid suspensions. A direct method to determine the liquid content of pyrolyzing coal particle is obtained from the screen reactor.

4.2 SCREEN REACTOR DATA

Figures 3.3.3. shows the evolution of the volatiles, pyridine extracts, and the pyridine insoluble char as a function of the heating time, for four sets of experiments with rapid quenching. The corresponding temperature-time histories for each set are also shown.

An extractables yield of about 25 % was obtained from the raw coal. As the coal was heated, the amount of extract increased to a maximum and then decreased, the rate of this process being strongly dependent on temperature, as indicated in Figure 4.2.1. The time interval over which the extract concentration was high (> 30 wt % of coal) decreased rapidly with increasing final holding temperatures of the experiments. The first order depletion rate constants for the extracts are indicated. The maximum amount of fluid material (extract plus volatiles) was as high as 80 % by weight of the raw coal. However, this quantity decreased with increasing holding temperature, or with increasing time at a given holding temperature, primarily due to conversion of
Figure 4.2.1 Pyridine extractables generation and depletion at different temperatures

(heating rate, holding temperature, cooling rate)

(470, 813, 1100)
(446, 858, 1100)
(514, 992, 1100)
the extractables to coke.

Figure 4.2.2. is an Arrhenius plot of the first order depletion rate constants of Figure 4.2.1. A global activation energy of 42.2 Kcal/mole is obtained. Figure 4.2.3. shows the total amount of transportable material (extract + volatiles) for different temperature-time histories.

The effect of pre-extracting the raw coal sample on its pyrolysis behavior is shown in Figure 4.2.4. for two different temperature-time histories. For the pyridine pre-extracted sample (25% of extract removed from raw coal sample), the yield of extracts is much less. Pretreating the coal particles with tetralin (coal soaked in tetralin with 4.8% weight gain) does not change the mass rate of extract generation significantly but does prolong the extract survival as seen in Figure 4.2.5. This may reflect partial hydrogenation of metaplast by the tetralin resulting in a somewhat more thermally stable extract.

4.3 PYROLYSIS OF OTHER MATERIALS

For comparing the plastic behavior and related extract generation/destruction kinetics, pyrolysis on the stainless screen of lignite, which is a non-softening material, and wood, which is a slightly caking sweet-gum wood were also studied. Particles size used were 63-75 µm, and 90-105 µm respectively. Figure 4.3.1. shows the evolution of the volatiles, pyridine extracts and the pyridine insoluble char as a function of heating time. All samples were heated at 736 K/s to 555°C and allowed
Arrhenius plot for extract depletion rate constant

Figure 4.2.2 Arrhenius plot for extract depletion rate constant
Figure 4.2.3 Yield of pyridine extract + volatiles at different temperature histories
Figure 4.2.4 Comparison of pyridine extracts for chars from raw bituminous coal and pyridine pre-extracted coal
Holding Temperature 626°C, heating rate 2000 K/s
cooling rate 4500 K/s

Figure 4.2.5 Comparison of pyridine extracts for raw bituminous coal, tetralin soaked coal, and pyridine pre-extracted coal
Figure 4.3.1a-c Volatiles, pyridine extractables and insolubles yield for (a) wood, (b) bituminous coal, and (c) lignite as functions of pyrolysis time.
to cool by natural convection in the screen reactor. Figure 4.3.2. is a comparison of the amount of extracts of bituminous coal, wood and lignite, all subjected to the same temperature time history. In Figure 4.3.2. the samples are cooled by natural convection. Note a smaller amount of liquid was generated in the bituminous coal than in the rapid quenching experiments. These results offer an interesting comparison with the basic data for bituminous coal.

A test material exhibiting chemical and physical properties similar to those of the intermediate liquid metaplast generated during the pyrolysis of softening coal, is an industrial coal tar from bituminous coal. The coal tar studied is a heat treated tar with initially 3% of pyridine insolubles. Subsequent reactions of the metaplast after softening of the bituminous coal can be studied by observing the pyrolysis behavior of the coal tar in the screen reactor. The advantage of this system is that the complex softening step (initial liquid generation step) need not be considered. Therefore the starting material already has well defined properties (molecular weight distribution and solids content) and their pyrolysis behavior would not be obscured by softening reactions. Some detailed experiments were performed. Figures 4.3.3. and 4.3.4. show the weight loss, pyridine extracts and pyridine insoluble char as a function of pyrolysis-time, for different holding temperatures and heating rates. This phase of work is conducted in collaboration with Dr. Jean-Louis Saint-Romain.
Samples heated at 736 K/s to 555°C and allowed to cool by convection

Figure 4.3.2 Pyridine extractables for different materials
Figure 4.3.3  Pyrolysis of a heat-treated tar

Heating rate 455 K/s
Holding Temp 1022 K
Cooling rate 4500 K/s
Figure 4.3.4 Pyrolysis of a heat treated coal tar (Saint-Romain, 1985)

A - weight loss of sample
B - pyridine extractable portion of material left on screen
C - pyridine insoluble portion of material left on screen
4.4 GPC DATA

The molecular weight distribution of the pyridine extracts were determined for bituminous coal, coal tar and wood at different extents of pyrolysis. Figures 4.4.1. to 4.4.3. show a few GPC curves (concentration vs elution volume) at different pyrolysis times. Different raw materials show different molecular weights and distributions reflecting their structural differences in their pyridine extractables (Figure 4.4.1.). The molecular weight is related to the elution volume \( V \) by the equation

\[
\log(MW) = -0.0965 \times V + 4.184
\]

obtained from a linear calibration method from different size fractions of coal tars (Oh, 1985, Boroson, 1985). The data were also transformed and normalized with respect to the total weight of extract in Figures 4.4.4. and 4.4.5. Hence, the distance between the distribution curves at two different pyrolysis times indicates the amount of material generated or lost during the time interval. Changes in the moments of MWD, such as number and weight averaged molecular weights are shown in Figures 4.4.6. and 4.4.7. (Saint Romain, 1985) For both bituminous coal and coal tar pyrolysis, the extract average molecular weights increased to a maximum and then decreased, as a result of polymerization, evaporation and cracking reactions.

4.5 OTHER EXPERIMENTS

A few "foil" experiments were designed to study the effects of
Figure 4.4.1  Raw GPC curves for bituminous coal, wood and lignite pyridine extract
Figure 4.4.2a–c Raw GPC curves for pyridine extract of bituminous coal pyrolyzed to (a) 555°C, (b) 658°C and (c) 749°C
Figure 4.4.3  GPC curves for pyridine extracts of different materials at different pyrolysis times.
Figure 4.4.4a,b Normalized molecular weight distributions of pyridine extracts at different pyrolysis times for bituminous coal.
Figure 4.4.5a,b Normalized molecular weight distributions of pyridine extracts at different pyrolysis times for coal tar
Holding temperatures indicated on curves

- △ heating rate 465 K/s
- ■ heating rate 455 K/s
- ○ heating rate 736 K/s, natural cooling

Figure 4.4.6 Changes in average molecular weights for bituminous coal and heat treated coal tar
Figure 4.4.7 Changes of extract weight and number averaged molecular weights during pyrolysis of a heat treated coal tar. Temperature histories are the same as in Figure 4.3.4 (Saint-Romain, 1985)
external mass transfer and secondary reactions on plasticity and pyrolysis. By trapping the volatiles in the foil, secondary reactions of those volatiles were promoted. For the pyrolysis of the heat treated coal tar, a pyridine insolubles yield exceeding 40 % was obtained vs the 29 % obtained in screen experiments, for the pyrolysis of coal tar at around 1000 K. This increase was observed at high temperatures above 950 K.
CHAPTER 5. DISCUSSION OF EXPERIMENTAL RESULTS

The mechanism of plasticity in coals is not well understood for rapid heating and high temperature conditions. This present study of plasticity at rapid heating, high temperature conditions is the first systematic approach attempted. Plasticity and related phenomena such as swelling and agglomeration are direct consequences of intra-particle liquid plasticizer formation by heating. The present study shows that physical melting of part of the coal first occurs when the temperature is sufficiently high to release mobile materials by overcoming weak bonds. Subsequent pyrolytic bond breaking generates additional liquid at more severe conditions. At the same time, liquid is lost through escape from the particle, and through repolymerization and cracking reactions to form light gases and solids inside the liquid phase.

