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Coal Plasticity at High Heating Rates and Temperatures
Final Technical Progress Report

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MASTER

Foreword

This report is the doctoral thesis of Sarakorn Gerjarusak, submitted by him to (partially) fulfill requirements for receipt of the degree of Ph.D. in Chemical Engineering at MIT c. May of 1993, except that this report contains revised versions of pages 38 and 115 of that thesis. These revisions reflect amendments by Dr. Gerjarusak (c. July 1993) to correct typographical errors, i.e. interchanging of two columns of numbers in Tables 1.3 and 4.2 respectively.

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PLASTICITY KINETICS OF DIFFERENT COAL TYPES

by

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by

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Submitted to the Department of Chemical Engineering at the Massachusetts Institute of Technology in June 1993, in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Abstract

Plastic coals are important feedstocks in coke manufacture, coal liquefaction, gasification, and combustion. During these processes, the thermoplastic behavior of these coals is also important since it may contribute to desirable or undesirable characteristics. For example, during liquefaction, the plastic behavior is desired since it leads to liquid-liquid reactions which are faster than solid-liquid reactions. During gasification, the plastic behavior is undesired since it leads to caking and agglomeration of coal particles which result in bed bogging in fixed or fluidized bed gasifiers.

The plastic behavior of different coals was studied using a fast-response plastometer. A modified plastometer was used to measure the torque required to turn at constant angular speed a cone-shaped disk embedded in a thin layer of coal. The coal particles were packed between two metal plates which are heated electrically. Heating rates, final temperatures, pressures, and durations of experiment ranged from 200-800 K/s, 700-1300 K, vacuum-50 atm helium, and 0-40 s, respectively. The apparent viscosity of the molten coal was calculated from the measured torque using the governing equation of the cone-and-plate viscometer. Using a concentrated suspension model, the molten coal's apparent viscosity was related to the quantity of the liquid metaplast present during pyrolysis. Seven coals from Argonne National Laboratory Premium Coal Sample Bank were studied. Five bituminous coals, from high-volatile to low-volatile bituminous, were found to have very good plastic behavior.

Effects of pressure, temperature, and coal type on coal plasticity were investigated. Elevated pressures up to 49 atm of helium above atmosphere did not affect coal plasticity, but reducing pressure from atmosphere to vacuum resulted in diminished plasticity, i.e. gave a shorter plastic period and a higher minimum apparent viscosity. It is hypothesized that for pressure increases above 1 atm there are approximately counterbalancing effects on the local inventory of plasticizer: inhibited mass transport of metaplast to tar vapors and augmented metaplast repolymerization into coke and char. Higher holding temperature decreased the coal plastic period. It is hypothesized that higher temperature increases mass transport of liquid metaplast to tar vapors and metaplast repolymerization to coke and tar. Heating rate had essentially no effect on the individual softening temperatures of five different plastic coals. A possible explanation is that, depending on coal type, metaplast generation, by chemical bond breaking or physical melting, or both, is not strongly affected by heating rate. Increasing the heating rate, however, decreased the plastic period of each coal. It is hypothesized that higher heating rate increases mass transport of liquid metaplast to tar vapors. In addition, higher temperature is reached faster with higher heating rates, resulting in enhanced metaplast repolymerization to coke and char.

The transient coal plastic behavior is well predicted using a multiple independent parallel reaction (MIPR) kinetics model. In this model, metaplast is generated by physical melting and chemical reactions, and depleted by chemical reactions. The model has five fitted parameters: the maximum amount of metaplast that can be generated (M^*), the mean

activation energy and its standard deviation of the generation chemical reactions (E_g and σ_{Eg}), and the mean activation energy and its standard deviation for the depletion chemical reactions (E_d and σ_{Ed}); all of which have been determined for each coal from the experimental data on apparent viscosity as affected by temperature-time history.

Coal type strongly affects the magnitude and duration of plasticity. Hvb coals were most plastic. Mvb and lvb coals exhibited comparable plasticity to hvb coals, though the maximum plasticity and plastic period were less. Low rank coals such as subbituminous and lignite did not exhibit any plasticity in the present studies. Coal plasticity is moderately well correlated with simple indices of coal type such as the elemental C, O, and H contents and linearly correlated with a coal specific parameter defined in terms of simple indices of coal type such as labile bridge fraction and H and O contents.

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Chapter 1. Summary

1.1 Introduction

Upon heating, bituminous coals soften and create a fluid-like mass often referred to as metaplast. The coal remains softened for a period of time and then resolidifies to form coke. The softened coal is a combination of solid materials (mineral matter and organic constituents that do not soften) and metaplast. The softened coal may also contain bubbles of gaseous products from pyrolysis. The thermoplastic behavior of coal is strongly connected with the coal's pyrolysis kinetics. At elevated temperature (>650 K), the parent coal starts to physically melt and devolatilize (Loison et al., 1963 and Fong, 1986). The resulting products include metaplast and gaseous species which can escape or undergo further secondary reactions to produce tar, char, and other gaseous species.

A good understanding of coal's transient plastic behavior is therefore important for understanding the pyrolysis kinetics of softening coals. Heating rate and holding temperature are expected to significantly affect coal plasticity and, by inference, the behavior of softening coal in modern coal conversion processes. For example, plasticity can affect reactivity and agglomeration of the coal in fixed or fluidized bed gasification. Swelling and agglomeration associated with coal plasticity can lead to bed bogging in fixed or fluidized bed gasifiers and combustors, but are desired in metallurgical coke manufacture since they contribute to strong and hard products. In addition, conditions in which the coal's fluidity is high are desirable for high reactivity in coal liquefaction (Whitehurst, 1980). Devolatilization and plasticity can affect reactions and thus pollutant generation in coal combustion, coal gasification, mineral matter size distributions in high temperature coal, and the survival of unburned char.

1.2 Objectives

The goal of this research is to provide new, quantitative understanding of the high heating rate transient plastic behavior of different bituminous coals, in particular experimental determinations of apparent viscosity as affected by temperature-time history and a global model relating observed plasticity behavior to transient intra-coal metaplast inventories.

The specific objectives are:

1. Experimental

To measure the apparent viscosity of different bituminous coals during thermally induced softening for different shear rates ($1-10 \text{ s}^{-1}$), heating rates (200-1000 K/s), maximum temperatures (600-1300 K), total reaction times (1-10 s), and pressures of inert gas (1-100 atm helium).

2. Theoretical

To relate the transient viscosity of molten coal to the kinetics of metaplast generation and depletion, using existing models and as appropriate to attempt to develop improved models to take into account effects heating rate, pressure, and shear rate and attempt to relate plasticity behavior to simple indices of coal type.

1.3 Experimental Technique and Apparatus

The apparent viscosity of coal has been measured by a modified version of the plastometer originally developed and built by Fong (1986). The instrument measures the torque required to turn at a constant angular velocity a thin disk embedded in a thin layer of coal particles.

A modified version of the plastometer (Figure 1.1) developed in the present study uses the same heating circuits (up to 1000 K/s and 1300 K maximum temperature) and torque transducer (up to 10 oz·in or $70 \cdot 10^{-3}$ N·m continuously) as that of Fong. However, a more powerful motor (24 V, 200 oz·in maximum torque) is used to provide shear rates of up to 10 s^{-1} .

The torque transducer measures the torque supplied by the gear motor, to rotate at constant angular speed and thus for the present geometry, constant shear rate, a shearing disk embedded in a thin layer of coal. The torque transducer is a noncontact strain gauge torquemeter. The stated response time is less than 10 ms, and the stated maximum error is 0.2 % of reading. The torque transducer's maximum permissible load is 10 oz·in or approximately $70 \cdot 10^{-3}$ N·m. The shearing disk configuration has been modified from the flat disk used by Fong to the cone-shaped disk shown in Figure 1.2. This geometry allows the viscosity of the coal melt to be calculated without the assumption that the melt is Newtonian. The apparent viscosity, η , is obtained by applying the equation for a concentric cone-and-plate viscometer in which the disk rotates between two stationary plates (Bird et. al., 1977 and 1988). For a cone-and-plate geometry of very small cone angle, Newtonian behavior of the sample is not a requirement to compute η from the observed torque and:

$$\eta = \frac{3T_a/4\pi R^3}{\gamma_R} \quad 1.1)$$

where T_a is the torque, $\gamma_R = \Omega/\theta$ is the shear rate of the cone-shaped disk of radius R and cone angle θ , and Ω is the disk angular velocity. The shearing disk and chamber were machined from nickel superalloy (Rene 41) for high temperature strength and resistance to corrosion. The plastometer is enclosed in a high-pressure vessel (316

Figure 1.1: Schematic of the Plastometer

Figure 1.2: Gerjarusak's cone-shaped disk plastometer

stainless steel) that can be evacuated to 0.0001 atm or charged with hydrogen or helium up to 100 atm.

The temperature is measured using a 0.012-mm thin-foil thermocouple attached to the outside surface of the shearing chamber. The response time of the thermocouple is between 2-5 ms for a stepwise temperature change. With the coal's and metal's thermal diffusivities of $1.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ and $5 \cdot 10^{-6} \text{ m}^2/\text{s}$ respectively, the temperature gradient across the coal sample and shearing chamber is approximately 50 K at a 1000 K/s heating rate (Carslaw and Jaeger, 1959). This is a conservative estimate since the thermal diffusivity of coal increases with increasing temperature (Badzioch et. al., 1964).

The heating and holding circuits employ a total of six 12-V lead acid automobile batteries. The heating circuit uses two sets of batteries connected in parallel. Each set consists of two batteries connected in series for a 24-V output. The temperature holding circuit uses only one set of batteries since the total amperage required to maintain a certain temperature is much less than that required for heatup. The magnitude of the electrical current is preset by adjusting two carbon rheostats. The durations of heating and temperature holding are preselected by setting two solid-state digital relays adjustable from 0.00 to 99.9 s in 0.01-s increments.

During a typical run, the shearing chamber containing the shearing disk and coal is placed between the electrodes. The shaft of the shearing disk is attached to a coupling connected to the transducer (Figure 1.1). The thermocouple is attached to the surface of the shearing chamber. The top of the pressure vessel is lowered, and the vessel is sealed and evacuated to a pressure of 0.0005 atm. Helium is added until the pressure is approximately 1 atm, and the vessel is then evacuated again. This helium flushing and evacuation is repeated once, and the test gas is admitted until the desired pressure is

reached. The motor and heating circuits are then activated. The torque vs. time and temperature vs. time histories are recorded, using a digital recorder capable of an acquisition rate of 1000 points/s. The data are later transferred to a personal computer. Typical raw data from the plastometer are shown in Figure 1.3.

The plastometer's new configuration has been calibrated for friction and an apparatus constant. The friction contributes to the torque value of approximately $1 \cdot 10^{-4}$ N·m. Various runs were performed with a viscosity standard, and with the torque from friction subtracted from the measured torque, the apparent viscosity of the standard was calculated. The apparatus constant (α) was found to be equal to $\frac{\eta_{\text{actual}}}{\eta_{\text{calc}}} = 0.93$.

From the transient torque data obtained from the standard calibration and the determination of the plastometer's friction, it is observed that the noise associated with the plastometer is approximately $1 \cdot 10^{-4}$ N·m or 200 Pa·s. In addition, the maximum error of the torque transducer's measurement is 0.2% of reading (100 Pa·s at 50000 Pa·s) (S. Himmelstein and Company, 1983). Choosing a low shear rate of 2.01 s^{-1} , the plastometer's viscosity resolution is approximately ± 300 Pa·s. The digital recorder records a data point every tenth of a second, and therefore the plastometer's time resolution is also 0.1 s.

1.4 Experimental Conditions

To prevent the torque transducer from overloading during start up (shearing solid coal particles), a low shear rate of 2.01 s^{-1} is used in most experimental runs. To study pressure effects, a constant heating rate of 400 K/s and a holding temperature of 1098 K

Figure 1.3: Raw data from plastometer for three different coals. Heating Rate: 400 K/s; Holding Temperature: 1098 K; Presssure: 1 atm helium

are used. The plastic behavior of the coals have been studied at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium.

Temperature-time history effects on coal plasticity were studied in two ways: by varying the holding temperature or the heating rate. To study the effects of holding temperature, the heating rate and pressure used are 400 K/s and 1 atm helium, respectively. The holding temperature is varied between 898 to 1298 K. To study the effects of heating rates, the holding temperature and pressure used are 1098 K and 1 atm helium, respectively. The heating rate is varied between 200 and 800 K/s.

1.5 Coal Selection and Preparation

Coals from the Argonne Premium Coal Sample Program were chosen for the experiments. They are chosen for the purity of and consistency among the samples. First, the samples are stored and grounded in a nitrogen atmosphere where the oxygen content of the facility is below 100 ppm. The final samples are stored in sealed glass ampules for further distribution (Vorres, 1989). Second, the samples of each coal are prepared from the same batch of raw sample. They are prepared carefully in the same way to ensure the consistency of each batch. An additional benefit of the Argonne coals is that most coal researchers have chosen them as "standard", and many scientific data pertinent to these coals are available.

The seven coals studied were: Beulah-Zap lignite (ND), Wyodak subbituminous (WY), Illinois No. 6 hvb (IL), Pittsburgh No. 8 hvb (PT), Lewiston-Stockton hvb (WV), Upper Freeport mvb (UF), and Pocahontas No. 3 lvb (PO). These coals fall within coal ranks ranging from lignite to low volatile bituminous. Hvb coals are known for their good plastic behavior, and therefore three different coals (IL, PT, and WV) are chosen from

this rank. In particular, Pittsburgh No. 8 hvb coal is chosen for its good coking ability and for comparing the data to those of Fong (1986) and Fong et al. (1985, 1986a, and 1986b). From the sealed ampule, the coal is spread as a thin layer in the recess of each of the shearing chamber's metal plates. The shearing disk is placed between the two coal layers when the two metal plates are clamped together.

The ultimate (elemental) analyses and selected structural data for the Argonne premium coals used in this work are shown in Table 1.1.

1.6 Experimental Results and Discussion

For the plastic coals, the present findings will help explain how pressure, temperature, and coal type affect the formation and depletion kinetics of the liquid metaplast which is primarily responsible for coal plasticity.

Shear Rate Effects: The coal selected for this experiment was Pittsburgh No. 8 hvb, a highly plastic coal. The plastometer's shear rate ($\dot{\gamma}_R$) was varied from 2.01 s^{-1} to 10.66 s^{-1} . The heating rate used was 400 K/s , and the holding temperature was 1098 K . The pressure was 1 atm helium.

For $\dot{\gamma}_R$ from 2.01 s^{-1} to 10.66 s^{-1} , no shear rate effect on the viscosity of Pittsburgh No. 8 hvb coal was observed. There was no effect on the plastic period, the viscosity at various times and temperatures, and the maximum plasticity. Figure 1.4 shows the viscosity of Pittsburgh No. 8 hvb at different times and temperatures to be independent of shear rate.

At the plastometer's range of shear rates, the molten coal suspension is therefore considered Newtonian. This property of the coal melt allows for the use of many

TABLE 1.1: Ultimate Analyses and Selected Structural Data for Argonne Premium Coals

	ND lig	WY sub	IL hvb	PT hvb	WV hvb	UFm vb	PO l vb
%C dmmf ^a	74.05	76.04	80.73	84.95	85.47	88.08	91.81
%O dmmf ^a	19.13	16.90	10.11	6.90	6.68	4.72	1.66
%H dmmf ^a	4.90	5.42	5.20	5.43	5.44	4.84	4.48
%N dmmf ^a	1.15	1.12	1.37	1.64	1.56	1.55	1.33
% Organic S ^a	0.70	0.47	2.38	0.89	0.65	0.74	0.50
Carbon Aromaticity ^b , C _{f,a}	0.57	0.60	0.67	0.74	0.75	0.80	0.88
Proton Aromaticity ^c , H _{f,a}	0.24	0.27	0.30	0.35	0.36	0.39	0.45

a: Vorres, 1989

b: Ko, 1988

c: Niksa, 1991

Figure 1.4: Viscosity of Pittsburgh No. 8 hvb at different shear rates.
Heating Rate: 400 K/s; Holding Temperature: 1098 K; Pressure: 1
atm helium

available suspension models (e.g. Frankel-Acrivos concentrated suspension model) which require the suspension to be Newtonian.

Pressure Effects: Compared to the runs at 1 atm helium, the results for different coals at vacuum displayed lower plasticity (higher minimum viscosity and shorter plastic period) as seen in Figures 1.5 and 1.6. The lower plasticity in vacuum is hypothesized to be due to enhanced mass transport of metaplast to tar vapors. The enhanced mass transport decreases the liquid metaplast inventory in the molten coal sample, resulting in lower plasticity.

Compared to the runs at 1 atm helium, the runs with different coals at elevated pressures (10 atm and 50 atm helium) did not display any significant change as seen in Figures 1.5 and 1.6. Fong (1986) also observed similar results in his work on Pittsburgh No. 8 coal. It is hypothesized that high pressure inhibits mass transport of metaplast out of the coal, resulting in increased intraparticle inventories of metaplast. These inventories could in turn give rise to increased plasticity, but also to more rapid rates of metaplast depletion, e.g. by polymerization or other rate processes greater than first order in metaplast concentration (Griffin, 1989). Here, since effects of increasing pressure are not observed above 1 atm, these two effects apparently compensate to give no net influence of increasing pressure on plasticity.

Temperature Effects: With different holding temperatures, the maximum plasticity, i.e. minimum viscosity, of different coals was essentially unchanged (Table 1.2 and Figure 1.7) to within the resolution of the plastometer. However, higher holding temperature decreased the plastic period (the period when the viscosity of molten coal is below 50000 Pa·s) for all coals (Figures 1.7 and 1.8; Table 1.2). For example, increasing the holding temperature from 898 K to 1098 K decreased the plastic period from 6.9 s to 1.9 s for

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 1.5: Maximum plasticity (minimum viscosity) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 1.6: Plastic period (period when the viscosity of molten coal is below 50000 Pa·s) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

Table 1.2: Minimum Apparent Viscosity and Plastic Period
at Different Holding Temperatures^a

	<u>Holding Temperatures</u>			
<u>Coal/Viscosity (Pa·s)</u>	<u>898 K</u>	<u>948 K</u>	<u>998K</u>	<u>1098K</u>
Illinois No. 6 hvb	1836	1800	1766	1759
Pittsburgh No. 8 hvb	1397	1364	1297	1286
Lewiston-Stockton hvb	1711	1660	1698	1694
Upper Freeport mvb	2722	2666	2661	2583
Pocahontas No. 3 lvb	5646	5553	5444	5337

	<u>Holding Temperatures</u>			
<u>Coal/Plastic Period (s)</u>	<u>898 K</u>	<u>948 K</u>	<u>998K</u>	<u>1098K</u>
Illinois No. 6 hvb	5.3	3.0	2.1	1.6
Pittsburgh No. 8 hvb	6.9	3.6	2.5	1.9
Lewiston-Stockton hvb	6.8	3.7	2.6	1.9
Upper Freeport mvb	7.0	3.8	2.6	2.0
Pocahontas No. 3 lvb	5.1	2.8	1.9	1.5

a: Heating rate: 400 K/s and Pressure 1 atm helium

Figure 1.7: Apparent viscosity of different coals at different holding temperatures. Heating Rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 1.8: Plastic period (period when the viscosity of molten coal is below 50000 Pa·s) of different coals at different holding temperatures. Heating Rate: 400 K/s; Pressure: 1 atm helium. ND and WY coals do not exhibit any plasticity.

Pittsburgh No. 8 hvb coal. It is hypothesized that higher temperatures diminish plasticity by increasing mass transport of liquid metaplast out of the coal and by increasing repolymerization of metaplast to coke (Fong, 1986).

The effect of heating rate on the softening temperature (temperature where the viscosity of molten coal first reaches 50000 Pa·s) was studied. For each coal, heating rate has essentially no effect on the softening temperature (Figure 1.9). This seems to indicate that for a given coal the initial generation of metaplast is independent of heating rate and further suggests, especially for hvb coals where the softening temperature is below 650 K, that the initial phase of softening probably occurs by physical melting of the pyridine extractables initially present in the parent coal (Fong, 1986). For example, other workers have found that for hvb coals pyridine extractables of the raw coal amount to 25-30% dmmf (Fong, 1986 and Niksa, 1991). Little or no dependence of softening temperatures on heating rate was observed experimentally by Fong (1986) and theoretically by Oh et. al (1989) for Pittsburgh No. 8 hvb coal.

The existence of different softening temperatures for different coal types could reflect different metaplast melting points for the different coals, different kinetics of metaplast generation, or both. The similarity in softening temperatures of hvb coals (approximately 630 K) suggests that the overall rates of generation of the metaplast responsible for initial softening are also similar. For hvb coals which have a high yield of pyridine extracts from the raw coal, most or all of this metaplast may be generated by physical melting. However, the UF mvb coal also has a similar softening temperature (approximately 650 K), but has a much lower initial weight fraction of pyridine extractables (i.e. 7%, Snape and Bartle, 1989). It is hypothesized that the UF mvb coal generates a major fraction of the metaplast needed for initial softening by chemical bond breaking and further that the kinetics of this process is very rapid.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 1.9: Softening Temperature of Various Coals at Different Heating Rates. Holding Temperature: 1098K; Pressure: 1 atm helium.

The PO lvb coal has a much higher softening temperature (740 K). This is probably due to the lack of metaplast generation by physical melting since the PO coal only has an initial fraction of pyridine extractables of 1%. The coal begins to soften only when the temperature is high enough for the metaplast generation by chemical bond breaking to become important.

Figure 1.10 displays plots of apparent viscosity vs. time for five different softening coals at three different heating rates. These plots, together with Table 1.3, show that heating rate has little effect on maximum plasticity (i.e. minimum apparent viscosity) of each coal to within the resolution of our plastometer (approximately ± 300 Pa·s). For each coal, the apparent viscosity drops rapidly to a minimum and then rises rapidly shortly after reaching the holding temperature of 1098 K. Figure 1.10 clearly shows that the plastic period decreases with increasing heating rate for each coal. At a higher heating rate, the metaplast generation and especially the depletion kinetics are enhanced since a higher temperature is reached faster. Fong (1986) among others has hypothesized that higher temperatures diminish plasticity by increasing the depletion rates of plasticizing agent (i.e. metaplast), e.g. by mass transfer out of the coal and by repolymerization of metaplast to coke (Fong, 1986).

Figure 1.10 also shows that after heating to final temperature at a lower rate, e.g. 400 and especially 200 K/s, the apparent viscosity of the molten coal increases less rapidly, implying slower overall resolidification kinetics. This may reflect differences in the metaplast properties, caused by secondary reactions during the longer period that proceeds the onset of fluidity. For example, Fong (1986) observed that the average molecular weight of liquid extractables from pyrolysis of molten coal, taken as approximately representative of metaplast, increased with decreasing heating rate. Griffin (1989) made similar observations for newly evolved coal pyrolysis tar. Thus the

**Table 1.3: Minimum Apparent Viscosity and Plastic Period
at Different Heating Rates^a**

<u>Coal/Viscosity (Pa·s)</u>	<u>Heating Rates</u>		
	<u>200 K/s</u>	<u>400 K/s</u>	<u>800 K/s</u>
Illinois No. 6 hvb	1766	1759	1753
Pittsburgh No. 8 hvb	1456	1286	1449
Lewiston-Stockton hvb	1680	1694	1650
Upper Freeport mvb	2614	2583	2497
Pocahontas No. 3 lvb	5322	5337	5223

<u>Coal/Plastic Period (s)</u>	<u>Heating Rates</u>		
	<u>200 K/s</u>	<u>400 K/s</u>	<u>800 K/s</u>
Illinois No. 6 hvb	2.8	1.6	0.7
Pittsburgh No. 8 hvb	3.3	1.9	0.7
Lewiston-Stockton hvb	3.4	1.9	0.7
Upper Freeport mvb	3.1	2.0	0.8
Pocahontas No. 3 lvb	2.7	1.5	0.7

a: Holding temperature: 1098 K and Pressure: 1 atm helium

Figure 1.10: Apparent viscosity of different coals at different heating rates. Holding Temperature: 1098 K; Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

slower resolidification rates at lower heating rates exhibited in Figures 1.10 may reflect greater resistance of metaplast to depletion by mass transfer or possibly by secondary reactions, due in either case to the higher molecular weight of the metaplast. In overall summary, higher heating rates would be expected to shorten the plastic period by bringing the coal more rapidly to higher temperatures where metaplast depletion is accelerated while having less effect on the temperature where softening begins.

Coal-Type Effects: From the results of the previous sections, hvb coals (IL, PT, and WV) are very plastic. Mvb and lvb coals (UF and PO) also exhibit very good plastic behavior. Subbituminous coal (WY) and lignite (ND) used in this study do not exhibit any plastic behavior. From the observation of the pyrolyzed samples, these low-rank coals do not swell or agglomerate at the experimental conditions used for other bituminous coals.

From replicate runs and previous calibration results, the maximum noise of the plastometer is 300 Pa·s. Therefore, the observed maximum plasticity data show a trend in which at vacuum and also at elevated pressures (1, 10, and 50 atm He) the hvb coals have the lowest viscosity readings when compared to the mvb coal which has a lower viscosity reading than the lvb coal.

From the present data, however, there is no evidence for a continuous increase (or decrease) in the plastic period with increasing coal rank over the entire range of bituminous coal ranks studied. From replicate runs and the sampling interval of the digital recorder, the maximum error in measuring the plastic period is about 0.1 s. The mvb coal exhibits the longest plastic period when compared to the hvb and lvb coals, which have the similar plastic periods.

At present, a trend exists for the plastic behavior of coals of different ranks.

Subbituminous and low-rank coals, as well as lignites and peats, have a high fraction of labile bridges for forming small molecular fragments. However, they are also abundant in oxygen which promotes cross-linking. The net effect is that a small quantity of liquid fragments are produced on pyrolysis, and thus low tar yields are obtained. The coals do not exhibit any plastic behavior, and their main volatile products are noncondensable gases (Niksa and Kerstein, 1991; Ko, 1988; and Fong, 1986).

Hvb coals are abundant in labile bridges, but they have lower oxygen content than low-rank coals. In addition, they are rich in hydrogen which can stabilize radicals formed during pyrolysis (Vorres, 1989 and Ko, 1988). They also have high tar yields as well as high yields of extractables from the raw coal. Hvb coals therefore produce a lot of liquid fragments from physical melting and from labile bridge scissions. These liquid molecules can be transported out of the coal sample to form tar or further react to form noncondensable gases and coke and char (Niksa and Kerstein, 1991).

The mvb and lvb coals in this study produce less tar than a typical hvb coal (Ko, 1988 and Niksa, 1991), but exhibit strong plastic behavior comparable to that of the three hvb coals studied. Since higher rank (mvb and lvb) coals have a smaller fraction of labile bridges than hvb coals, they are less likely to produce the small liquid fragments identifiable as tar precursors, and hence lower tar yields on pyrolysis would be expected (Ko, 1988; Niksa and Kerstein, 1991). However, mvb and lvb coals are still able to produce larger fragments (possibly a cluster of aromatics) which contribute to their good plastic behavior. They are rich in hydrogen to stabilize the radicals formed from labile bridge scissions and can therefore produce stable molecules in the liquid boiling range. They also have lower oxygen content which means cross-linking to these liquid fragments to form light gases and char is less likely.

It has been proposed that the scission of kinetically similar bonds in the coal is the preferred route for release of molecular fragments which ultimately form metaplast-like liquids (Darivakis, 1989). According to this picture, coals which have more kinetically similar and thermally labile bonds (e.g. because of a more uniform molecular structure), as is expected in mvb and lvb coals, have a higher probability to form liquid products than low-rank coals. This hypothesis, along with considerations of their labile bridge fraction and hydrogen and oxygen contents, explains why low-rank coals such as subbituminous coals and lignites do not exhibit any plastic behavior under the present conditions. Hvb coals have a high probability of forming liquids, have lower oxygen content, and are abundant in labile bridges and hydrogen. They therefore are the most plastic coals of all ranks in the sense of exhibiting the lowest values of minimum apparent viscosity. Mvb and lvb coals have lower liquid yields because they are lower in labile bridges. Having the lowest labile bridge fraction of the coal ranks studied, lvb coals exhibit even less plastic behavior than mvb coals.