As shown in Figure 5.1., or by a comparison of plasticity data and intra-particle liquid formation and depletion data in Figures 4.1.3. and 4.2.1., the respective times for initial generation and near final depletion of extractables within the coal corresponds well with the time for initiation and termination of the coal's plastic phase. This supports our assumption that the pyridine extract of the rapidly quenched coal is a reasonably accurate measure of the amount of liquid product within the pyrolyzing coal at the time of quenching.

However, 25 wt % of the raw unpyrolyzed coal can be extracted by pyridine, yet the unpyrolyzed coal contains no liquids at room temperature. It is quite likely that the initial 25 % extract corresponds
Figure 5.1a Comparison of viscosity and extract data

IN 0.1 MPa HELIUM

HOLDING TEMPERATURE
- 910 K
- 855 K

Extract yield, wt. % raw coal

Apparent viscosity (10^4 Pas)

Start heating at ~ 450Ks⁻¹
Figure 5.1b Comparison of viscosity and pyridine insolubles, extracts growth for the higher temperature case in Figure 5.1a
to some loosely bonded, low melting point material. Upon heating to a sufficiently high temperature, this material undergoes physical melting and causes initial softening of the coal. Our observation with the plastometer that initial softening occurs around 570 K independent of heating rate (50–700 K, Figure 4.1.2.) is consistent with the above hypothesis. If this initial 25% of material is pre-extracted, and afterwards the coal is subjected to pyrolysis, the extract is less and the time duration of a high liquid content inside the coal is shorter (Figure 4.2.4.). The pre-extracted coal is expected to soften at a later time (higher temperature), and the duration of plasticity is shorter, as is observed in Figure 4.1.11. Other workers found the Gieseler plasticity (low heating rate type experiments) during the early softening stage to be reversible as the temperature is raised or lowered. Again, this supports the picture that some part of the liquid is formed by physical melting.

At higher temperatures, pyrolytic bond breaking generates significant quantities of intra-particle liquids which cannot be reversibly converted back to resolidified coal. The maximum yields of extractables from the coal studied can be as high as 80% daf. In similar screen heating experiments on a lignite, which does not soften, almost no extract was obtained from the residual char on the screens. Similarly, only a small extract yield up to 7% was observed in the pyrolysis of wood (Figure 4.3.2.). This wood exhibits slight caking behavior during pyrolysis in a fixed bed reactor (Boroson, 1985). Thus plasticity behavior is well reflected by the amount of intra-particle liquid content during pyrolysis.
The wood or lignite pyrolyzed at a much faster rate than the bituminous coal (Figure 4.3.1), reflecting the structural difference of the fuels (they are more aliphatic than the bituminous coal in chemical composition, and they remain more or less a porous solid during pyrolysis, offering less resistance to products escape). It is possible that biomass, lignite and low rank coals may still undergo an initial conversion to very high yields of potentially transportable liquid intermediates. However, these liquids may be much more reactive than those from high rank coals, and thus are removed by polymerization within the sample, and transport away from the sample in times so short that they escape detection by the char extraction technique.

Although internal mass transfer resistance predominates the external mass transfer resistance for bituminous coal pyrolysis under the experimental conditions studied in the screen heater (Oh, 1985), in a closed system, liquids may have a longer survival time before they undergo further reactions such as polymerization or cracking. The foil experiments for a heat treated coal tar indeed showed more liquids are retained than in open screen pyrolysis (more solids are formed, too) due to trapping of volatiles. In Figures 5.1a,b, the plasticity curve from the plastometer at the higher temperature has a longer duration of low viscosity than the duration for a high pyridine extract. This probably reflects the transfer resistance to volatiles escape from the plastometer, which is a semi-open chamber. At very rapid heating rates ($10^4$ K/s) or high temperatures, then it may be more appropriate to infer the plasticity from data on pyridine extract generation/depletion kinetics.
from the screen heater reactor than the fast response plastometer.

Another clear manifestation of the resolidification reactions of softened bituminous coal at longer holding times and higher temperatures is the corresponding increase in the yield of pyridine insolubles. Studies of the pyrolysis behavior of the heat-treated coal tar using the screen reactor showed similar evidence of the competition between coke formation via polymerization, cracking, and volatiles escape via transport away from the reacting substrate (Figure 4.3.4.).

However, differences in plasticity are expected between tar, pitch and bituminous coal (Figure 3.2.8.) since the raw tar is already a viscous liquid containing 97% pyridine solubles, and the pitch is a solid with a low softening point at 342 K. The bituminous coal requires that a minimum inventory of liquids capable of initiating and sustaining plasticity throughout a reacting, three-phase suspension be available within the coal matrix. Generation of this liquid requires that at least some melting or bonding breaking precede the onset of plasticity. A further complication is that heterogeneous reactions of these plasticizing agents may be more significant for the coal due to its higher content of char (pyridine insolubles) or higher cracking reactivity of this char (Serio, 1984). This may explain the higher ultimate yields of pyridine insolubles in coal than in coal tar, 56% vs 28% respectively, and is consistent with the fact that the resolidification rates for the coal tar or pitch are slower than for bituminous coal (Figure 3.2.8.).

It is thus clear that better understanding of the reactions
occurring within the coal can shed light on the underlying mechanisms of coal plasticity. An important measurement is the molecular weight distribution (MWD) of the extract as a function of the extent of pyrolysis.

The trends for extract average molecular weight evolution are strong functions of temperature-time history. In general, with increasing time at a given holding temperature, the molecular weight increases to a very well defined maximum, and then decreases (Figures 4.4.6. and 4.4.7.). Figure 4.4.4. shows that besides formation of pyridine insolubles, some heavier molecular weight material are formed (1.20 s and 3.00 s in Figure 4.4.4a, and 1.10 s in Figure 4.4.4b) at intermediate times. These high molecular weight materials are probably intermediate products in the solid formation reaction by polymerization. The decrease arises from cracking of the liquids since further generation of low molecular weight liquids by primary decomposition of the parent coal is no longer possible at these severities. At higher holding temperatures, more severe cracking drives the molecular weight to even lower values. The maxima of these curves are thus determined by competition between evaporation, polymerization, and cracking reactions. At small heating times (0.8 s in Figure 4.4.4b.), the extract molecular weight distribution from the quenched char is identical to that of the extract of unsoftened coal at 0.5s, while the coal has already become plastic from plastometer studies. This supports our hypothesis that initial softening is due to physical melting of part of the coal corresponding to the raw coal extract.

The rate of cooling in the experiments may also affect the
molecular weights (Figure 4.4.6.) and extract amount (compare Figures 4.2.1. and 4.3.2.). A slow-cooling rate experiment allows more time for lighter volatiles to escape, hence the molecular weights tend to be higher, and liquid yield less than those in rapid quenching experiments. Also, the heavier molecules in the liquid may have more time to realign themselves to form pyridine insolubles.

The molecular weight of the bituminous coal extract is much higher than that for the coal tar extract, or for wood and lignite extracts (Figure 4.4.6.). This probably reflects two differences expected in their thermal behavior because of differences in their structure and initial state. Cracking and repolymerization of the high molecular weight coal extract especially in the presence of surfaces of unsoftened macerals and already available coke can give more residual coke and high molecular weight coke precursors. A larger liquid molecule also has a lower vapor pressure, and thus a slower evaporation rate, and thus has more chance to form pyridine insolubles in the liquid state. Both are consistent with the lower pyridine insolubles yield and the faster evaporation rate observed in the coal tar pyrolysis.

Plasticity mechanism inferred from this study suggest the following points regarding the behavior of a coal particle during heating:

(1) Initial softening at low temperature is due to physical melting.
(2) Further generation of liquids is by pyrolytic bond breaking, associated with the release of gases and tar from coal.
(3) Liquid depletion is associated with the growth of pyridine insoluble material or solids (from extract yield and plasticity curves), and the cracking reactions (from decreasing molecular weights), and tar transport away from coal.

(4) A substantial weight fraction of softening coal is transformed into intermediate liquids in the plastic coal before these liquids are depleted by the above pathways.

(5) The structure and molecular weight of these liquids influence their devolatilization behavior and reactivity in polymerization and cracking reactions. Competition among these processes in turn can determine the observed yields, quality, and overall generation rate of devolatilization liquids and gases.

(6) For conditions where external mass transport is, or is made to become rate limiting in intra-particle liquids depletion, then plasticity can be modified by changing the mass transfer for liquids escape (foil experiments). Pretreatment of the raw coal (pre-extraction runs), and manipulation of intra-particle mass transfer rates can also change plasticity.

(7) Solvent extraction of rapidly quenched char is a promising technique to determine plasticity at the higher ranges of heating rate and temperature (such as combustion conditions) where direct measurements even with the present plastometer would be difficult.
The following schematic for plasticity mechanism is proposed:

![Schematic of plasticity mechanism](image)

This picture is also consistent with the above points as well as the observed pressure effects on vacuum or high pressure pyrolysis (Suuberg, 1977). High tar yields in vacuum pyrolysis is due to rapid transport of tar away from coal, and this also reduces the plastic period (Figure 4.1.9.). Under high pressures, tar diffusion is suppressed, gas yield increases and according to the above picture, solids yields will also be higher because of augmented time for repolymerization. Hence a shorter plastic period is expected and found. Therefore, an optimum pressure for maximum plasticity would exist for rapid-heating, high temperature conditions. The effect of pressure on the polymerization step is not clear. Effects of hydrogen or hydrogen donors in this reaction certainly is of practical interest. However, under the range of heating rate and reaction times studied, no difference in the plastic behavior was observed for experiments in 35 atm of hydrogen or 35 atm helium. Pre-treating the coal particles with tetralin does not change the mass rate
of extraction but does prolong the survival of extract. This may reflect partial hydrogenation of metaplast by the tetralin resulting in a somewhat more thermally stable extract.

In the case of pyrolysis of coal tar, a similar scheme can be proposed.

\[
\begin{align*}
&\text{transport} \\
&\hspace{1cm} \text{tar} \\
&\hspace{2cm} \text{polymerization} \\
&\hspace{3cm} \text{heavier} \\
&\hspace{4cm} \text{tar} \\
&\hspace{5cm} + \\
&\hspace{6cm} \text{coke} \\
\end{align*}
\begin{align*}
&\hspace{1cm} \text{tar vapor} \\
&\hspace{2cm} \text{cracking} \\
&\hspace{3cm} \text{gas + coke}
\end{align*}
\]
CHAPTER 6. MATHEMATICAL MODELING

6.1 COAL PLASTICITY KINETICS

The apparent viscosity data are first fitted with the simple first order kinetic scheme of Fitzgerald (1956):

\[ \text{coal} \rightarrow_{k_1} \text{metaplast} \rightarrow_{k_2} \text{coke} \]

The term metaplast refers to the intraparticle liquid content M. Apparent viscosity \( \mu \) is related to the viscosity of the solids free liquid \( \mu^* \) by a concentrated suspension model (Frankel and Acrivos, 1967)

\[ \frac{\mu}{\mu^*} = \frac{9/8}{(1 - M)^{-1/3} - 1} \]  

(6.1.1)

At a late stage of resolidification, the rate of increase of \( \log(\text{viscosity}) \) is approximately

\[ \frac{d\ln \mu}{dt} = k_2 \]  

(6.1.2)

Thus \( k_2 \) can be found from experimental resolidification rates. Values of \( \mu^* \) are estimated from Nazem's work (1980) on carbonaceous mesophase pitch (average value taken, 1200 poise). The parameter \( k_1 \) is then obtained by fitting data for the plastic period. Figure 6.1.1. shows calculated viscosity curves, and calculated plastic periods vs experimental values for 450 K/s holding temperature runs.
Figure 6.1.1  Calculated viscosity curves for 450 K/s heating rate to different holding temperatures, and comparison with observed plastic period (solid circles)

\[ K_1 = 245 \exp(-\frac{4900}{T}), \text{S}^{-1} \]
\[ K_2 = 2 \times 10^8 \exp(-\frac{16350}{T}), \text{S}^{-1} \]
However, the Fitzgerald kinetic scheme does not fit runs at different heating rates, because physical melting of part of the coal is not taken into account.

The plasticity mechanism presented in Chapter 5 is a starting point for a more realistic model. Both primary bond breaking and physical melting are important in coal softening. Coke formation in the primary reaction can be neglected as a first approximation since most of the organic material of the coal passes through the liquid phase, (i.e., the non-softening macerals such as fusinite and inertinite are a small fraction of the total mass) although in lower rank coals it should be considered. Polymerization in the liquid phase can result in a higher liquid viscosity, even if no solids are formed. At higher temperatures, (> 658°C, compare 555°C and 658°C, Figures 4.4.4.a,b) cracking predominates over polymerization. For this reason, and because the detailed MWD information required for a quantitative model is not available, polymerization kinetics in the liquid phase is not modelled. Both tar escape and cracking are pathways to resolidification. High pressure or closed reactor geometry can prevent tar evaporation. Since no individual tar or gas species were collected in the present study, both tar escape and cracking are lumped into one reaction with volatiles (tar and gas that leaves the particle) and coke as products. Further reaction between intraparticle liquid and coke or mineral matter are not considered.

Here the global model assumes the coal to undergo both physical
melting and pyrolytic bond breaking to form an intermediate liquid in a suspension of unsoftened coal, coke and inert mineral matter. The liquid forms a volatile product which, according to the model, escapes from the coal infinitely rapidly, and leaves a solid coke. The weight ratio of coke to volatiles thus formed is assumed to be constant (= a). The initial 25% pyridine extract from raw coal is assumed to be the maximum that can be obtained without chemical decomposition of the initial structure, and is generated by physical melting. This material is assumed to melt over a narrow range of temperatures. To account for melting, a gaussian distribution of melting points with a mean at 623 K and a standard deviation of 30 K are assumed in the calculations. These values reflect the range of the initial softening temperatures of coals (Read et al., 1985; Rees and Pierron, 1954). The rate of generation of liquids by melting alone would therefore be the product of the heating rate and this distribution function. The mineral matter (wt. fraction \( f_a \) = 0.13 for the coal studied, Franklin, 1980) is assumed to be inert. The reaction scheme and corresponding rate expressions based on weight fractions of the raw coal (moisture free, mineral matter containing basis) are

\[
\begin{align*}
&\text{coal} \quad \longrightarrow \quad \text{intermediate liquid} \quad \longrightarrow \quad \text{volatiles + coke} \\
&\text{melting}
\end{align*}
\]

\[
\begin{align*}
\frac{dC}{dt} &= -k_1 \left( C - f_a \right) - r_m \\
\frac{dM}{dt} &= k_1 \left( C - f_a \right) + r_m - k_2 M \quad \text{(6.1.3)} \\
\frac{dV}{dt} &= k_2 M \left( \frac{1}{1 + a} \right) \\
\frac{dE}{dt} &= k_2 M \left( \frac{a}{1 + a} \right)
\end{align*}
\]
where C, M, V and E are the weight fractions of the unsoftened coal, liquid, volatiles and coke, respectively, and \( r_m \) is the rate of physical melting, given by the product of heating rate and the melting point distribution function.

The model is first applied to intraparticle liquid formation and depletion data from the screen reactor. At a late stage of pyrolysis, when most of the coal has reacted \((C - f_a = 0)\) and all the material that can physically melt has done so \((r_m = 0)\), the rate of liquid depletion is

\[
\frac{dM}{dt} = -k_2 M
\]  

(6.1.4)

The rate constant \( k_2 \) can thus be found from a plot of \( \ln(M) \) vs time for constant temperatures. Typical values thus obtained are shown in Figure 4.2.1. An Arrhenius plot gives an activation energy of 42.2 Kcal/mole, and \( k_2 \) is found to be

\[
k_2 = 1.9 \times 10^{10} \exp \left( -21200/T \right), \text{s}^{-1}
\]  

(6.1.5)

The rate constant \( k_1 \) was obtained from a best fit to the experimental data, using values of \( k_2 \) already found. The result was

\[
k_1 = 6.6 \times 10^7 \exp \left( -14500/T \right), \text{s}^{-1}
\]  

(6.1.6)

Figure 6.1.2. gives values of pyridine insolubles and extractables, (corresponding to \( C + E \) and \( M \) respectively) observed in the
Figure 6.1.2  Calculated vs experimental volatiles, pyridine extract, and insolubles yield for two temperature histories
experiments and corresponding model predictions (solid lines), using an "a" value of 1.25 (obtained from long holding time data) for two sets of reaction conditions.