1.7 Mathematical Modeling

From suspension modeling results, a two phase model has been used to relate metaplast concentration and the apparent viscosity of different coals. In particular, analyzing the plasticity kinetics of coal, the concentrated suspension model of Frankel and Acrivos (1967) has been chosen to relate the viscosity of molten coal to the metaplast concentration:

$$\mu/\mu^* = (9/8)/[(\frac{1-M}{1-M_c})^{-1/3} - 1] \quad 1.2)$$

where μ^* is the viscosity of the solids-free liquid. From the work of Nazem (1980) who measured the viscosities of carbonaceous mesophase pitch at 623 K to be in the order of 100 Pa·s and assuming that the solids-free metaplast has a similar viscosity, μ^* was chosen to be 200 Pa·s. The quantity M is the intraparticle inventory of softened material (metaplast), having the critical value M_c , at which μ goes to ∞ . At this critical value, the liquid fraction is insufficient to separate the solid particles. The number ranges from .36 to 0.25 for close packing spheres and 0.20 to 0.10 for close packing rods. The solid elements in the coal sample are expected to be more like thin slabs (lamellae) than spheres (Fong et al., 1985). Therefore, to be representative of these ranges, the number for M_c was chosen arbitrarily to be 0.20. In addition, it is seen from Fong's pyridine extractable data that Pittsburgh No. 8 coal only starts to soften when $M > 0.20$ (Fong, 1986). From this equation, one can calculate the transient metaplast inventory, $M(T,t)$, from plasticity data, $\mu(T,t)$, or vice versa.

Multiple Independent Parallel Reaction Kinetics

The multiple independent parallel reaction model has been used to describe the kinetics of metaplast generation and depletion. In the generation step, physical melting of coal is also incorporated. Using a nonlinear least squares regression routine (DUNLSF by IMSL), the activation energy and its variance for each chemical reaction step are fitted to the experimental data. The modeling results are then compared to the experimental results.

With the need for a model which describes the plasticity and metaplast kinetics more realistically, the multiple independent parallel reaction (MIPR) kinetics model was used. The MIPR model has been used widely by previous students in combustion at MIT to describe kinetics of weight loss and of tar production during coal pyrolysis (Anthony,

1975, Ko, 1988, and Griffin, 1989). The model is described in detail elsewhere (Anthony, 1975 and Howard, 1981). For the proposed studies, all the chemical reactions involved in the plasticity kinetics and metaplast generation and destruction will be modeled using MIPR. For an irreversible, first-order reaction:

the rate equation and its solution are:

$$dA/dt = -k_A A \quad 1.4)$$

$$A = \exp\left(-\int_0^t k_A dt\right) \quad 1.5)$$

where A is the amount of A at time t and k_A is the rate constant. Using the MIPR model:

$$A = A_1 + A_2 + A_3 + \dots + A_n = \sum_0^n A_i \quad 1.6)$$

$$dA_i/dt = -k_{Ai} A_i, \quad i = 1, 2, 3, \dots, n \quad 1.7)$$

$$A_i = \exp\left(-\int_0^t k_{Ai} dt\right) \quad 1.8)$$

$$k_{Ai} = k_{0Ai} \exp(-E_i/RT) \quad 1.9)$$

where i denotes a particular reaction i, k_{0Ai} and E_i are respectively the preexponential factor and activation energy for reaction i. Assuming that all the reactions have the same preexponential factor ($k_{0Ai} = k_{0A}$) and that the number of reactions are large enough to permit the activation energies to be expressed as a continuous distribution with a probability density function $F(E)$:

$$A = \int_0^{\infty} \exp\{-k_0 A \cdot \int_0^t \exp(-E/RT) dt\} \cdot F(E) dE \quad 1.10$$

Following Anthony et al. (1975) one can choose $F(E)$ to be a Gaussian such that:

$$F(E) = (2\pi\sigma_E^2)^{-1/2} \exp\{-(E_0 - E)^2/2\sigma_E^2\} \quad 1.11$$

where E_0 and σ_E^2 are respectively the mean activation energy and its variance. Only four parameters ($A(t=0)$, E_0 , σ_E^2 , $k_0 A$) are required to correlate the MIPR model to kinetics data for a reaction contributing to plasticity and/or metaplast generation and depletion data.

Metaplast Reaction Kinetics: Formulation, Results, and Discussion

The following sequence of kinetic steps are used to determine the intraparticle metaplast inventory, $M(T,t)$:

$$M^* = C_r(t) + (M_{mo}-M_m(t)) + M(t) + P(t) \quad 1.13$$

$$dM/dt = -dC_r/dt + dM_m/dt - dP/dt \quad 1.14$$

$$dM/dt = r_m + r_g + r_d \quad 1.15$$

where M^* is the maximum amount of metaplast that can be formed and $C_r(t)$ is the remaining amount of coal that can react to form metaplast. The quantity $(M_{mo}-M_m(t))$

is the remaining amount of coal that can melt to form metaplast, M_{mo} being the maximum amount of meltable coal and M_m being the amount of metaplast formed by melting. $P(t)$ is the product from the pyrolysis (i.e. light gases, tar, and coke). The rate of change of metaplast concentration is given by equations 1.14 and 1.15, where r_m is the rate of physical melting, r_g is the rate of metaplast generation by chemical reaction, and r_d is the rate of metaplast depletion.

For a Gaussian distribution of melting points, the rate of physical melting, r_m , is given to a very good approximation by:

$$dM_m/dt = r_m = \{M_{mo}m_h/(2\pi\sigma_m^2)^{1/2}\} \cdot \exp\{-(T_m-T)^2/2\sigma_m^2\} \quad 1.16)$$

M_{mo} is the amount of meltable components (e.g. pyridine extractables) in the parent coal, m_h is the heating rate at time t , and T_m the mean melting temperature of coal. The quantity r_m is thus described as the product of M_{mo} , m_h , and the melting point probability density function. Since coal is assumed to melt over a narrow range of temperatures, the melting point distribution is estimated to be normal, with a mean $T_m = 600$ K and the variance $\sigma_m^2 = (30K)^2$ (Fong et. al., 1986b). The quantity M_m is found by integrating r_m over time, knowing the temperature-time histories.

Defining M_r as the amount of metaplast formed by the pyrolysis of C_r , the rate of metaplast generation by chemical reaction of the parent coal is given by:

$$-dC_r/dt = r_g = dM_r/dt \quad 1.17)$$

Defining M_{ri} as the amount of M_r formed by an independent reaction i :

$$dM_{ri}/dt = k_{gi}(M_{ri}^* - M_{ri}) \quad 1.18)$$

$$\frac{M_{ri}^* - M_{ri}}{M_{ri}^*} = \exp \left\{ \int_0^t -k_{gi} dt \right\} \quad 1.19)$$

$$\frac{M_r^* - M_r}{M_{ri}^*} = \int_0^\infty \exp \left\{ \int_0^t -k_{gi} dt \right\} \cdot F(E_g) dE_g \quad 1.20)$$

$$F(E_g) = (2\pi\sigma_{E_g}^2)^{-1/2} \exp \{ - (E_{go} - E_g)^2 / 2\sigma_{E_g}^2 \} \quad 1.21)$$

$M_r^* = M^* - M_{mo}$, the maximum amount of metaplast produced by chemical reaction of the parent coal. Using low temperature (< 900 K) transient viscosity data to find $M(t)$, $M_r(t) = M(t) - M_m$, in which M_m was calculated from integrating r_m over time. The generation rate constant (k_g) was found by fitting the parameters M_r^* , the mean activation energy (E_{go}) and its variance ($\sigma_{E_g}^2$) to data on $M_r(t)$ for various temperature-time histories. The preexponential factor of k_g was fixed at 10^{13} s^{-1} to simplify the generation of a set of best-fitted kinetics parameters. Otherwise, several sets of best-fitted parameters can be found with markedly different values of k_{go} , each set being a local minimum of the M_r vs. (k_{go} , E_{go} , σ_{E_g} , M_r^*) parameter space.

The metaplast depletion step would in general be given by:

$$r_d = -k_d M = -dP/dt \quad 1.22)$$

However, a useful simplification becomes possible by inspection of the plots of apparent viscosity vs. time (Figures 1.7 and 1.10). These figures exhibit a plateau-like region where the minimum apparent viscosity is essentially unchanged with time. This implies that the maximum metaplast concentration, M^* , is observed before any substantial

resolidification of the molten coal has begun and hence that the chemical driving force generation of the products:

$$dP/dt = k_d(P^* - P) \quad 1.23)$$

can be reasonably approximately by setting:

$$P^* = M^* = M_r^* + M_{mo} \quad 1.24)$$

Equation 1.14 and 1.24 imply that:

$$P(t) = M^* - M(t) \quad 1.25)$$

The approximations allow the kinetics of metaplast depletion and hence products formation to be modeled without the need to simultaneously solve differential equations for $C(t)$, $M(t)$, and $P(t)$.

In particular here, high temperature (>1000 K) transient viscosity data were used to calculate $M(t)$ and thus $P(t)$ from equation 1.25, again assuming that the metaplast generation step had been completed.

Defining P_i as the amount of P formed by an independent reaction i :

$$dP_i/dt = k_{di}(P_i^* - P_i) \quad 1.26)$$

$$\frac{P_i^* - P_i}{P_i^*} = \exp \left\{ \int_0^t -k_{di} dt \right\} \quad 1.27)$$

$$\frac{P^* - P}{P^*} = \int_0^{\infty} \exp \left\{ \int_0^t -k_d dt \right\} \cdot F(E_d) dE_d \quad 1.28)$$

$$F(E_d) = (2\pi\sigma_{Ed}^2)^{-1/2} \cdot \exp \{ - (E_{do} - E_d)^2 / 2\sigma_{Ed}^2 \} \quad 1.29)$$

The depletion rate constant (k_d) were found by fitting the mean activation energy (E_{do}) and its variance (σ_{Ed}^2) to these high temperature data on $P(t)$ for different holding temperatures, estimated from equation 1.25. The preexponential factor of k_d was fixed at 10^{13} s^{-1} , again to generate only one set of kinetics parameters (see discussion of fitting to obtain kinetics parameter of the metaplast generation step).

With each contribution to the metaplast generation and depletion kinetics defined according to equation 1.14, metaplast concentration, $M(t)$, is found by:

$$M(t) = M_r(t) + M_m(t) - P(t) \quad 1.30)$$

The best fitted parameters (M_r^* , E_{go} , σ_{Eg} , E_{do} , and σ_{Ed}) are shown on Table 1.4. The calculated apparent viscosity of different coals is shown in Figure 1.11 for constant heating rate runs and different final holding temperatures and in Figure 1.12 for heating at different rates to the same final temperature.

The calculated apparent viscosity of different plastic coals agrees well with the experimental data. The standard error of the estimate (SEE) is calculated for the plastic periods and minimum apparent viscosities for all runs on each coal at 1 atm pressure.

$$SEE = \sum_{j=1}^n \left\{ \frac{(\text{experimental value}_j - \text{predicted value}_j)^2}{n-k} \right\}^{1/2} \quad 1.31)$$

Table 1.4: MIPR BEST-FITTED KINETICS PARAMETER VALUES

COAL	(dmmf)		Ego	(Kcal/mole)		Edo	σEd
	Mmelt	M*		σEg			
IL hvb	.28 ^a	.41	42.7	0.4	59.0	8.0	
PT hvb	.30 ^a	.48	43.0	0.4	60.1	7.6	
WV hvb	.30 ^b	.45	42.8	0.3	60.0	7.5	
UF mvb	.07 ^a	.35	37.7	0.3	63.2	5.5	
PO lvb	.01 ^a	.29	38.1	0.3	59.2	4.4	

a: data from Snape and Bartle, 1989

b: no data available, estimated to be approximately equal to that of Pittsburgh No. 8 coal.

$$k_{go} = k_{do} = 10^{13} \text{ s}^{-1}$$

Figure 1.11: Smooth lines: Apparent viscosity of different coals at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 1.12: Smooth lines: Apparent viscosity of different coals at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ h.

where n is the number of data points and k the number of best fitted parameters used in the model. The average standard error of estimate (ASEE), for the plastic periods and for the minimum apparent viscosity, is found by averaging the SEE's for all five coals. In previous work, a SEE was calculated for a set of data on tar yields where each measured tar yield corresponded to a specific and complete temperature-time history (Ko, 1988). However, for each temperature-time history in this work a set of many viscosity data points is obtained. It was therefore concluded that SEE's should be computed, not for the entire set of individual viscosity readings associated with each temperature-time history, but rather for two parameters characteristic of the composite viscosity vs. time behavior for each temperature-time history. These two parameters are the minimum apparent viscosity and the plastic period. The resulting SEE's and corresponding ASEE's are listed in Table 1.5. The ASEE's for the plastic period and the minimum apparent viscosity are 0.13 s and 317 Pa·s, respectively. These values are comparable to the measurement resolution of the plastometer (0.1 s and ± 300 Pa·s). It is therefore concluded that the model does a good job of fitting the overall plastic behavior of this set of five coals, as affected by temperature-time history.

In general, the model predictions fit the experimental results well, except for predicting that at lower heating rates (200 and 400 K/s), the apparent viscosity begins to increase at a later time than that observed. At lower heating rates, the experimentally observed viscosity during resolidification increases slowly at approximately 1000 K, then increases very rapidly when the holding temperature of 1098 K is attained. This earlier rise in viscosity is hypothesized to be caused by secondary reactions, which the model does not address, degrading the plasticizing power of the metaplast by forming higher molecular weight liquid which is more viscous.