To calculate the apparent viscosities, Equation 6.1.1 is again used with the present scheme and rate constants in Equations 6.1.5 and 6.1.6. Figure 6.1.3 shows calculations corresponding to the experimental conditions and lab results presented in Figures 4.1.2. and 4.1.3. The rate constants obtained from the screen reactor describe constant heating rate plastometer runs well but underpredict viscosity for 450 K/s runs at low holding temperatures. Three possible reasons are (a) the polymerization in the liquid phase is neglected, which can affect the solids free viscosity μ*, (b) resistance to volatiles escape can exist in the plastometer, and (c) μ* is assumed independent of temperature.

If the solids free viscosity μ* is assumed to be proportional to a positive power of the intraparticle liquid weight average molecular weight, as in polymer melts, then from Figure 4.4.4. the lower temperature runs would have a higher viscosity than predicted since the liquid has higher average molecular weights. Temperature variation of μ* is correlated by the Andrade equation with an activation energy of 38 Kcal/mole (Bhatia et al., 1985). However, the expression is not valid over a wide range of temperatures, and the resulting fit is not improved. If the rate constant k1 is retained (because little volatiles are formed during early softening) and k2 allowed to vary, then k2 = 8 x 10^6 exp(-14000/T)s^-1 fits the data well (Figure 6.1.4.). A lower activation energy is consistent with mass transfer resistance to volatiles escape from the plastometer.
Figure 6.1.3  Calculated viscosity curves for conditions of Figures 11 and 12, with liquid formation and depletion rate constants (Eq. 6.1.5, 6.1.6)
Figure 6.1.4 Calculated viscosity curves for conditions of Figures 11 and 12, with $k_2$ fitted
Therefore both polymerization at lower temperatures and resistance to volatiles escape cannot be ruled out.

6.2 MODELING OF COAL PARTICLE AGGLOMERATION

Heating regimes of practical interest cause many bituminous coals to soften. As a result, pyrolyzing particles can swell and form agglomerates under selected contacting conditions. Softening, swelling and agglomeration can result in desired or unwanted effects in coal utilization. For example, stable agglomerate formation is critical to obtaining a mechanically strong product in metallurgical coke manufacture. Conversely, agglomerate buildup in fluidized-, entrained-, and fixed- (more properly moving-) bed gasifiers or combustors can degrade process operability by bed bogging, defluidization, plugging of chambers and transfer lines, and erosion of refractories and heat transfer surfaces. Lightman and Street (1968) observed coal agglomerates in the combustion of pulverized coal in large flames.

Few studies on the agglomeration kinetics of softening coal have been reported in the literature. Klose and Lent (1984) investigated agglomeration of stationary particles at low heating rates (2.5 - 6 K/min) and final temperatures (around 520 C) and modelled their results in terms of a viscous sintering mechanism. Their study is pertinent to low temperature coal carbonization processes. Tyler (1979, 1980) and McCarthy (1980) measured extents of coal agglomeration due to flash pyrolysis in a laboratory scale fluidized bed and an entrained flow reactor, respective-
ly. Scharff et al. (1981) developed a detailed coal agglomeration model based on surface binding energies for the particle aggregates. However, none of these studies has treated plasticity and agglomeration kinetics in such a way that their influence on pulverized coal combustion can be predicted.

The essential features of the agglomeration model are presented by first treating the case of formation of an agglomerate by collision of two spherical particles of softening coal of constant radii, \( a \). Extensions to generation of larger multi-particle agglomerates and to account for particle swelling are then presented.

(A) Two single particles agglomerating in isotropic turbulence

For a system initially composed solely of single spherical particles of radius \( a \), agglomeration is modeled by assuming there are only binary collisions of single particles to form two-particle agglomerates (Figure 6.2.1) at a rate per unit volume of,

\[
\frac{dn}{dt} = -K_c \xi n^2 \tag{6.2.1}
\]

where \( K_c \) is the collision constant, \( \xi \) the probability of forming an agglomerate per collision, and \( n \) the number of single particles per unit volume at any time \( t \). The particles are assumed to be entrained in an isotropic turbulent flow field. For the particle size and turbulent intensity ranges in this study, the particles are much smaller than the Kolmogorov microscale of turbulence. Permanent sticking of two particles
Figure 6.2.1  A pair of agglomerated particles
to form an agglomerate is proposed to occur in the following sequence:

(1) After Saffman and Turner (1956), particles collide with a dimensional collision constant, $K_C$

$$K_C = 10.4 \frac{a^3 \sqrt{\varepsilon_0}}{v} \quad (6.2.2)$$

where $\varepsilon_0$ is the turbulent energy dissipation rate per unit volume, and $v$ is the kinematic viscosity of the entrainment gas.

(2) In reality, the particles are irregularly shaped. Thus, two particles may approach at many different orientations resulting in a large number of possible contact areas. For simplicity, this is dealt with by assuming each two-particle agglomerate consists of two distorted spheres of radii $a$, joined by a neck of diameter $2x$. A range of possible collision contact areas is treated by introducing a dimensionless neck radius, defined as $x/a$, and further assuming that quantity is normally distributed with a mean $\overline{\sigma}_1$ and a standard deviation $\sigma$. 

(3) The strength of the neck region $\sigma_m$ at the instant when a potential agglomerate is formed, is assumed to be

$$\sigma_m = \sigma_0 M(t) \quad (6.2.3)$$

where $\sigma_0$ is an empirical constant and $M$ is the time-dependent weight fraction of liquid plasticizer in the coal (i.e. only the liquid
portion of the contacting surface is assumed to adhere effectively).

(4) Among the different stresses imposed by the flow field on a fused pair of particles (Figure 6.2.1) of radii $a$, the maximum stress is the bending stress $\sigma_b$ (Yoshida et al., 1979),

$$\sigma_b = 10.8 \mu / \varepsilon_0 / \nu / c_1^3 \quad (6.2.4)$$

where $\nu$ is the viscosity of the carrier gas.

(5) If the bending stress is larger than the strength of the bonding neck region, no agglomeration will take place, i.e. $\xi = 0$, otherwise $\xi = 1$. Thus from Eqs. 6.2.3 and 6.2.4, successful agglomeration collisions will only occur for

$$c_1 > 2.21(\mu / \sigma_0 M)^{1/3} (\varepsilon_0 / \nu)^{1/6} = c_1^* \quad (6.2.5)$$

(6) For any temperature–time history of the agglomerating coal particles, their instantaneous metaplast content $M(t)$ can be calculated from the global kinetic model for liquid generation and depletion as described in Section 6.1.

(7) In practice the neck radius cannot exceed the particle radius, so the result in Equation 6.2.5 complies with
\[
\xi(c_1) = 0 \quad 0 < c_1 < c_1^* \quad (6.2.6)
\]
\[
\xi(c_1) = 1 \quad c_1 < c_1^* < 1.0
\]
These constraints are included in the agglomeration kinetics by replacing in Eq. 6.2.1 with an effective probability of forming a successful agglomerate \(\xi(t)\), obtained by averaging \(\xi(c_1)\) over all allowed values of \(c_1\). Since the probability of having a given value of \(c_1\) is described by a continuous distribution function, and since the collision times are much smaller than the plastic period, the required averaging can be performed as an integral.

\[
\xi(t) = \int_{c_1^*}^{1.0} P(c_1) \xi(c_1) dc_1
\]

and using Equation 6.2.6

\[
\xi(t) = \frac{1}{\sqrt{2\pi} \delta} \int_{c_1^*}^{1.0} \exp \left( -\frac{(c_1 - c_1^*)^2}{2 \delta^2} \right) dc_1
\]

where \(P(c_1)\) is the normalized gaussian distribution function for \(c_1\) values. The quantity \(\xi(t)\) is time and flow field dependent because the lower limit of the integral depends on \(M\), and on \(\varepsilon_0/v\) (Eq. 6.2.5)

Thus for a given turbulent energy dissipation rate and initial number density of coal particles, the binary agglomeration equation can be solved by substituting Eqs. 6.2.2, 6.2.5, 6.2.8, into Eq. 6.2.1.