Table 1.5: Standard Error of Estimate for MIPR Kinetics Model^a

<u>Coal</u>	<u>SSE(Plastic Period), s</u>	<u>SSE(Min Viscosity), Pa·s</u>
Illinois No. 6 hvb	0.14	203
Pittsburgh No. 8 hvb	0.14	279
Lewiston-Stockton hvb	0.07	395
Upper Freeport mvb	0.21	424
Pocahontas No. 3 lvb	0.07	283
Average (ASEE)	0.13	317

a: see equation 1.31 in text.

The activation energy values of the metaplast chemical generation step for hvb are higher than those for mvb and lvb coals. There are two processes for forming metaplast: physical melting and chemical reaction. While metaplast generation for mvb and lvb coals is mostly due to chemical bond breakings, for hvb coals it is mostly due to melting. If two coals have comparable plastic behaviors, the one with a lower metaplast formation from physical melting maintains a comparable metaplast inventory by having a higher metaplast formation from chemical reactions. Lower activation energy values (i.e. higher chemical reaction rates) would then be expected for mvb and lvb coals to compensate for the lower inventories of meltable components in these coals. The standard deviation values of E_g are very small, supporting the interpretation that chemical generation of metaplast occurs by a small number of, or even one, pathway. Thus the sometimes observed phenomenon of higher product yield at higher heating rate, attributed by some interpretations to competing chemical pathways with different activation energies, is expected to be of little importance here. By modeling the metaplast generation kinetics as a single reaction, the modeling results are essentially the same. However, the SEE's and ASEE's improve by 18%, since the number of fitted parameters (k) decreases from 5 to 4, with the removal of σ_{E_g} from the parameter space.

The activation energy values of the depletion step for all coals are about the same except for the mvb coal which is slightly higher. Since Upper Freeport mvb coal solidifies at much later time than other coals, its depletion step's activation energy is higher (implying a lower rate of depletion kinetics). The standard deviation of E_d , σ_{E_d} , decreases with increasing rank, ranging from 4.4 kcal/mole for Pocahontas No. 3 lvb coal to 8.0 kcal/mole for Illinois No. 6 hvb coal (Table 1.4). A tendency toward greater uniformity in the molecular structure of the parent coal structures with increasing rank is supported by these σ_{E_d} results. Higher rank coals have a more uniform molecular structure, and therefore their liquid metaplast should be made up of more similar molecules. These

similar molecules react by more similar pathways, thus the lower σ_{Ed} , indicating that there are fewer independent reactions contributing to metaplast depletion. Hvb coals have higher σ_{Ed} values, implying that the depletion reactions may involve a larger number of different reactions.

Coal-Type Specific Parameter Modeling: Formulation, Results, and Discussion

For plastic coals, relationships between simple indices of coal type and observed plasticity would be beneficial. From the present data, there is no evidence for a continuous increase (or decrease) in plasticity with increasing coal rank. This section will concentrate on the investigation of the relationships between maximum plasticity (and thus maximum metaplast concentration) and simple indices of coal type for different coals.

Different Indices of Coal Type

One of the simplest indices of coal type for different coals is their elemental content. Coal consists of inorganic materials (e.g. 5-20 wt%) and organic materials, i.e. macerals, made up of largely C, O, H, N, S, and mineral matter. In general, as the rank increases, the carbon content of a coal increases, while its oxygen content decreases. The balance of the mass consists mainly of hydrogen, nitrogen, and, in high sulfur coals such as Illinois No. 6 hvb, organic sulfur. Carbon and hydrogen NMR studies also allow for more refined classifications of coal elements such as fraction of aromatic carbon (carbon aromaticity, C_{fa}) and fraction of hydrogen attached to aromatic carbon (proton aromaticity, H_{fa}). Ultimate analyses and structural data for the coals studied here are shown in Table 1.6.

TABLE 1.6: Ultimate Analyses, Structural, and Plasticity Data for Argonne Premium Coals

	ND lig	WY sub	IL hvb	PT hvb	WV hvb	UFm vb	PO l vb
%C dmmf ^a	74.05	76.04	80.73	84.95	85.47	88.08	91.81
%O dmmf ^a	19.13	16.90	10.11	6.90	6.68	4.72	1.66
%H dmmf ^a	4.90	5.42	5.20	5.43	5.44	4.84	4.48
%N dmmf ^a	1.15	1.12	1.37	1.64	1.56	1.55	1.33
% Organic S ^a	0.70	0.47	2.38	0.89	0.65	0.74	0.50
Carbon Aromaticity ^b , C _f _a	0.57	0.60	0.67	0.74	0.75	0.80	0.88
Proton Aromaticity ^c , H _f _a	0.24	0.27	0.30	0.35	0.36	0.39	0.45
Max Plasticity (Pa·s), vacuum	n/a	n/a	2690	2500	2550	5019	7455
Max Plasticity (Pa·s), 1 atm He	n/a	n/a	1758	1286	1694	2583	5337

a: Vorres, 1989

b: Ko, 1988

c: Niksa, 1991

Plot of maximum plasticity at 1 atm pressure of helium and at vacuum vs. %C for different coals is shown in Figure 1.13. Hvb coals are seen to be very plastic. Although mvb and lvb coals are less plastic than hvb coals, they still exhibit a strong plastic behavior. However, the %C content does not correlate well with plasticity.

Labile Bridges: Labile bridges are mostly aliphatic, with some alicyclic and heteroatomic functionalities. They are the bridges which link the larger aromatic clusters or molecules together. The initial fraction of labile bridges are important since they are the key reaction centers. When a labile bridge is heated, its dissociation can produce reactive fragments which may further dissociate to produce smaller aromatic fragments or condenses to form char and release noncondensable gases (Niksa and Kerstein, 1991). Scissions of labile bridges can therefore create smaller aromatic molecules including liquid metaplast. Thus, coals with higher fractions of labile bridges should exhibit greater plasticity. Figure 1.14a shows a plot of maximum plasticity vs. fraction of aliphatic carbon content ($1-C_f$). In general, hvb coals with higher aliphatic carbon fraction (and thus higher labile bridge fractions) exhibit greater plasticity than mvb and lvb coals with lower aliphatic carbon fraction.

Oxygen Content: Oxygen also plays an important role in coal devolatilization. Oxygen promotes cross-linking of labile bridges which suppresses formation of liquid fragments or metaplast (Niksa and Kerstein, 1991). Coals with higher oxygen content might therefore be expected to exhibit lower plasticity. Figure 1.14b shows a plot of maximum plasticity vs. %O content of a coal. Here, hvb coals with higher oxygen content still exhibit significant plasticity, more than mvb and lvb coals with lower oxygen content. This is probably because the magnitude of plasticity is coupled with other indices of coal type (e.g. labile bridge content and hydrogen content), and the effects of oxygen content on coal plasticity is not clear cut in Figure 1.14b. In discussing possible explanations for

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 1.13: Maximum plasticity (minimum viscosity) of different coals at vacuum and 1 atm helium. Heating Rate: 400 K/s; Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

1.14a: Maximum Plasticity vs. Aliphatic Carbon Fraction

1.14b: Maximum Plasticity vs. %O

1.14c: Maximum Plasticity vs. %H

Figure 1.14: Plasticity vs. coal-specific parameters at vacuum and 1 atm helium. Heating rate of 400 K/s and holding temperature of 1098 K.

coal type effects on pyrolysis, Suuberg et al. (1979) noted that reactions of two hydroxyl groups can result in water and an etheric oxygen bridge between two moieties in the coal structure. Thus phenolic groups are expected to inhibit plasticity by participating in cross-linking of metaplast or its precursors, and by consuming hydrogen which could otherwise stabilize radicals. Thus a possible relation of OH content of the coals and decreased plasticity was investigated. However, decreasing plasticity was not found to be correlated with increasing OH content. Therefore it was decided to concentrate only on the contribution of total oxygen content to plasticity in the formulation of a coal specific parameter to correlate the magnitude of plasticity of different coals.

Hydrogen Content: Hydrogen is important because it can stabilize radicals. The abstractable hydrogen is hydrogen which is not attached to aromatic carbons. Its inventory depends on Hf_a and the total amount of hydrogen in the parent coal.

Abstractable hydrogen stabilizes aromatic molecules, and is thus believed to promote plasticity. Coals with higher content of non aromatic hydrogen would therefore be expected to exhibit higher plasticity (Ko et al., 1988 and Niksa, 1991). Figure 1.14c shows a plot of maximum plasticity vs. %H content. In general, hvb coals with higher hydrogen content exhibit greater plasticity, i.e. lower apparent viscosity, than mvb and lvb coals with lower hydrogen content.

Formulation of A Parameter to Correlate Plasticity with Coal-type

Ko (1988) and Ko et al. (1989) correlated maximum tar yield in rapid pyrolysis of powdered coal (diameter < 100 μ m) with a coal-type parameter X_{tar} :

$$X_{tar} = \frac{(\text{no. of labile bridges})(\text{amt. of abstractable H})}{(\text{no. of cross-linked bridges})} \quad 1.28)$$

from the assumption of that tar generation proceeds via the global mechanism:

Here, the importance of labile bridges, oxygen, and hydrogen is recognized in determining the three factors used to determine X_{tar} . The number of labile bridges is assumed to be proportional to the aliphatic carbon content of the raw coal. The amount of the abstractable hydrogen is assumed to be proportional to the amount of elemental hydrogen in the raw coal. The number of cross-linked bridges is assumed to be proportional to amount of the elemental oxygen and organic sulfur in the raw coal. The analysis of Ko et al. provided a good linear correlation between maximum tar yield at various pressures and X_{tar} . (Ko, 1988 and Ko et al., 1989)

In light of Ko's previous correlation and the strong relationship between metaplast and tar, it seems plausible to try to correlate maximum plasticity with a coal-type parameter. This coal-type parameter should incorporate the importance of labile bridges, oxygen, and hydrogen content. First, the coal-type parameter for plasticity was formulated as:

$$X_P = \frac{(\text{no. of labile bridges})(\text{total amount of hydrogen})}{(\text{total amount of oxygen})} \quad 1.30)$$

with:

$$\text{no. of labile bridges} = ((1 - C_{f_2}) \cdot [C \text{ wt\% dmmf}])^{1.8} \quad (\text{Ko, 1988}) \quad 1.31)$$

$$\text{amount of hydrogen} = [H \text{ wt\% dmmf}] / 1.0079 \quad 1.32)$$

$$\text{amount of oxygen} = [O \text{ wt\% dmmf}] / 15.994 \quad 1.33)$$

A plot of maximum plasticity vs. X_p is shown in Figure 1.15a. A linear correlation between plasticity and X_p is quite good at vacuum and better at 1 atm He pressure. However, knowing that not all hydrogen participates in stabilizing free radicals, it seems logical to replace the amount of hydrogen in equation 1.32 by the amount of abstractable hydrogen. Here, the amount of abstractable hydrogen is formulated as the amount of hydrogen which is attached only to aliphatic carbon atoms minus a correction suggested by Ko (1988) to account for experimental observations that OH group may compete for the abstractable hydrogen:

$$\begin{aligned} \text{amount of abs hydrogen} = & (1-H_{f_a}) \cdot [\text{H wt\% dmmf}] / 1.0079 \\ & - [\text{OH wt\% dmmf}] / 17.002 \end{aligned} \quad 1.34)$$

$$[\text{OH wt\% dmmf}] = 33.2 - 35[C] \quad (\text{Ko, 1988}) \quad 1.35)$$

Ko (1988) assumed that abstractable hydrogen should be proportional to aliphatic hydrogen. In formulating an equation for estimating abstractable hydrogen from coal elemental composition, he assumed that aliphatic hydrogen concentration in the coal was proportional to total hydrogen concentration in the coal. For the present set of coals, data are available on the actual fraction of aromatic hydrogen in the coals of interest. Therefore we can directly calculate the fraction of aliphatic hydrogen as $1-H_{f_a}$. The revised X_p was formulated as:

$$X_p(\text{corrected}) = \frac{(\text{no. of labile bridges})(\text{amount of abstractable hydrogen})}{(\text{total amount of oxygen})} \quad 1.35)$$

A plot of maximum plasticity vs. a revised X_p , corrected to better account for the abstractable hydrogen ($X_p(\text{corrected})$) is shown in Figure 1.15b. The linear fit between

maximum plasticity and $X_p(\text{corrected})$ is better than that of the uncorrected X_p , especially in correlating data under vacuum.

The present correlations represent an attempt to explain coal-type effects on coal plasticity. Here it has proved fruitful to formulate a coal-type parameter for apparent viscosity analogous to that for tar yields devised by Ko (1988). The effects of labile bridges, oxygen, and hydrogen in the specific coal are incorporated into the present coal type parameter in reflection of their hypothesized effects on metaplast and hence on coal plasticity. Although rich in labile bridges and hydrogen, lignites and subbituminous coals have abundant oxygen which promotes cross-linking, causing the formation of liquid fragments or metaplast to be suppressed, leading to a lack of plastic behavior in these coals. The primary volatile products of their pyrolysis are noncondensable gases. With much lower oxygen content than that of low rank coals, Hvb coals are also rich in labile bridges and hydrogen which leads to very good plastic behavior. High rank coals have lower plasticity than hvb coals because they have considerably less labile bridges.

A coal-type parameter for correlating plasticity is intended to be used as a rough guide, or at least to predict trends in plasticity for a coal when experimental data are not available on the plasticity of that coal. One is able to use the correlation knowing only the ultimate analysis and a few structural data for the given coal.

1.15a: Maximum Plasticity vs. X_p 1.15b: Maximum Plasticity vs. $X_p(\text{corrected})$

Figure 1.15: Plasticity vs. coal-specific parameters at vacuum and 1 atm helium. Heating rate: 400 K/s; holding temperature: 1098 K.

1.8 Conclusions and Recommendations

Conclusions

- 1) By varying the shear rates of the plastometer and observing the apparent viscosity, molten Pittsburgh No. 8 hvb coal was found to be Newtonian for shear rates from 2 to 10 s^{-1} .
- 2) At higher temperature (i.e. 1098 K), pressure effects are important at vacuum where the plastic period decreases and minimum apparent viscosity increases when compared to those at 1 atm of inert gas. Increasing inert gas pressure from 1 atm up to 50 atm does not significantly change coal plasticity. It is hypothesized that higher pressure inhibits mass transport of metaplast to tar vapors, but also enhances metaplast repolymerization into coke and char.
- 3) The plastic period decreases with increasing holding temperature. It is hypothesized that higher temperature increases mass transport of liquid metaplast to tar vapors and metaplast repolymerization to coke and char.
- 4) Heating rate has essentially no effect on the individual softening temperature of each plastic coal, thus implying that metaplast generation, by physical melting (as would be expected) or by chemical bond breaking, or both, is not strongly affected by heating rate.
- 5) The plastic period decreases with increasing heating rate. It is hypothesized that higher heating rate increases mass transport of liquid metaplast to tar vapors. In addition, higher temperature is reached faster, resulting in enhanced metaplast repolymerization to coke and char.

- 6) Coal type strongly affects the magnitude and duration of plasticity. Hvb coals are most plastic. Mvb and lvb coals exhibit comparable plasticity to hvb coals, though the maximum plasticity and duration of the plastic period are less. Low rank coals such as subbituminous and lignite do not exhibit any plasticity under the present heating conditions.
- 7) The number density and volume fraction of bubbles in molten coal are not consistent with those usually associated with foams. During high heating rate pyrolysis of coal (heating rate $> 10^3$ K/s), the bubble number density is high, but the volume fraction of bubbles in the molten coal is too small to be foam-like. During low heating rate pyrolysis of coal (heating rate $< 10^2$ K/s), the volume fraction is high, but the number density of bubbles in the molten coal is too low to be considered foam-like.
- 8) The apparent viscosity of molten coal can be reasonably modeled by approximating the melt as a two phase suspension of a solid in a liquid. Although the contribution to the apparent viscosity of the coal melt by gas bubbles is not negligible, it is not significant enough for this research to use a three phase suspension model, considering the difficulty of determining the time-dependent gas volume fraction either experimentally or theoretically.
- 9) The transient coal plastic behavior is well predicted using a kinetics model that assumes metaplast is generated by physical melting and by chemical reactions, and depleted by chemical reactions. The model assumes that the chemical reaction steps can be mathematically described by multiple independent parallel reaction kinetics (MIPR). The model has five fitted parameters: the maximum amount of metaplast that can be generated (M^*), the mean activation energy and its variance for the chemical

generation reactions (E_g and σ_{Eg}), and the mean activation energy and its variance of the chemical depletion chemical (E_d and σ_{Ed}). All of these parameters have been determined by best fitting the model to experimental data on viscosity vs. temperature-time histories.

10) The MIPR model's standard errors of estimate (SEE's) have been determined for the minimum apparent viscosity and the plastic period of each coal. The average of the SEE's for the minimum apparent viscosity and the plastic period of all five plastic coals have been found to be approximately the same to the viscosity and time resolutions of the plastometer which are 300 Pa·s and 0.1 s, respectively.

11) Coal plasticity is moderately well correlated with simple indices of coal type such as the elemental C, O, and H contents and well correlated linearly with a coal specific parameter defined in terms of simple indices of coal type such as labile bridge fraction and H and O contents. These indices are combined to calculate a coal specific parameter $X_p(\text{corrected})$:

$$X_p(\text{corrected}) = \frac{(\text{no. of labile bridges})(\text{total amount of abstractable hydrogen})}{(\text{total amount of oxygen})}$$

which has a good predictive ability for coal maximum plasticity as affected by coal type at vacuum and at 1 atm pressure.

Recommendations

1) The Newtonian behavior of molten should be further investigated. The range of shear rates for this study should be increased, and the measurements should be conducted for other coals. Currently, the maximum shear rate of the plastometer is approximately 11 s⁻¹

11 s^{-1} due to a limit set by the gear motor's maximum angular speed and the size of the current apparatus. The possibility of incorporating a higher performance gear motor to the current plastometer setting should be investigated.

2) The effects of pressure on plasticity should be further investigated, particularly at lower temperatures. With a trade-off between mass transport of metaplast to tar and repolymerization of tar to coke and char, there should be an optimum pressure (and temperature) for maximum plasticity.

3) The effects of reactive gases such as H_2 and O_2 should be investigated. Hydrogen is hypothesized to enhance plasticity, and oxygen is hypothesized to diminish plasticity. Plasticity data obtained under these reactive gas atmospheres will shed light on these hypotheses.

4) The effects of coal pretreatment such as alkylation and preoxidation should be investigated. These pretreatments are hypothesized to affect plasticity by altering the metaplast generation and depletion reaction processes.

5) The plastometer can be used to investigate the rheological behavior of other thermoplastic materials such as thermal softening polymers at high heating rates and temperatures.

6) High heating rate studies of lower rank coals should be performed to potentially induce plasticity for systematic measurement in an apparatus similar to the current plastometer, but modified to provide higher heating rates.

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Chapter 2. Introduction and Background

2.1 Introduction

Upon heating, bituminous coals soften and create a fluid-like mass often referred to as metaplast. The coal remains softened for a period of time and then resolidifies to form coke. The softened coal is a combination of solid materials (mineral matter and organic constituents that do not soften) and metaplast. The softened coal may also contain bubbles of gaseous products from pyrolysis. The thermoplastic behavior of coal is strongly connected with the coal's pyrolysis kinetics. At elevated temperature (>650 K), the parent coal starts to physically melt and devolatilize (Loison et al., 1963 and Fong, 1986). The resulting products include metaplast and gaseous species which can escape or undergo further secondary reactions to produce tar, char, and other gaseous species.

A good understanding of coal's transient plastic behavior is therefore important for understanding the pyrolysis kinetics of softening coals. Heating rate and holding temperature are expected to significantly affect coal plasticity and, by inference, the behavior of softening coal in modern coal conversion processes. For example, plasticity can affect reactivity and agglomeration of the coal in fixed or fluidized bed gasification. Swelling and agglomeration associated with coal plasticity can lead to bed bogging in fixed or fluidized bed gasifiers and combustors, but are desired in metallurgical coke manufacture since they contribute to strong and hard products. In addition, conditions in which the coal's fluidity is high are desirable for high reactivity in coal liquefaction (Whitehurst, 1980). Devolatilization and plasticity can affect reactions and thus pollutant generation in coal combustion, coal gasification, mineral matter size distributions in high temperature coal, and the survival of unburned char.

2.2 Literature Review

Bituminous coals heated to 650 K or higher exhibit transient plastic behavior. The coal particles soften, swell, and resolidify to form coke (Loison et al., 1963). When coal melts and devolatilizes, its fluidity increases to a maximum for a period of time and then decreases. Fitzgerald (1956) modeled the thermoplastic behavior of coal by the metaplast theory:

The fluidity of the coal melt is dependent on the amount of the liquid metaplast existing throughout the coal at any time during devolatilization. Fong et al. (1986b) found that the amount of pyridine extractables of pyrolyzed coal could be correlated with the fluidity of the coal for various temperature-time histories. Darivakis (1989) also reported that the amount of pyridine extractables and tar yields depended on the temperature-time history of the coal during pyrolysis.

Previous observations of the coal's thermoplastic behavior have been made under conditions pertinent to metallurgical coke making. The heating rates used were low (< 0.1 K/s), and the maximum temperatures were generally below 800 K (ASTM, 1974). A commonly used instrument is the Gieseler plastometer (Figure 2.1). Powdered coal is compacted into a small cylindrical chamber containing a stirrer with blades or arms. The axis of the stirrer is subjected to a constant torque. The coal is heated rapidly to a temperature of about 573 K, and then the heating rate is kept constant at about 3 K/min. The rotational speed of the stirrer is recorded as a function of time or temperature. The plastic period of coal is observed between 650-750 K (Loison et al., 1963).

Figure 2.1: Gieseler plastometer and its plasticity data (Loison et al., 1963)

Lloyd and his research group at Western Kentucky University studied the rheological behavior of bituminous coals using the Gieseler plastometer. The effects of inert gas pressure (argon and helium) were extensively studied. Increasing pressure increases coal plasticity, as seen by higher angular speed of the stirrer and longer plastic period (Read et al., 1985 a & b).

The Gieseler plastometer's data provide only a qualitative understanding of coal's thermoplastic behavior. The viscosity of the coal melt cannot be readily obtained directly from the measured angular velocity. The Gieseler plastometer can be calibrated using a standard of known viscosity, and the measured angular velocity can be translated into an apparent viscosity. However, it is difficult to infer the physical significance of this apparent viscosity since the angular speed of the stirrer depends not only the true viscosity of the coal sample, but also on the complex flow field created in the cylindrical chamber.

Other investigators such as Davis and Echterhoff have created a number variable-torque plastometers. By keeping the angular velocity of the stirrer constant, the thermoplastic behavior of coal is observed by recording the transient torque data. Again, the heating rates and maximum temperatures of such plastometers are low, and the quantitative interpretation of the transient torque data is difficult due to the nature of the stirrer (Loison et al., 1963). Other plastometers include the Brabner plastograph, the Sapozhinokov plastometer, the concentric cylinder viscometer (Stephens, 1963), the capillary viscometer (Davies et al., 1983), and the microdilatometer of Khan and Jenkins (1984).

Using the microdilatometer, Khan and Jenkins (1984 and 1986) reported that increasing the heating rate increased the apparent fluidity of coal. However, they found that pressure had little effect, if any, on the thermoplastic behavior of coal.

In general it is difficult to interpret the data from the previously described plastometers quantitatively in term of the coal viscosity. Solomon et al. (1992) translated the Gieseler plastometer's data to viscosity and employed the metaplast theory to explain coal plasticity with moderate success. Their empirical model fitted the Geiseler plastometer's data well. However, the model performed poorly in predicting coal plasticity at high temperatures and heating rates such as those studied by Fong (1986).

Fong (1986) studied the transient plastic behavior of coal using a rapid-heating, fast-response plastometer he developed. The configuration of Fong's plastometer is a flat disk configuration in which the angular velocity of the shearing disk is constant (Figure 2.2). The viscosity of the pyrolyzing coal sample is calculated from the recorded torque required to rotate the disk at constant speed. Fong et al. (1986a) related the formation/depletion kinetics of pyridine extractables (assumed to approximate the metaplast) to the observed transient plastic behavior of rapidly pyrolyzed coal (Figure 2.3). The transient viscosity of the coal melt was related to the concentration of metaplast by an equation adapted from an equation of Frankel and Acrivos (1967) for the viscosity of solid in liquid suspensions:

$$\mu_{rel} = \frac{9}{8} \cdot \frac{\phi^{1/3}}{1 - \phi^{1/3}} \quad 2.2)$$

where μ_{rel} is the ratio of the actual viscosity and solid-free viscosity of the coal melt, ϕ is $1 - M$, and M is the mass fraction of metaplast in the melt.

Fong et al. studied the thermoplastic behavior of only one particular coal (Pittsburgh bituminous No. 8). In addition, they performed experiments at only one shear rate (1.98 s^{-1}). Coal plasticity data are needed for other coal types and shear rates and for temperature-time histories and pressures other than those studied by Fong. In general, the

FIGURE 2.2: Fong's flat-disk plastometer configuration, redrawn from Fong (1986) for presentation here.

FIGURE 2.3: Comparison of plastic behavior and pyridine-extractables formation and destruction. Holding temperature: —, 910 K; ----, 855 K. Heating Rate = 450 K/s and Pressure = 1 atm helium (Fong et al., 1985c)

factors influencing the plastic properties of coal include heating rate, particle size, coal type, pressure, shear rate, and pretreatment of the coal sample (Loison et al., 1963 and Howard, 1981).

With regards to coal-type effects, Ko et al. (1987 and 1988) correlated tar yields with coal type by assuming that tar is generated during pyrolysis via the global mechanism:

The structural-chemical factors considered in the coal type correlation were: 1) the identities and numbers of bridges between aromatic clusters of the coal and 2) the concentration of hydrogen available to stabilize free radicals created by bridge scission reactions (Ko et al., 1987).

Ko et al. defined a coal-type parameter for correlating tar yields as:

$$X_{\text{tar}} = \frac{\# \text{ of labile bridges}}{\# \text{ of cross-linked bridges}} \cdot \# \text{ of abstractable H atoms} \quad 2.4)$$

The formulation and computation of each of these three factors are described by Ko (1988). Each factor can be calculated solely from a C, H, O, and S elemental analysis of the raw coal. Maximum tar yield at a given pressure is linearly correlated with the coal-type parameter by:

$$\text{Tar Yield (wt\% dmmf)} = \alpha(P) + \beta(P)X_{\text{tar}} \quad 2.5)$$

The coefficients α and β are pressure (P) dependent and are determined by best fitting equation 2.5 to experimental tar yield data. Typical results are shown in Figure 2.4 from Ko et al. (1988).

Equation 2.3 shows that the amount of metaplast generated during coal pyrolysis can be determined from the tar yield if the transport term is unimportant as was taken to be the case in many of Ko's studies or if one has knowledge of the pertinent transport rates. The goal in the present work is to use a coal-specific parameter analogous to X_{tar} and an equation like 2.5 to estimate maximum metaplast yields for different coal types, and thereby to estimate the maximum fluidity for different coals.

2.3 Objectives

The goal of this research is to provide new, quantitative understanding of the high heating rate transient plastic behavior of different bituminous coals, in particular experimental determinations of apparent viscosity as affected by temperature-time history and a global model relating observed plasticity behavior to transient intra-coal metaplast inventories.

The specific objectives are:

1. Experimental

To measure the apparent viscosity of different bituminous coals during thermally induced softening for different shear rates ($1-10 \text{ s}^{-1}$), heating rates (200-1000 K/s), maximum temperatures (600-1300 K), total reaction times (1-10 s), and pressures of inert gas (1-100 atm helium).

FIGURE 2.4: Correlation of measured tar yields at different pressures against semi-empirical coal type parameter, X_{TAR} (Ko et al., 1988)

2. Theoretical

To relate the transient viscosity of molten coal to the kinetics of metaplast generation and depletion, using existing models and as appropriate to attempt to develop improved models to take into account effects heating rate, pressure, and shear rate and attempt to relate plasticity behavior to simple indices of coal type.