(B) Multiple agglomeration process

The preceding discussion is for agglomeration of two single particl-
es of equal radii. In reality, two-particle agglomerates can grow larger by colliding with other single particles or agglomerates. The process can be expressed as:

$$A_i + A_j \rightarrow A_{i+j}$$  \hspace{1cm} (6.2.9)

where $A_j$ are the $j$-particle agglomerates with a population density $n_j$. Assuming no agglomerates breakup after permanent agglomerates are formed and neglecting particle loss due to adherance to the reactor walls, the formation rate of $A_j$ is:

$$\frac{dn_j}{dt} = \frac{1}{2} \sum_{i=1}^{j-1} K_{i,j} n_i n_{j-i} - \sum_{i=1}^{N-j} K_{i,j} n_i n_j$$  \hspace{1cm} (6.2.10)

where $K_{i,j}$ is the overall agglomeration constant, i.e. the product of collision frequency $K_c$, and probability of forming an agglomerate per collision, $\xi(t)$, for the agglomeration of $A_i$ and $A_j$. For computation purpose, a maximum agglomerate size of ten single particles sticking together is allowed in the present calculations. It is assumed that all $j$-particle agglomerates are spherical and related to the initial single particle radius by

$$a_j = a_0(j)^{1/3}$$  \hspace{1cm} (6.2.11)

The collision constant $K_c$ for $A_i$ with $A_j$ is (Saffman and Turner, 1956)
The quantity \( \xi(t) \) is still given by Eq. 6.2.8 assuming the distribution of \( c_1 \) values is unchanged.

(C) **Effect of particle swelling**

Significant swelling of softened bituminous coal particles can occur during rapid pyrolysis due to expansion of the plastic coal mass by pyrolysis-derived vapors. This changes the collision cross section of the particles. To account for swelling, a single volatile bubble is assumed to grow in a viscous, spherical droplet. Defining \( Q \) as the ratio of particle radius at time \( t \) to the initial particle radius, it is shown in Section 6.3.1. that,

\[
\frac{dQ}{dt} = \frac{P_\infty \left\{ \frac{\varepsilon(T/T_0)}{(1-y_1)[Q^3-(1-\varepsilon)]} - 1 \right\} - \frac{2\sigma_s}{R_0} \left\{ \frac{1}{[Q^3-(1-\varepsilon)]^{1/3}} + \frac{1}{Q} \right\}}{4\mu_1 Q^2 \left\{ \frac{1}{Q^3-(1-\varepsilon)} - \frac{1}{Q^3} \right\}}
\]  

(6.2.13)

where \( P_\infty, \varepsilon, \sigma_s, T, T_0, \mu_1 \) respectively are the ambient pressure, initial porosity, surface tension, temperature, initial temperature and viscosity of the liquid-solid suspension of the softening coal. Volume shrinkage due to pyrolysis weight loss is not considered. Because of the presence of mineral matter and non softening macerals, the softened coal is in reality a solid/liquid suspension. Its apparent viscosity is related to the liquid content by Eq. 6.1.1.
During the agglomeration process, the particle or agglomerate radius is thus modified according to,

\[ a_j = a_0 (j)^{1/3} Q \]  \hspace{1cm} (6.2.14)

(D) Agglomeration in laminar flow

In a laminar flow particle particle collision rate is expected to be lower than under turbulent conditions. Defining \( \gamma \) as the velocity gradient in the direction perpendicular to the direction of particle travel, Smoluchowski (1917) obtained

\[ K_c = 4(a_1 + a_j)^3\gamma/3 \]  \hspace{1cm} (6.2.15)

The corresponding bending stress for a pair of agglomerated spheres is given by Yoshida (1979),

\[ \sigma_b = 30\mu\gamma/c_1^3 \]  \hspace{1cm} (6.2.16)

and the allowed range of \( c_1 \) values for successful agglomeration becomes

\[ 3.11(\mu \gamma / \sigma_0 M)^{1/3} < c_1 < 1.0 \]  \hspace{1cm} (6.2.17)

ESTIMATION OF PARAMETERS

(A) Parameters in agglomeration equations
Depending on each particular process, the initial particle size and number density of the feed can vary. For stoichiometric combustion of 40 μm diameter pulverized coal particles in air, an initial feed of 2800 particles/cm$^3$ is required. The turbulent energy dissipation rate per unit volume can also vary widely between different processes and within different regions of the same process. For example, $\varepsilon_o$ values for regions adjoining injection nozzles can greatly exceed those for the main combustion chamber. Values of $\varepsilon_o$ can be as high as $10^{10}$ cm$^2$/sec$^3$ in MHD combustors but can be significantly lower in fluidized beds. A rough estimate of the average value of $\varepsilon_o$ in turbulent pipe flow with a volume average velocity $U$ is (Leslie, 1983)

$$\varepsilon_o = \frac{2}{d}U^3f$$  \hfill (6.2.18)

where $f$ is the standard Fanning friction factor and $d$ is the pipe diameter. For values of $U$ up to a few meters/sec and with a pipe diameter of order 0.1 m, the range of $\varepsilon_o$ is between $10^3$ and $10^6$ cm$^2$/sec$^3$. Kinematic viscosities of entrainment gas are in the range of 0.1 - 1 cm$^2$/sec, depending on the temperature. In the laminar flow case, the velocity gradient $\gamma$ is estimated from the stress at the wall of laminar flow in a pipe. The range of $\gamma$ for practical flows is estimated at from 1 to 100 sec$^{-1}$. The viscosity of the entrainment gas (helium) is calculated by the Chapman-Enskog theory. The empirical constant $\sigma_o$ in Eq. 6.2.3 is estimated from data of Sheomaker et al. (1976). The ultimate strength in uniaxial compression for a Pittsburgh bituminous coal in the softening range decreases with temperature. At 343 °C, the value reaches $5 \times 10^5$
dynes/cm$^2$. A value of $10^5$ dynes/cm$^2$ is taken for the present computation.

The parameters for the distribution of neck sizes $c_1$ and $\delta$ are arbitrarily chosen to be 0.1 and 0.01, respectively.

Kinetic parameters for metaplast formation and depletion obtained from rapid pyrolysis experiments with an electrical screen heater reactor are given above. In the particle swelling equation, the surface tension is assumed to be 50 dynes/cm and the initial porosity is 0.3. The quantity $y_1$, which represents the mole fraction of volatiles dissolved in the metaplast, is arbitrarily taken to be 0.8.

(B) Process variables

Results are presented for an initial feed of 40 $\mu$m particles of Pittsburgh No.8 Seam bituminous coal at a particle number density of 2800 particles/cm$^3$, heated at either 10000 K/s or 15000 K/s from 298 K to constant final temperatures between 600 - 1700 K, in helium at atmospheric pressure. The largest agglomerate size is limited to a 10-particle aggregate, A$_{10}$.

DISCUSSION OF RESULTS

Computed swelling ratios and intra-particle liquid inventories for heating from room temperature (a) to a final temperature of 1000 K at 10000 K/s, and (b) to 1700 K at 15000 K/s are shown in Figures 6.2.2a,b. In both cases, the particle shows a maximum swelling of more than 1.3 times its original diameter. For the 1000 K final temperature, there is
Figure 6.2.2  Liquid content and swelling ratio for two temperature histories
more time for the particle to contract after maximum swelling, before the cessation of its plastic stage while at 1700 K the short duration of plasticity results in essentially no contraction. These swelling predictions are in qualitative accord with recently reported measurements on individual vitrain particles of larger diameter rapidly pyrolyzed under 10 atm helium (Lowenthal et al., 1985).

Maximum liquid yield is less for the higher heating rate case where the liquid generation and depletion reactions are completed before the final temperature is reached.