Chapter 3. Experimental Technique and Apparatus

3.1 Apparent Viscosity Measurement

The apparent viscosity of coal have been measured by a modified version of the plastometer originally developed and built by Fong (1986). The instrument measures the torque required to turn at a constant angular velocity a thin disk embedded in a thin layer of coal particles.

The modified plastometer (Figure 3.1) uses the same heating circuits (up to 1000 K/s and 1300 K maximum temperature) and torque transducer (up to 10 oz·in or $70 \cdot 10^{-3}$ N·m continuously) as that of Fong. However, a more powerful motor (24 V, 200 oz·in maximum torque) is used to provide shear rates of up to 10 s^{-1} . A high pressure vessel allows the instrument to be operated at pressures from near vacuum to 100 atm.

The torque transducer measures the torque supplied by the gear motor, to rotate at constant angular velocity and thus shear rate, a shearing disk embedded in a thin layer of coal. The torque transducer is a noncontact strain gauge torquemeter. The stated response time is less than 10 ms, and the stated maximum error is 0.2 % of reading. The torque transducer's maximum permissible load is 10 oz·in or approximately $70 \cdot 10^{-3}$ N·m. The shearing disk configuration has been modified from the flat disk used by Fong to cone-shaped disk shown in Figure 3.2. This allows the viscosity of the coal melt to be calculated without the assumption that the melt is Newtonian. The apparent viscosity, η , is obtained by applying the equation for a concentric cone-and-plate viscometer in which the disk rotates between two stationary plates (Bird et. al., 1977 and 1988). Since for a cone-and-plate geometry of very small cone angle, Newtonian behavior of the sample is not a requirement to compute η from the observed torque:

Figure 3.1: Schematic of the Plastometer

Figure 3.2: Gerjarusak's cone-shaped disk plastometer

$$\eta = \frac{3T_a/4\pi R^3}{\gamma_R} \quad 3.1)$$

where T_a is the torque, $\gamma_R = \Omega/\theta$ is the shear rate of the cone-shaped disk of radius R and cone angle θ , and Ω is the disk angular velocity. The shearing disk and chamber were machined from nickel superalloy (Rene 41) for high temperature strength and resistance to corrosion. The plastometer is enclosed in a high-pressure vessel (316 stainless steel rated for 200 atm) that can be evacuated to 0.0001 atm or charged with hydrogen or helium.

The temperature is measured using a 0.012-mm thin-foil thermocouple attached to the outside surface of the shearing chamber. The response time of the thermocouple is between 2-5 ms for a stepwise temperature change. With the coal's and metal's thermal diffusivities of $1.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ and $5 \cdot 10^{-6} \text{ m}^2/\text{s}$ respectively, the temperature gradient across the coal sample and shearing chamber is approximately 50 K at a 1000 K/s heating rate (Carslaw and Jaeger, 1959). This is a conservative estimate since the thermal diffusivity of coal increases with increasing temperature (Badzioch et. al., 1964).

The heating and holding circuits employ a total of six 12-V lead acid automobile batteries. The heating circuit uses two sets of batteries connected in parallel. Each set consists of two batteries connected in series for a 24-V output. The temperature holding circuit uses only one set of batteries since the total amperage required to maintain a certain temperature is much less than that required for heating. The magnitude of the electrical current is controlled by two carbon rheostats. The durations of heating and temperature holding are controlled by two solid-state digital relays adjustable from 0.00 to 99.9 s in 0.01-s increments.

During a typical run, the shearing chamber containing the shearing disk and coal is placed between the electrodes. The shaft of the shearing disk is attached to a coupling connected to the transducer (Figure 3.1). The thermocouple is attached to the surface of the shearing chamber. The top of the pressure vessel is lowered, and the vessel is sealed and evacuated to a pressure of 0.0005 atm. Helium is added until the pressure is approximately 1 atm, and the vessel is then evacuated again. This helium flushing and evacuation is repeated once, and the test gas is admitted until the desired pressure is reached. The motor and heating circuits are then activated. The torque vs. time and temperature vs. time histories are recorded, using a digital recorder capable of an acquisition rate of 1000 points/s. The data are later transferred to a personal computer. The raw data from the plastometer is shown in Figure 3.3.

3.2 Calibration of the Plastometer

A calibration has been developed for the new cone-shaped shearing disk version of the plastometer. This instrument was operated at three different shear rates (2.01 s^{-1} , 5.16 s^{-1} , and 8.00 s^{-1}) without any material in the shearing chamber. The torque readings were recorded and are plotted in Figure 3.4a. The torque due to friction and misalignment was "steady", i.e. exhibited only small variations with time, and had an average value of $3.18 \cdot 10^{-4} \text{ N}\cdot\text{m}$. Even at elevated temperature (e. g. 1098 K), the torque due to friction and misalignment did not change (Figure 3.5). The torque did not increase with shear rate, and the average value due to friction and misalignment was subtracted from the torque readings obtained with the shearing chamber filled with the calibration fluid or coal to determine the actual torque required to shear the material of interest.

Figure 3.3: Raw data from plastometer for three different coals.
 Heating Rate: 400 K/s; Holding Temperature: 1098 K;
 Pressure: 1 atm helium

Figure 3.4: Calibration of the Plastometer.

a) Noise due to friction and misalignment of the plastometer as determined by measured torque values when operating the empty shearing chamber at various shear rates.

b) Apparent viscosity determined for a high viscosity polymer liquid at various shear rates.

Figure 3.5: Torque values for empty plastometer runs at various shear rates with heating of the shearing chamber at 400 K/s to a holding temperature of 1098 K.

To calibrate the new cone-shaped disk configuration, a viscosity standard obtained from a commercial vendor (Cannon, $\eta = 5.22 \cdot 10^3 \text{ Pa}\cdot\text{s}$) was placed inside the shearing chamber. Three runs were performed at different shear rates (2.01 s^{-1} , 5.16 s^{-1} , and 8.00 s^{-1}). The average frictional torque value was subtracted from the torque data obtained, and using equation 3.1, the apparent viscosity of the standard was obtained and plotted in Figure 3.4b. Again, the viscosity values from the plastometer did not vary with the shear rates, and the average viscosity value calculated was $5.58 \cdot 10^3 \text{ Pa}\cdot\text{s}$. The calculated value was only 7% higher than the actual value of $5.22 \cdot 10^3 \text{ Pa}\cdot\text{s}$ provided by the manufacturer. Therefore, the apparatus constant used through out this work is:

$$a = \frac{\eta_{\text{actual}}}{\eta_{\text{calc}}} = 1.07^{-1} = 0.93 \quad 3.2)$$

This good agreement strongly suggests the reliability of using the new cone-shaped shearing disk configuration and the above data analysis methods to determine the apparent viscosity of molten coal and other thermal softening polymers.

From the transient torque data obtained from the standard calibration and the determination of the plastometer's friction, it is observed that the noise associated with the plastometer is approximately $1 \cdot 10^{-4} \text{ N}\cdot\text{m}$ or $200 \text{ Pa}\cdot\text{s}$. In addition, the maximum error of the torque transducer's measurement is 0.2% of reading ($100 \text{ Pa}\cdot\text{s}$ at $50000 \text{ Pa}\cdot\text{s}$) (S. Himmelstein and Company, 1983). Choosing a low shear rate of 2.01 s^{-1} , the plastometer's viscosity resolution is approximately $\pm 300 \text{ Pa}\cdot\text{s}$. The digital recorder records a data point every tenth of a second, and therefore the plastometer's time resolution is also 0.1 s .

To test the reproducibility of the plastometer, several experimental runs with the same temperature-time histories were performed. The replicate runs shown in Figure 3.6 show

**Torque vs. time
Illinois No. 6 hvb Coal**

Figure 3.6: Raw plasticity data of Illinois No. 6 hvb coal for replicate runs. Heating rate: 400 K/s; Holding temperature: 1098 K; Pressure: 1 atm helium.

that the torque (and thus viscosity) vs. time curves are reproducible. The slight fluctuations in the plastic region of the curves (where the corresponding viscosity is less than 50000 Pa·s) were probably due to some unsoftened macerals which could be different in one run from the other. In general, the reproducibility of the plastometer is good. Some runs were discarded due to the misalignment between the shearing disk's rotating shaft and the torque transducer's rotating shaft. The misalignment was due to the incorrect tightening of the coupling between the two shafts. The screws used to tighten the couplings to the torque transducer's shaft must come in contact with the shaft at a specific area designed by the manufacturer of the torque transducer manufacturer. In addition, the misalignment could result from the incorrect tightening of the couplings to the shearing disk's shaft. The shearing disk's shaft is threaded so that it tightens itself to the couplings by screwing the shaft into the coupling. The misalignment of in either of these tightening processes will cause the torque transducer's shaft and the shearing disk's shaft to be rotating on the different axis. The misalignment can be observed as the torque transducer's overload on the digital recorder.

3.3 Experimental Conditions

To prevent the torque transducer from overloading during start up (shearing solid coal particles), a low shear rate of 2.01 s^{-1} is used in most experimental runs. To study pressure effects, a constant heating rate of 400 K/s and a holding temperature of 1098 K are used. The plastic behavior of the coals have been studied at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium.

Temperature-time history effects on coal plasticity were studied in two ways: by varying the holding temperature or the heating rate. To study the effects of holding temperature, the heating rate and pressure used are 400 K/s and 1 atm helium, respectively. The holding

temperature is varied between 898 to 1298 K. To study the effects of heating rates, the holding temperature and pressure used are 1098 K and 1 atm helium, respectively. The heating rate is varied between 200 and 800 K/s.

3.4 Coal Selection

Coals from the Argonne Premium Coal Sample Program were chosen for the experiments. They are chosen for the purity of and consistency among the samples. First, the samples are stored and ground in a nitrogen atmosphere where the oxygen content of the facility is below 100 ppm. The final samples are stored in a sealed glass ampules for further distribution (Vorres, 1989). Second, the samples of each coal are prepared from the same batch of raw sample. They are prepared carefully in the same way to ensure the consistency of each batch. An additional benefit of the Argonne coals is that most coal researchers have chosen them as "standard", and many scientific data pertinent to these coals are available.

The seven coals studied were: Beulah-Zap lignite (ND), Wyodak subbituminous (WY), Illinois No. 6 hvb (IL), Pittsburgh No. 8 hvb (PT), Lewiston-Stockton hvb (WV), Upper Freeport mvb (UF), and Pocahontas No. 3 lvb (PO). These coals fall within coal ranks ranging from lignite to low volatile bituminous. Hvb coals are known for their good plastic behavior, and therefore three different coals (IL, PT, and WV) are chosen from this rank. In particular, Pittsburgh No. 8 hvb coal is chosen for its good coking ability and for comparing the data to those of Fong (1986) and Fong et al. (1985, 1986a, and 1986b). From the sealed ampule, the coal is spread as a thin layer in the recess of each of the shearing chamber's metal plates. The shearing disk is placed between the two coal layers when the two metal plates are clamped together.

The ultimate (elemental) analyses and selected structural data for the Argonne premium coals used in this work are shown in Table 3.1.

3.5 Safety

1) Electrical: The automobile batteries in parallel used for the heating circuits of the plastometer are capable of producing up to 500 A of electrical current. There are three switches which must be activated in sequence to close the electrical circuit. None of these switches should remain closed after an experiment, and these switches should be open when adjustments are being made to the plastometer and its heating circuits. The electrical connections of the heating circuits are well insulated to minimize the possibility of electrical shock.

2) Chemical: The pyrolyzed coal residues contain carcinogens and should only be handled while one is wearing gloves. In addition, viton gloves should be worn when one is handling methylene chloride and acetone used as cleaning solvents for the coal pyrolysis residues. These solvents should only be handled under the fume hood.

TABLE 3.1: Ultimate Analyses and Selected Structural Data for Argonne Premium Coals

	ND lig	WY sub	IL hvb	PT hvb	WV hvb	UFmvb	PO lvb
%C dmmf ^a	74.05	76.04	80.73	84.95	85.47	88.08	91.81
%O dmmf ^a	19.13	16.90	10.11	6.90	6.68	4.72	1.66
%H dmmf ^a	4.90	5.42	5.20	5.43	5.44	4.84	4.48
%N dmmf ^a	1.15	1.12	1.37	1.64	1.56	1.55	1.33
% Organic S ^a	0.70	0.47	2.38	0.89	0.65	0.74	0.50
Carbon Aromaticity ^b , Cf _a	0.57	0.60	0.67	0.74	0.75	0.80	0.88
Proton Aromaticity ^c , Hf _a	0.24	0.27	0.30	0.35	0.36	0.39	0.45

a: Vorres, 1989

b: Ko, 1988

c: Niksa, 1991

Chapter 4. Experimental Results and Discussion

4.1 Introduction

The new plastometer described in Chapter 3 was used to measure the apparent viscosity of molten coals as affected by pressure, temperature, time, and coal type. The seven coals, from the Argonne National Laboratory premium coal sample bank described in section 3.4, were studied. The hvb, mvb, and lvb coals showed very good plastic behavior, but the lignite and subbituminous coal did not exhibit any plasticity. For the plastic coals, the present findings will help explain how pressure, temperature, and coal type affect the formation and depletion kinetics of the liquid metaplast which is primarily responsible for coal plasticity.

4.2 Shear Rate Effects

The coal selected for this experiment was Pittsburgh No. 8 hvb, a highly plastic coal. The plastometer's shear rate ($\dot{\gamma}_R$) was varied from 2.01 s^{-1} to 10.66 s^{-1} . The heating rate used was 400 K/s , and the holding temperature was 1098 K . The pressure was 1 atm helium.

For $\dot{\gamma}_R$ from 2.01 s^{-1} to 10.66 s^{-1} , no shear rate effect on the viscosity of Pittsburgh No. 8 hvb coal was observed. There was no effect on the plastic period, the viscosity at various times and temperatures, and the maximum plasticity. Figure 4.1 shows the viscosity of Pittsburgh No. 8 hvb at different times and temperatures to be independent of shear rate.