The growth of agglomerates containing from 2 to 10 of the original particles (i.e. $A_2$, $A_3$, $A_4$, ...) in turbulent flow under the same temperature-time histories is plotted for different values of $\frac{c_0}{\nu}$ as a function of heating time in Figures 6.2.3a,b. The ordinate is the mass fraction of the originally fed coal that remains unagglomerated. For example in Figure 6.2.3a at 0.6s and $c_0/\nu = 10^5$ s$^{-2}$ about 20% of the original coal is predicted to exist as two to ten particle agglomerates. As the intensity of turbulence increases, the collision frequency increases and results in more agglomeration. However, at very high values of $c_0/\nu$, the agglomeration probability per collision, $\xi$ is low because of the high shear stress imposed on potential agglomerates by the entrainment gas and less agglomeration occurs. By definition agglomeration must cease when the metaplast in the coal is depleted and Figures 6.2.3a,b bear out this picture. At the higher heating rates and final temperatures, the duration of plasticity is much shorter, resulting in a decrease in the extent of agglomeration.
Figure 6.2.3 Weight fraction of unagglomerated particles at different intensities of turbulence, numbers on curves indicate $\varepsilon/\nu$, in s$^{-2}$
Figures 6.24a,b show the time evolution of different size agglomerates with $\varepsilon_0/\nu$ at $10^6$ sec$^{-2}$, with the vertical separation between any two curves depicting the mass fraction of the originally fed coal particles which has been combined to form the indicated agglomerate, $A_j$. Significant amounts of two, three, four and five-particle agglomerates are formed. Six-particle or larger agglomerates constitute a small mass fraction of the total initial feed at either heating rate.

Effects of final temperature on the predicted mass fractions of agglomerates are plotted in Figures 6.25a,b for heating rates of 10000 K/s and 15000 K/s respectively. Agglomeration does not stop until the collision efficiency, which depends on the magnitude of $\varepsilon_0/\nu$ and the metaplast content, reaches a small value. Hence, to allow comparison of the different cases, a residence time, 0.24 s is specified. Experimentally, this would correspond to allowing the mixture of coal particles to pyrolyze, collide, and agglomerate under the given temperature-time history, then quenching the mixture infinitely rapidly and collecting and counting the agglomerates.

The effect of heating rate can be seen by comparing curves of identical $\varepsilon_0/\nu$ in Figures 6.26a,b. At lower heating rate, (10000 K/s) the plastic period is longer and more agglomeration is predicted. Figure 6.26a shows predictions for a much lower heating rate of 1000 K/s to the same temperatures. A longer residence time (0.9 s) is imposed so that the highest final temperature will still be reached at this lower heating rate. Even more agglomeration is predicted. Particle agglomeration in
Figure 6.2.4  Weight fractions of different size agglomerates formed at $E_k/y$ equal to $10^6$ s$^{-2}$
Figure 6.2.5  Weight fractions of agglomerates vs final temperature
Numbers on curves indicate $\varepsilon/\gamma$, in $s^{-2}$
laminar flow is much less, as seen in Figure 6.2.6b.

Effects of feed particle size distribution on agglomeration behavior are of interest since practical devices utilize a distribution of sizes. Particles 250 - 500 μm or larger are of interest to fluid bed combustion. On the other hand, sizes of 10 - 35 μm command attention in research on coal fired diesel engines. Assuming a single particle size and a constant coal/gas mass ratio, then \( a_0^3n = \text{constant} \). From Eqs. 6.2.1 and 6.2.2, it can be seen that the fraction of agglomeration is independent of particle size \( a_0 \). When Eq. 6.2.10 is solved, the fraction of agglomeration is not sensitive to the initial particle size for the same coal/gas feed ratio. For larger particles, (\( > 200 \) μm) the particle size may be larger than the eddy size at the higher range of \( \varepsilon_0/\nu \). Hence particle entrainment is not possible. The collision frequency will be less and so is the extent of agglomeration.

The agglomeration model presented is simple yet satisfying. Opportunities for improvement include a better description of particle swelling that elaborates upon the picture of expansion of a single volatile bubble. Electron micrographs of char particles from rapidly pyrolyzed coal suggest that a "foam-coated bubble" model may be more realistic. Particle fragmentation can also occur in pyrolysis or combustion processes, and thus contribute to changes in the particle number density. For simplicity this possibility and the detailed motion of agglomerating pairs (spinning, rotation) are not considered here. At very intense levels of turbulence, flow field effects on mass transfer of volatiles away from the coal; and for very fluid coals, on recircu-
Figure 6.2.6  Weight fractions of agglomerate vs final temperature for (a) 1000 K/s heating rate, (b) laminar flow.

Numbers on curves indicate $\xi_0/\gamma$, in s$^{-2}$ or velocity gradient $\gamma$, in s$^{-2}$. 

Final Temperature, K

$1000k/s, t=0.9s$  
$10000k/s$, laminar case
lation within the molten coal, would have to be accounted for. Both effects could modify the global plasticity kinetics. Collision due to sedimentation of different size particles can also be important at lower levels of turbulence.

The model predictions show that both swelling and agglomeration are important in explaining changes in particle size distributions in coal combustion and gasification. The model provides a priori prediction of a maximum in extent of agglomeration with increasing temperature. The model also predicts that formation of large agglomerates (> 6-particle) is of relatively minor importance for many flow fields of practical interest. Although there are opportunities for improving its physical and chemical features, the model in its present form is applicable to laminar and turbulent entrained flow pyrolysis or combustion of pulverized coal particles.

Devolatilization kinetics including rates of metaplast formation and depletion are important for agglomeration modelling. They determine local metaplast inventories as a function of temperature-time history (and pressure, particle size, and coal type). The metaplast, or liquid formation/depletion kinetics influence at least two phenomena, namely the swelling dynamics due to effects on melt viscosity and volatiles release into bubbles; and the agglomeration dynamics due to effects on the strength of the agglomerate pairs.
6.3 OTHER POSSIBILITIES OF MODELING

Other chemical and physical behavior of bituminous coal during thermal processing can also be modelled with the liquid generation and destruction kinetics. A few possibilities are briefly mentioned.

6.3.1. Swelling of pulverized coal particles

Electron micrographs of char particles fed through entrained flow reactors show existence of both cenospheres (particles with a large cavity in the center) and particles with numerous small cavities which impart a foam-like appearance to the particles.

Two equations for describing separately the swelling of the large cavity (bubble), and the swelling of the liquid material surrounding the bubble are given below.

(a) Swelling of the large bubble

The model here is for the expansion of a spherical, viscous droplet with a gas bubble trapped inside. For pulverized coal particles with diameters about 100 µm or less, the temperature inside the particle can be assumed to be spatially uniform at heating rates of up to 1000 K/s. An increase in the particle temperature causes (1) the coal to soften, (2) the trapped gas to expand, and (3) the softened melt to evolve volatiles, creating a higher gas pressure inside the particle. These events contribute to the swelling of the particle. Besides the assumption
of uniform temperature inside the whole particle, it is also assumed that the flow of the softened coal melt is incompressible and Newtonian, and the loss of liquid due to evaporation and diffusion away from the liquid phase does not change the volume of the liquid to a significant extent. The last assumption should be true at the early stage of swelling when relatively little devolatilization has occurred.

Consider the following coordinate system (Figure 6.3.1.), where

\[ P_b = \text{pressure inside bubble} \]
\[ P_\infty = \text{pressure outside particle} \]
\[ R_o = \text{original radius of particle} \]
\[ R_1 = \text{radius of bubble inside particle} \]
\[ R_2 = \text{radius of softened particle} \]
\[ \varepsilon = \text{initial porosity of particle} \]
\[ T_0 = \text{initial temperature of particle} \]
\[ T = \text{temperature of particle} \]
\[ u = \text{viscosity of coal melt} \]
\[ \sigma_s = \text{surface tension of melt} \]

By symmetry the velocity field

\[ \mathbf{v} = (v_r, v_\theta, v_\phi) = (v_r, 0, 0) \quad (6.3.1) \]

Applying the continuity equation for the liquid, \( \mathbf{v} \cdot \mathbf{v} = 0 \) gives

\[ r^2 v_r = R_1^2 \dot{R}_1 = R_2^2 \dot{R}_2 = C(t) \quad (6.3.2) \]
A. Single Bubble Swelling

B. Reacting Foam Model

Figure 6.3.1 Limiting cases of swelling (a) single bubble swelling (b) reacting and solidifying foam
At the interface \( r = R_1 \), a momentum balance gives

\[
P_b = P \bigg|_{R_1} - 2 \mu \left. \frac{\partial v_r}{\partial r} \right|_{R_1} + \frac{\sigma s}{R_1} \tag{6.3.3}
\]

and similarly at \( r = R_2 \),

\[
P_\infty = P \bigg|_{R_2} - 2 \mu \left. \frac{\partial v_r}{\partial r} \right|_{R_2} + \frac{\sigma s}{R_2} \tag{6.3.4}
\]

here \( P \bigg|_{R_1} \) and \( P \bigg|_{R_2} \) are the pressure inside the liquid at \( r = R_1 \) and \( r = R_2 \), respectively.