At the plastometer's range of shear rates, the molten coal suspension is therefore considered Newtonian. This property of the coal melt allows for the use of many available suspension models (e.g. Frankel-Acrivos concentrated suspension model) which require

Figure 4.1: Viscosity of Pittsburgh No. 8 hvb at different shear rates. Heating rate: 400 K/s; Holding temperature: 1098 K; Pressure: 1 atm helium

the suspension to be Newtonian. However, at a much higher shear rates ($> 10^2 \text{ s}^{-1}$), the coal melt may exhibit a shear-thinning behavior in which the apparent viscosity decreases with shear rate. The behavior is common in polymeric solutions, in which some exhibit the shear-thinning effect at the shear rate as low as 1 s^{-1} (Bird et al., 1977 and 1988).

From the observation that coal plasticity is independent of shear rate at the range which the plastometer is capable of producing, the lower shear rate (2.01 s^{-1}) has been selected as the operating shear rate of the plastometer. The lower shear rate has been selected to reduce the overloading to the torque transducer which has the maximum torque limit at $70.6 \cdot 10^{-3} \text{ N}\cdot\text{m}$ (S. Himmelstein, 1983). Using a higher shear rate will result in exceeding the maximum torque limit of the transducer, especially at the beginning of a run when the plastometer is shearing solid coal particles and at the end of a run when the plastometer is shearing solid coke residues.

4.3 Pressure Effects

Using a constant heating rate of 400 K/s and a holding temperature of 1098 K , the plastic behavior of the Argonne coals was studied at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium.

Compared to the runs at 1 atm helium, the results for of different coals at vacuum displayed lower plasticity (higher minimum viscosity and shorter plastic period) as seen in Figures 4.2 and 4.3. The lower plasticity in vacuum is hypothesized to be due to enhanced mass transport of metaplast to tar vapors. The enhanced mass transport decreases the liquid metaplast inventory in the molten coal sample, resulting in lower plasticity.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.2: Maximum plasticity (minimum viscosity) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.3: Plastic period (period when the viscosity of molten coal is below 50000 Pa·s) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

Compared to the runs at 1 atm helium, the runs with different coals at elevated pressures (10 atm and 50 atm helium) did not display any significant change as seen in Figures 4.2 and 4.3. Fong (1986) also observed similar results in his work on Pittsburgh No. 8 coal. It is hypothesized that high pressure inhibits mass transport of metaplast out of the coal, resulting in increased intraparticle inventories of metaplast. These inventories could in turn give rise to increased plasticity, but also to more rapid rates of metaplast depletion, e.g. by polymerization or other rate processes greater than first order in metaplast concentration (Griffin, 1989). Here, since effects of increasing pressure are not observed above 1 atm, these two effects apparently compensate to give no net influence of increasing pressure on plasticity.

From these findings, it seems that increasing pressure of inert gas above atmospheric does not play a major role in coal plasticity at high temperatures where rate of depletion of liquid metaplast by mass transport is believed to be small compared to that by kinetics at atmospheric and elevated pressures. However, at extremely low pressure (such as vacuum), mass transport is greatly enhanced, and the metaplast depletion via this route becomes significant enough to diminish plasticity as seen above. At lower temperatures, where metaplast depletion kinetics are slower, increasing inert gas pressure above 1 atm may augment plasticity by slowing metaplast transport from the coal and thus providing more time for metaplast to facilitate fluid like behavior before it is depleted by secondary reactions.

4.3 Temperature Effects

Temperature-time history effects on coal plasticity were studied in two ways: by varying the holding temperature at constant heating rate and by varying the heating rate with a fixed holding temperature. To study the effects of holding temperature, the heating rate and

pressure used were 400 K/s and 1 atm helium, respectively. With different holding temperatures, the maximum plasticity, i.e. minimum viscosity, of different coals was unchanged (Table 4.1 and Figure 4.4a-e). However, higher holding temperature decreased the plastic period (the period when the viscosity of molten coal is below 50000 Pa·s) for all coals (Figures 4.4a-e and 4.5). For example, increasing the holding temperature from 898 K to 1098 K decreased the plastic period from 6.9 s to 1.9 s for Pittsburgh No. 8 hvb coal. It is hypothesized that higher temperatures diminish plasticity by increasing mass transport of liquid metaplast out of the coal and repolymerization of metaplast to coke (Fong, 1986).

To study the effects of heating rate, the holding temperature and pressure used were 1098 K and 1 atm helium, respectively. The heating rate effect on the softening temperature (temperature when the viscosity of molten coal first reaches 50000 Pa·s) was studied. For each coal, the heating rate has essentially no effect on the softening temperature (Figure 4.6). This seems to indicate that for a given coal the initial generation of metaplast is independent of heating rate and further suggests, especially for hvb coals where the softening temperature is below 650 K, that the initial phase of softening probably occurs by physical melting of the pyridine extractables initially present in the parent coal (Fong, 1986). For example, other workers have found that for hvb coals pyridine extractables of the raw coal amount to 25-30% dmmf (Fong, 1986 and Niksa, 1991). Little or no dependence of softening temperatures on heating rate was observed experimentally by Fong (1986) and theoretically by Oh et. al (1989) for Pittsburgh No. 8 hvb coal.

The existence of different softening temperatures for different coal types could reflect different metaplast melting points for the different coals, different kinetics of metaplast generation, or both. The similarity in softening temperatures of hvb coals (approximately

Table 4.1: Minimum Apparent Viscosity and Plastic Period
at Different Holding Temperatures^a

	<u>Holding Temperatures</u>			
<u>Coal/Viscosity (Pa·s)</u>	<u>898 K</u>	<u>948 K</u>	<u>998K</u>	<u>1098K</u>
Illinois No. 6 hvb	1836	1800	1766	1759
Pittsburgh No. 8 hvb	1397	1364	1297	1286
Lewiston-Stockton hvb	1711	1660	1698	1694
Upper Freeport mvb	2722	2666	2661	2583
Pocahontas No. 3 lvb	5646	5553	5444	5337

	<u>Holding Temperatures</u>			
<u>Coal/Plastic Period (s)</u>	<u>898 K</u>	<u>948 K</u>	<u>998K</u>	<u>1098K</u>
Illinois No. 6 hvb	5.3	3.0	2.1	1.6
Pittsburgh No. 8 hvb	6.9	3.6	2.5	1.9
Lewiston-Stockton hvb	6.8	3.7	2.6	1.9
Upper Freeport mvb	7.0	3.8	2.6	2.0
Pocahontas No. 3 lvb	5.1	2.8	1.9	1.5

a: Heating rate: 400 K/s and Pressure 1 atm helium

Figure 4.4a: Apparent viscosity of Illinois No. 6 coal at different holding temperatures. Heating rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Holding Temperatures **Pittsburgh No. 8 hvb Coal**

Figure 4.4b: Apparent viscosity of Pittsburgh No. 8 coal at different holding temperatures. Heating rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Holding Temperatures Lewis-Stockton hvb Coal

Figure 4.4c: Apparent viscosity of Lewis-Stockton coal at different holding temperatures. Heating rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Figure 4.4d: Apparent viscosity of Upper Freeport coal at different holding temperatures. Heating rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Holding Temperatures **Pocahontas No. 3 lvb Coal**

Figure 4.4e: Apparent viscosity of Pocahontas No. 3 coal at different holding temperatures. Heating rate: 400 K/s and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.5: Plastic period (period when the viscosity of molten coal is below 50000 Pa·s) of different coals at different holding temperatures. Heating Rate: 400 K/s and Pressure: 1 atm helium. ND and WY coals do not exhibit any plasticity.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.6: Softening Temperature of Various Coals at Different Heating Rates. Holding temperature: 1098K and Pressure: 1 atm helium.

630 K) suggests that the overall rates of generation of the metaplast responsible for initial softening are also similar. For hvb coals which have a high yield of pyridine extracts from the raw coal, most or all of this metaplast may be generated by physical melting. However, the UF mvb coal also has a similar softening temperature (approximately 650 K), but has a much lower initial weight fraction of pyridine extractables (i.e. 7%, Snape and Bartle, 1989). It is hypothesized that the UF mvb coal generates a major fraction of the metaplast needed for initial softening by chemical bond breaking and further that the kinetics of this process is very rapid.

The PO lvb coal has a much higher softening temperature (740 K). This is probably due to the lack of metaplast generation by physical melting since the PO coal only has an initial fraction of pyridine extractables of 1%. The coal begins to soften only when the temperature is high enough for the metaplast generation by chemical bond breaking to become important.

Solomon et. al (1992) reported for four of the same Argonne sample bank coals studied here softening temperatures measured with a Gieseler plastometer at an apparent heating rate of 3 K/s. Their softening temperatures and those of the present study agree qualitatively, and the results are consistent with the picture that heating rate has little effect on the softening temperatures of individual coals.

Figures 4.7a- 4.7e display plots of apparent viscosity vs. time for five different softening coals at three different heating rates. These figures, together with Table 4.2, show that heating rate has little effect on maximum plasticity (i.e. minimum apparent viscosity) of each coal to within the resolution of our plastometer (approximately ± 300 Pa·s). For each coal, the apparent viscosity drops rapidly to a minimum and then rises rapidly shortly after reaching the holding temperature of 1098 K. Figures 4.7a-4.7e clearly show that the

Table 4.2: Minimum Apparent Viscosity and Plastic Period
at Different Heating Rates^a

<u>Coal/Viscosity (Pa·s)</u>	<u>Heating Rates</u>		
	<u>200 K/s</u>	<u>400 K/s</u>	<u>800 K/s</u>
Illinois No. 6 hvb	1766	1759	1753
Pittsburgh No. 8 hvb	1456	1286	1449
Lewiston-Stockton hvb	1680	1694	1650
Upper Freeport mvb	2614	2583	2497
Pocahontas No. 3 lvb	5322	5337	5223

<u>Coal/Plastic Period (s)</u>	<u>Heating Rates</u>		
	<u>200 K/s</u>	<u>400 K/s</u>	<u>800 K/s</u>
Illinois No. 6 hvb	2.8	1.6	0.7
Pittsburgh No. 8 hvb	3.3	1.9	0.7
Lewiston-Stockton hvb	3.4	1.9	0.7
Upper Freeport mvb	3.1	2.0	0.8
Pocahontas No. 3 lvb	2.7	1.5	0.7

a: Holding temperature: 1098 K and Pressure: 1 atm helium

Figure 4.7a: Apparent viscosity of Illinois No. 6 coal at different heating rates. Holding temperature: 1098 K and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Heating Rates
Pittsburgh No. 8 hvb Coal

Figure 4.7b: Apparent viscosity of Pittsburgh No. 8 coal at different heating rates. Holding temperature: 1098 K and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Figure 4.7c: Apparent viscosity of Lewiston-Stockton coal at different heating rates. Holding temperature: 1098 K and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Figure 4.7d: Apparent viscosity of Upper Freeport coal at different heating rates. Holding temperature: 1098 K and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

Figure 4.7e: Apparent viscosity of Pocahontas No. 3 coal at different heating rates. Holding temperature: 1098 K and Pressure: 1 atm helium. Heating started at $t = 0.5$ s.

plastic period decreases with increasing heating rate for each coal. At a higher heating rate, the metaplast generation and depletion kinetics are enhanced since a higher temperature is reached faster. Fong (1986) among others has hypothesized that higher temperatures diminish plasticity by increasing the depletion rates of plasticizing agent (i.e. metaplast), e.g. by mass transfer out of the coal and by repolymerization of metaplast to coke (Fong, 1986).

Figures 4.7a-4.7e also show that after heating to final temperature at a lower rate, e.g. 400 and especially 200 K/s, the apparent viscosity of the molten coal increases less rapidly, implying slower overall resolidification kinetics. This may reflect differences in the metaplast properties, caused by secondary reactions during the longer period that proceeds the onset of fluidity. For example, Fong (1986) observed that the average molecular weight of liquid extractables from pyrolysis of molten coal, taken as approximately representative of metaplast, increased with decreasing heating rate. Griffin (1989) made similar observations for newly evolved coal pyrolysis tar. Thus the slower resolidification rates at lower heating rates implied by Figures 4.7a-4.7e may reflect greater resistance of metaplast to depletion by mass transfer or possibly by secondary reactions, due in either case to the higher molecular weight of the metaplast. Thus higher heating rates would be expected to shorten the plastic period by bringing the coal more rapidly to higher temperatures where metaplast depletion is accelerated while having less effect on the temperature where softening begins.

The effects of heating rate on the solidification of coal melt suggest that more than one pathway is involved in the metaplast depletion kinetics. A multiple independent parallel reaction (MIPR) model with a distribution of activation energies for depletion kinetics has been used to fit the data and test this hypothesis (see Section 5.3, Table 5.2). The high

standard deviation (4.4 kcal/mole to 8.0 kcal/mole) in activation energy of the depletion step for each coal supports this hypothesis.

4.4 Coal-Types Effects

From the results of the previous sections, hvb coals (IL, PT, and WV) are very plastic. Mvb and lvb coals (UF and PO) also exhibit very good plastic behavior. Subbituminous coal (WY) and lignite (ND) used in this study do not exhibit any plastic behavior. From the observation of the pyrolyzed samples, these low-rank coals do not swell or agglomerate at the experimental conditions used for other bituminous coals.

From replicate runs and previous calibration results, the maximum noise of the plastometer is 300 Pa·s. Therefore, the observed maximum plasticity data show a trend in which at vacuum and also at elevated pressures (1, 10, and 50 atm He) the hvb coals have the lowest viscosity readings when compared to the mvb coal which has a lower viscosity reading than the lvb coal (Figure 4.8).

From the present data, however, there is no evidence for a continuous increase (or decrease) in the plastic period with increasing coal rank over the entire range of bituminous coal ranks studied. (Figure 4.9). From replicate runs and the sampling interval of the digital recorder, the maximum error in measuring the plastic period is about 0.1 s. The mvb coal exhibits the longest plastic period when compared to the hvb and lvb coals, which have the similar plastic periods (Figure 4.9 and Table 4.1).