The Navier-Stokes equation gives

\[
\rho \left( \frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = - \frac{\partial P}{\partial r} \tag{6.3.5}
\]

Substituting \( C(t) \) from Equation 6.3.2 into 6.3.5, and integrating from \( R_1 \) to \( R_2 \) gives

\[
P \bigg|_{R_1} - P \bigg|_{R_2} = \rho \left[ \frac{dC(t)}{dt} \left( - \frac{1}{r} \right) + \frac{C^2(t)}{2r^4} \right] \bigg|_{R_1}^{R_2} \tag{6.3.6}
\]

By mass conservation one finds

\[
R_2^3 - R_1^3 = R_o^3(1 - \epsilon) \tag{6.3.7}
\]

Subtracting Equation 6.3.4 from 6.3.3, and subtracting \( P \bigg|_{R_1} - P \bigg|_{R_2} \) from Equation 6.3.6 into the resulting expression gives an equation in terms
of C(t), R₁ and R₂. Defining \( R^* = \frac{R_2}{R_0} \) and making use of Equation 6.3.7, finally we arrive at,

\[
P_b - P_\infty = \rho R_o^2 \left( 2 R^* \frac{\dot{R}^*}{R^*} + R^* \frac{\ddot{R}^*}{R^*} \right) \left( \frac{1}{[R^*^3 - (1 - \varepsilon)]^{1/3}} - \frac{1}{R^*} \right) + \frac{1}{2} (R^* R^* \frac{\ddot{R}^*}{R^*}) \left( \frac{1}{R^*^4} - \frac{1}{[R^*^3 - (1 - \varepsilon)]^{4/3}} \right)
+ 4 \mu R^* \frac{\dot{R}^*}{R^*} \left( \frac{1}{R^*^3 - (1 - \varepsilon)} - \frac{1}{R^*^3} \right)
+ \frac{2 \sigma_s}{R_o} \left( \frac{1}{[R^*^3 - (1 - \varepsilon)]^{1/3}} + \frac{1}{R^*} \right)
\]

(6.3.8)

The first term on the right is the inertia term, followed by the viscous term and the surface tension term. For an order of magnitude analysis, let

\( R_o = 100 \) um
\( \sigma_s = 50 \) dynes/cm
\( \rho = 1 \) gm/cm³
\( \mu = 10^4 \) poise
\( P_b - P_\infty = 1 \) atm

Rewriting Equation 6.3.8 as

\[
\frac{P_b - P_\infty}{\rho R_o^2} = a_1 + \frac{4 \mu}{\rho R_o^2} a_2 + \frac{2 \sigma_s}{\rho R_o^3} a_3
\]

(6.3.9)

\( 0(10^{10}) \quad 0(a_1) \quad 0(10^8)0(a_2) \quad 0(10^8)0(a_3) \)

where \( a_1, a_2 \) and \( a_3 \) respectively represent the terms in braces, from left to right in Equation 6.3.8.

It is easy to see \( O(a_3) \sim O(10^0) \). This forces \( O(a_2) \sim O(10^2) \). In the term \( a_2 \),
\[
\frac{R^*2}{R^*^3} \left( \frac{1}{1-R^*^3} - \frac{1}{R^*^3} \right) \sim O(10^1 - 10^0) \quad (6.3.10)
\]

Hence \(O(R^*) \sim O(10^2 - 10^3)\). This implies \(O(a_1) \sim O(10^6)\). So, the final numbers are,

\[
\frac{P_b - P_\infty}{\rho R_o^2} = a_1 + \frac{4\mu}{\rho R_o^2} a_2 + \frac{2\sigma}{\rho R_o^3} a_3 \quad (6.3.11)
\]

\[
0(10^{10}) \quad 0(10^6) \quad 0(10^{10}) \quad 0(10^8)
\]

if \(P_b - P_\infty = 1 \text{ atm}\)

The above shows that (1) inertia terms can be neglected, (2) surface tension effect cannot be neglected if the pressure difference is small (less than 0.1 atm).

To evaluate \(P_b - P_\infty\), consider \(n_0\) to be the number of moles of gas (assumed inert) initially trapped inside the particle occupying a volume \(4/3(\epsilon \pi R_o^3)\) at temperature \(T_o\) and a pressure \(P_0 (= P_\infty)\). Upon heating, this volume of gas expands. Also, volatiles diffuse across \(r = R_1\).

\[
\frac{dn}{dt} = 4\pi R_1^2 k_y (y_i - y_b)
\]

\[
n(0) = n_o \quad (6.3.12)
\]

\(y_i\) is the gas phase mole fraction of volatiles at the interface and \(y_b\) is the mole fraction of volatiles inside the bubble. \(k_y\) is the local mass transfer coefficient based on the gas phase. Solving for \(n\) in Equation 6.3.12 and using the ideal gas law allows \(P_b - P_\infty\) to be calculated. Two limiting cases exist.
(1) \( k_y \rightarrow 0 \) very slow volatiles transfer across interface.

(2) \( k_y \rightarrow \infty \) volatiles in the bubble attain equilibrium with volatiles in the liquid melt.

Define \( \Delta P^* = \frac{P_b - P_\infty}{P_\infty} \) then for the case (1),

\[
\Delta P^* = \frac{\varepsilon(T/T_0)}{R^3(1-\varepsilon)} - 1 \tag{6.3.13}
\]

and for case (2),

\[
\Delta P^* = \frac{\varepsilon(T/T_0)}{(1-y_i)(R^3-(1-\varepsilon))} - 1 \tag{6.3.14}
\]

In principle, \( y_i \) can be estimated from Henry's law constants and is a function of the metaplast concentration in the melt. Hence, the final equation would be,

\[
\frac{\varepsilon(T/T_0)}{(1-y_i)(R^3-(1-\varepsilon))} - 1 - \frac{2\sigma_S}{R_o[R^3-(1-\varepsilon)]^{1/3}} + \frac{1}{R^*} - \frac{1}{R^3} \frac{1}{R^*}
\]

\[
R^* = 4\pi R^2 \left[ \frac{1}{R^3-(1-\varepsilon)} - \frac{1}{R^3} \right] \tag{6.3.15}
\]

The viscosity \( \mu \) can be obtained from the plastometer data or calculated from the plasticity model as described in Section 6.1. Recalling our global model for coal plasticity kinetics,
The parameters $k_1$, $k_2$ are given in Section 6.1. The viscosity is then related to metaplast concentration $M$ (wt. fraction of coal) by Equation 6.1.1.

Figures 6.2.2a, b shows calculated results of swelling for 40 μm diameter coal particles heated at (a) 10000 K/s to 1000 K, and (b) 15000 K/s to 1700 K.

(b) Swelling of the foam layer

The swelling of the foam layer is analogous to the processing of plastic foams. Expansion of foams by chemical blowing agents is quite similar to swelling of a devolatilizing coal liquid. Both give a cellular structure at the end of expansion. Figure 6.3.2 shows expansion of a cross-linked polyethylene. During the expansion process the polymer has a low viscosity. As the degree of cure (as indicated by gel formation) increases, the foam is stabilized by the increases of viscosity and elasticity. An empirical approach is attempted here to describe the swelling ratio. Consider a reacting mixture of coal, liquid, gas and coke, their weight fractions denoted by $C, M, G, E$ respectively (Figure 6.3.1). The swelling of the liquid is due to the gas generation, and is assumed to be proportional to a $\alpha$ power of the generation rate, $dG/dt$ via a constant $\alpha$. The unreacted coal in the suspension is assumed having an
Figure 6.3.2 Schematic diagram of expansion of a polyethylene foam (Benning, 1969)
initial density $\rho_e$. The porous coke is continuously formed from the liquid, so its porosity reflects the instantaneous porosity of the liquid. Therefore, at any time, the volumetric swelling ratio $Q(t)$ is given by

$$Q(t) = \frac{C/\rho_0 + [1 + \alpha(dG/dt)^B] M/\rho_0 + \int_0^t [(dE/dt)/\rho_{M+E}] dt}{(1/\rho_0)}$$  \hspace{1cm} (6.3.16)

The volumetric contributions of $C$, $M$ and $E$ are in the three separate terms of the numerator. The instantaneous density of the liquid is related to $\rho_0$ by $\rho_{M+E} = \rho_0/[1 + \alpha(dG/dt)^B]$, therefore

$$Q(t) = C + [1 + \alpha(dG/dt)^B]M + \int_0^t (dE/dt)[1 + \alpha(dG/dt)^B] dt \hspace{1cm} (6.3.17)$$

Figure 6.3.3 shows calculated swelling ratios for the same conditions of Figures 6.2.2.

The two expressions above probably represent the two limiting cases of the physical picture of coal swelling.

6.3.2. Fragmentation of large coal particles

"possible model"

When a large (a few mm or larger) softening coal particle is rapidly heated, the non-isothermal temperature distribution creates a plastic layer that is progressing towards the center of the particle (Figure 6.3.4).
Figure 6.3.3  Liquid content and swelling ratio, same temperature histories as in Figures 31a,b
Progressing plastic zone

Outline of computation

UNSTEADY STATE HEAT TRANSFER  PLASTICITY KINETICS

CALCULATE LIQUID FORMATION RATE

PRESSURE DIFFERENCE FROM Darcy's Law

STRESS ON OUTER COKE SHELL

Figure 6.3.4 Possible model for coal particle fragmentation
As the liquid layer is formed, an increase in specific volume results. Initial density of the coal may be between 1.2 - 1.4 g/cm³, while the liquid may have a density near 1.0 g/cm³. Hence an increase of 20 - 30 % by volume can happen in the initial softening step. Both the liquid and the volatiles formed must flow outwards through the outer coke layer, since the inner unreacted core of coal has a much smaller porosity. The volatiles can escape much faster than the liquid, while the liquid undergoes coking and secondary reactions as it flows through the porous coke layer.

Even though the volatiles formed have a larger volume, the large differences in their viscosities (0.02 cp vs >1000 p) means that the pressure generated by the flow os species is mainly due to the viscous liquid. The volumetric formation rate of the liquid can be calculated from plasticity kinetics, this is equated to the flow through the porous coke layer by Darcy's law to obtained the pressure difference required for flow. The stress on the outer coke shell is then calculated from the pressure difference. If the stress exceeds the critical strength of coke, the outer shell cracks, and a few fragments are formed. The equations to be solved are given in Figure 6.3.5.
\[ \frac{\partial T}{\partial t} = \sigma \left( \frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) \]
\[ \sigma = \sigma(T) \]
\[ T(0,r) = 0 \quad \text{HEAT TRANSFER} \]
\[ T(t,a) = 1 \]
\[ \frac{\partial T}{\partial r}(t,0) = 0 \]
\[ \frac{\partial C}{\partial t} = -k_1(C - f_m) - r_m \]
\[ \frac{\partial M}{\partial t} = k_1(C - f_m) - k_2 M + r_m - \nu \frac{\partial M}{\partial r} \quad \text{LIQUID FORMATION} \]
\[ C(r,0) = 1.0 \quad \text{loss term due to flow, assumed small} \]
\[ M(r,0) = 0 \]
\[ Q(t) = \left( \frac{1}{\rho} - \frac{1}{\rho_0} \right) \int_{0}^{r^*(t)} 4\pi r^2 \frac{\partial M}{\partial t} dr \quad \text{CALCULATE FLOWRATE} \]
\[ r^* \text{ is the outer radius at which } M \text{ is less than some small value} \]
\[ \Delta P(t) = \left( \frac{1}{\eta} - \frac{1}{\eta_0} \right) \frac{WQ(t)}{\eta_0 \kappa} \quad \text{PRESSURE DROP} \]
\[ \text{viscosity of liquid } \quad \text{permeability of coke layer} \]
\[ \sigma_{\theta\theta} = \frac{\Delta P}{2} \left( \frac{(a/r^*)^2 + 2}{(a/r^*)^2 - 1} \right) \quad \text{STRESS ON COKE LAYER} \]
\[ - \text{particle breaks up if stress is greater than the strength of the coke} \]

Figure 6.3.5 Equations for fragmentation model
CHAPTER 7. CONCLUSIONS, POTENTIAL APPLICATIONS AND RECOMMENDATIONS FOR FUTURE WORK

CONCLUSIONS

(1) A new coal plastometer has been developed to measure the rapidly changing apparent viscosities at severe conditions, i.e. at high temperatures, pressures and heating rates pertinent to modern coal conversion processes but previously unattainable with conventional instruments.

(2) Coal plasticity can be described directly by its viscosity change. As a Pittsburgh Seam bituminous coal is heated, the coal softens to form a solid/liquid suspension the viscosity of which decreases from more than one million poise to minimum values of order a few thousand poise. Resolidification of the intermediate liquid phase is indicated by rapid rise in viscosity values.

(3) Characteristic times for softening and resolidification were obtained. The measured time interval of low viscosity varies from one minute to less than a second, depending on the temperature-time history.

(4) Initial softening of a Pittsburgh coal is by physical melting of an estimated 25\% by weight of the coal. Up to 40\% by weight of the coal is further converted to liquids by pyrolytic bond breaking. These liquids can polymerize to give higher molecular weight liquids.
and solids, crack to give gas and coke, or escape from the coal particle to give tar. The result is that the average liquid molecular weight can increase from 570 to above 800, and then decrease to around 600.

(5) The kinetics of intraparticle coal liquid formation and depletion can be quite accurately determined for a bituminous coal in an electrical screen heater with rapid sample quenching, followed by solvent extraction of the quenched char.

(6) The new information on coal plasticity kinetics finds quantitative application in modeling coal particle agglomeration and swelling behavior under rapid heating high temperature conditions. Predictions of model here developed were in qualitative accord with literature data on swelling and provide a possible explanation for coal agglomeration observed within a pulverized coal flame.

POTENTIAL APPLICATIONS

(1) The results provide an approach for describing agglomeration behavior in gasifiers and combustors.

(2) The improved physical and chemical picture of the pyrolysis of softening coals can be used in improved description of the chemical kinetics and transport processes that determine the rates and extents of coal softening, pyrolysis and liquefaction.

(3) The data showed that suitable thermal treatment followed by rapid
quenching can give high liquid yields, exceeding 80 % daf from bituminous coal without addition of catalyst or hydrogen. A possible application is improved production of liquids from coal.

(4) The high temperature, fast response plastometer can be applied to the study of other thermoplastic materials.
RECOMMENDATIONS FOR FUTURE WORK

The present study opens some interesting points for future research in softening coal pyrolysis:

1. Further experiments on the effects of pressure, reactive gases and heating rate on plasticity is needed (using the approach in the present thesis: viscosity curves, extract generation and depletion study in conjunction with the characterization of the extract).

2. The above approach can be applied to a range of coal types (lignite, sub-bituminous and bituminous coals of different fluidity) for a better understanding of coal pyrolysis in general.

3. Chemical characterization of the extracts, such as determining the H/C ratio and aromatic content will be useful for a more detailed understanding of the chemistry of coal plasticity, including runs with samples pretreated with tetralin.

4. More work is needed in the study of resolidification reactions of pre-treated coals, or for raw coal in the presence of (a) heterogenous surfaces, (b) catalysts, (c) hydrogen donors, and (d) secondary reactions, such as increased contact with its pyrolysis products in a closed system.

5. More detailed molecular weight information can be obtained from the newly completed screen heater reactor, since the escaping tar is also
collected and can be analyzed. This can shed light on the mode of tar secondary reaction and transport in coal.

6. For conditions pertinent to pulverized coal combustion, plasticity kinetics can be determined by studying the extract yields of particles passing through a drop tube furnace and rapidly quenched on a cold collector.

7. By combining the single bubble and foam swelling models, a more realistic description of particle swelling can be achieved. This with other modifications in the description of particle sticking (or fragmentation) can lead to a better understanding of the behavior of a system of softening, pyrolyzing coal particles under realistic conditions.

8. The effective diffusivity of pyrolysis products or gaseous reactants in a viscous coal melt can be estimated from its viscosity values (assuming no internal motion of the melt). This is useful for the modeling of softening coal pyrolysis.

9. The present work suggests that an optimum solids residence time exists at each reaction temperature for maximum liquids yield in the absence of hydrogen. A two-stage coal liquefaction process with first thermal treatment followed by rapid dissolution in a solvent seems possible. The quality of the liquids should be studied as mentioned in Point 3.
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