Because they are low in tar and extractable yields, the strong plasticity exhibited by the mvb and lvb coals is interesting. In general, a typical hvb coal (Illinois No. 6 or Pittsburgh

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.8: Maximum plasticity (minimum viscosity) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 4.9: Plastic period (period when the viscosity of molten coal is below 50000 Pa·s) of different coals at vacuum, 1 atm helium, 10 atm helium, and 50 atm helium. Heating Rate: 400 K/s and Holding Temperature: 1098 K. ND and WY coals do not exhibit any plasticity.

No. 8) has a maximum tar yield of around 30 % at vacuum (Ko, 1988). As for mvb and lvb coals (Upper Freeport and Pocahontas No. 3), a typical maximum tar yield at vacuum is around 10 %-20 % (Ko, 1988 and Niksa, 1991). The pyridine extract yields of mvb and lvb coals are also much lower than that of a typical hvb coal, generally amounting to less than 10 %, with a typical hvb coal exhibiting about 30 % yield of pyridine extract (Snape and Bartle, 1991 and Niksa, 1991).

At present, a trend exists for the plastic behavior of coals of different ranks.

Subbituminous and low-rank coals, as well as lignites and peats, have a high fraction of labile bridges for forming small molecular fragments. However, they are also abundant in oxygen which promotes cross-linking. The net effect is that a small quantity of liquid fragments are produced on pyrolysis, and thus low tar yields are obtained. The coals do not exhibit any plastic behavior, and their main volatile products are noncondensable gases (Niksa and Kerstein, 1991; Ko, 1988; and Fong, 1986).

Hvb coals are abundant in labile bridges, but they have lower oxygen content than low-rank coals. In addition, they are rich in hydrogen which can stabilize radicals formed during pyrolysis (Vorres, 1989 and Ko, 1988). They also have high tar yields as well as high yields of extractables from the raw coal. Hvb coals therefore produce a lot of liquid fragments from physical melting and from labile bridge scissions. These liquid molecules can be transported out of the coal sample to form tar or further react to form noncondensable gases and coke and char (Niksa and Kerstein, 1991).

The mvb and lvb coals in this study produce less tar than a typical hvb coal (Ko, 1988 and Niksa, 1991), but exhibit strong plastic behavior comparable to that of the three hvb coals studied. Since higher rank (mvb and lvb) coals have a smaller fraction of labile bridges than hvb coals, they are less likely to produce the small liquid fragments identifiable as tar

precursors, and hence lower tar yields on pyrolysis would be expected (Ko, 1988; Niksa and Kerstein, 1991). However, mvb and lvb coals are still able to produce larger fragments (possibly a cluster of aromatics) which contribute to their good plastic behavior. They are rich in hydrogen to stabilize the radicals formed from labile bridge scissions and can therefore produce stable molecules in the liquid boiling range. They also have lower oxygen content which means cross-linking to these liquid fragments to form light gases and char is less likely.

It has been proposed that the scission of kinetically similar bonds in the coal is the preferred route for release of molecular fragments which ultimately form metaplast-like liquids (Darivakis, 1989). According to this picture, coals which have more kinetically similar and thermally labile bonds (e.g. because of a more uniform molecular structure), as is expected in mvb and lvb coals, have a higher probability to form liquid products than low-rank coals. This hypothesis, along with considerations of their labile bridge fraction and hydrogen and oxygen contents, explains why low-rank coals such as subbituminous coals and lignites do not exhibit any plastic behavior under the present conditions. Hvb coals have a high probability of forming liquids, have lower oxygen content, and are abundant in labile bridges and hydrogen. They therefore are the most plastic coals of all ranks in the sense of exhibiting the lowest values of minimum apparent viscosity. Mvb and lvb coals have lower liquid yields because they are lower in labile bridges. Having the lowest labile bridge fraction of the coal ranks studied, lvb coals exhibit even less plastic behavior than mvb coals.

Chapter 5. Mathematical Modeling

5.1 Introduction

To further understand the plasticity results from chapter 4, mathematical modeling using chemical engineering principles is required. The modeling objectives are: 1) to correlate magnitude and duration of plasticity with heating rate, temperature, and coal type and 2) to seek relationships between plasticity simple indices of coal type and plasticity.

To accomplish these objectives, we first start with the suspension modeling to relate the viscosity of coal melt to the amount of metaplast. The next step is the kinetics modeling of metaplast generation and depletion. Finally, the correlations between coal plasticity and various simple indices of coal type are explored to identify a coal-type specific parameter to predict coal plasticity.

5.2 Suspension Modeling

5.2.1 Introduction

It is generally accepted that the apparent viscosity of molten coal is related to the coal's liquid or "metaplast" inventory. In the past, the concentrated suspension of solid spheres model by Frankel and Acrivos (1967) was used to express this relationship quantitatively. Fong (1986) reasoned after the works on coal carbonization by Kirov and Stephens (1967) and Szladow and Ignasiak (1976) that the coal melt is well described as a concentrated suspension of solids. However, there is a need to determine the influence on viscosity of gas bubbles generated at elevated temperature in the coal melt during pyrolysis of the coal. The reasons are to gain further insight on the mechanisms of coal

plasticity at elevated temperature and if gas bubbles are important, to be sure that the mathematical expressions used to relate the viscosity of molten coal to its metaplast inventory properly reflect contributions from gas bubbles.

5.2.2 Different Two Phase Suspension Models

Models for the Viscosity of Suspensions Developed by Einstein and Hatschek

Einstein's viscosity model for a dilute suspension of solid in liquid is:

$$\eta_{rel} = \frac{\eta}{\eta_0} = 1 + K\phi \quad 5.1)$$

where η_0 is the viscosity of the solid-free liquid, ϕ is the volume fraction of solid in the suspension, and the constant K depends on the shape and rigidity of the particles (e.g. $K = 2.5$ for rigid spheres) (Hauser, 1939). The Einstein model is valid when ϕ is less than 0.05 (Frankel and Acrivos, 1967, Sherman, 1968, and Van Krevelen, 1990).

For a concentrated suspension of rigid spheres in a liquid, Hatschek's viscosity model is:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{1}{(1 - \sqrt[3]{\phi})} \quad 5.2)$$

where η_0 and ϕ have the same meaning as defined above. This model is generally valid when ϕ is greater than 0.5 (Hauser, 1939 and Sherman, 1968).

These equations are the early works on which many later models are based.

The Concentrated Suspension Model of Frankel and Acrivos

Frankel and Acrivos (1967) used an asymptotic mathematical analysis of governing equations of change to derive a suspension viscosity model similar to that of Hatschek. According to the model by Frankel and Acrivos, the effective Newtonian viscosity of a suspension of uniform solid spheres is:

$$\mu_{\text{rel}} = \frac{\mu}{\mu_0} = \frac{9}{8} \frac{\sqrt[3]{\phi/\phi_m}}{1 - \sqrt[3]{\phi/\phi_m}} \quad 5.3)$$

where μ_0 is the viscosity of the solid-free liquid, ϕ is the volume fraction of solids in the suspension, and ϕ_m is the maximum solid volume fraction. The most important assumption of this model is that the suspension exhibits Newtonian behavior. Based upon comparisons with experimental data, Frankel and Acrivos found that equation 3 is valid for ϕ/ϕ_m greater than 0.5.

The Foam Model

One approach to assessing the role of gas bubbles in molten coal viscosity is to assume they create foam-like behavior to the coal melt. Foams by definition are "agglomerations of gas bubbles separated from each other by thin liquid films" (Bikerman, 1973). However, to classify a suspension of gas bubbles in liquid as foams usually requires a gas volume fraction exceeding 0.75 (Heller and Kuntamukkula, 1987 and Walstra, 1989). Bikerman (1973) even suggests a gas volume fraction of 0.9 or higher to quantify gas in

liquid suspensions as foams. In addition, the bubble diameter of foams is typically between 0.1 mm to 3 mm (Walstra, 1989).

Experiments by Griffin (1989) suggest that the number density and size distribution of bubbles in molten coal do not match those of bubbles in typical foams. His methodology was optical microscopy of chars quenched from molten coal and the assumption that the size and number of cavities in those chars were representative of the size and number of bubbles in the molten coal just prior to quenching. His findings indicate that: 1) when bubble number density is large enough to be considered foam-like, the volume fraction gas is below 75%; and 2) if the gas volume fraction exceeds 75%, the bubble diameter is comparable to the particle diameter, but there are too few bubbles to produce a foam.

Taylor's Emulsion Model

Taylor (1932) extended Einstein's hydrodynamic treatment for dilute suspensions of solid spheres to dilute suspensions of globules that may be deformable, i.e. liquids, in a liquid (Sherman, 1968):

$$\eta_{rel} = \frac{\eta}{\eta_o} = 1 + K \frac{\eta' + (2/5)\eta_o}{\eta' + \eta_o} \phi \quad 5.4)$$

where η_o is the viscosity of the globule-free liquid, η' is the viscosity of the fluid inside the globule, ϕ is the globule volume fraction in the suspension, and the constant K depends on the shape of the particles ($K = 2.5$ for rigid spheres, $K < 2.5$ when the globule is deformable). The equation is generally valid when ϕ is less than 0.2 (Meyer, 1950 and Sherman, 1968).

5.2.3 Viscosity of an Emulsion with Two Dispersed Phases.

From the past studies of suspension and emulsion, one can write a general model describing the effective viscosity of a suspension or an emulsion as:

$$\eta_{o+i} = \eta_o [1 + \text{factor}(\phi_i)] \quad 5.5)$$

where $\text{factor}(\phi_i)$ means a factor that is a function of the quantity ϕ_i . η_{o+i} is the effective viscosity of the suspension or emulsion, η_o is the viscosity of the continuous phase free of the dispersed phase, and ϕ_i is the volume fraction of the dispersed phase i . From the studies of hydrocolloids and pigment in different emulsions, the viscosity of an emulsion with two dispersed phases (a and b) can be described in two ways: based on whether series or parallel interaction is viewed as more important. In the series model, one of the dispersed phases and the continuous phase forms a new continuous phase. The new continuous phase then interacts with the remaining dispersed phase. The effective viscosity can be modeled as (Sherman, 1968):

$$\begin{aligned} \eta_{o+a+b} &= \eta_{o+a} [1 + \text{factor}(\phi_b)] \\ &= \eta_o [1 + \text{factor}(\phi_a)] \cdot [1 + \text{factor}(\phi_b)] \end{aligned} \quad 5.6)$$

In the parallel model, η_o remains the viscosity of the continuous phase which interacts simultaneously with both dispersed phases. The effective viscosity can be modeled as (Sherman, 1968):

$$\eta_{o+a+b} = \eta_o [1 + \text{factor}(\phi_a) + \text{factor}(\phi_b)] \quad 5.7)$$

The difference in the two models is the extra factor of $[\text{factor}(\phi_a) \cdot \text{factor}(\phi_b)]$ in the series model which accounts for the fact that the second suspended component (here b) interacts with the first suspended component (here a) as well as with the continuous phase. In general, the series model seems plausible in a suspension or emulsion which is not highly concentrated. When the continuous phase is present at very high concentration, it interacts with one of the dispersed phases (the more dilute one) first to form a new continuous phase. The new continuous phase then interacts with the other, more concentrated, dispersed phase. The parallel model is more appropriate for a concentrated suspension or emulsion in which a continuous phase, present at lower concentration, is likely to interact with both dispersed phases simultaneously. An illustration of an emulsion/suspension with two dispersed phases is shown in Figure 5.1.

Whether the suspended phases are dilute or concentrated, equations 6 and 7 are best applied when the volume fraction of the continuous phase is high i.e. $\phi_0 > 0.5$. In molten coal, however, the volume fraction of the continuous phase (liquid metaplast) is generally expected to be ≤ 0.5 . It is therefore necessary to modify equations 6 and 7 before they can be confidently applied to a molten coal system.

The first step is to define the concept of relative volume fraction. When the continuous phase is not present at high concentration, its interactions with *each* of the dispersed phases are important and depend on the amount of each dispersed phase relative to the amount of the continuous phase. Thus for a suspension of two dispersants in one continuous phase it proves convenient to define a volume (V_i) of one of the dispersed phases, *i*, relative to the volume occupied by the continuous phase (V_0) and the dispersed phase *i* (V_i) as:

Figure 5.1: An illustration of an emulsion/suspension with two dispersed phases (1 and 2). When applied to molten coal, the two dispersed phases are gas bubbles and unsoftened solids, and the continuous phase is the liquid metaplast.

$$\phi_{io} = \frac{V_i}{V_i + V_o} = \frac{\phi_i}{\phi_i + \phi_o} \quad 5.8)$$

When there is only one dispersed phase $\phi_{io} = \phi_i$ because $\phi_i + \phi_o = 1$. When the continuous phase is present at very high concentration, $\phi_o \gg \phi_i$, and ϕ_{io} is well approximated by ϕ_i . In the series model, when the continuous phase interacts with one of the dispersed phases to form a new continuous phase, the effective viscosity of the new continuous phase depends on the volume fraction of the dispersed phase relative to the volume fraction of the original continuous phase. This is significant when the volume fractions of the two dispersed phases are vastly different. Thus for suspensions with lower concentrations of continuous phase, the volume fraction ϕ_a in equation 6 should be replaced by the volume fraction of dispersed phase a relative to the original solids free continuous phase, ϕ_{ao} :

$$\begin{aligned} \eta_{o+a+b} &= \eta_{o+a} [1 + \text{factor}(\phi_b)] \\ &= \eta_o [1 + \text{factor}(\phi_{ao})] \cdot [1 + \text{factor}(\phi_b)] \end{aligned} \quad 5.9)$$

The volume fraction of the second dispersed phase ϕ_b is unchanged since it already is the volume fraction of phase b relative to the new continuous phase.

In the parallel model, the continuous phase interacts simultaneously with both dispersed phases. The effective viscosity of the suspension/emulsion therefore depends on the relative volume fraction of each dispersed phase with respect to the continuous phase. Consequently, the relative volume fractions replace the volume fractions in equation 5.7 which now becomes:

$$\eta_{o+a+b} = \eta_o [1 + \text{factor}(\phi_{ao}) + \text{factor}(\phi_{bo})] \quad 5.10)$$

5.2.4 Incorporating the Taylor Model into the Concentrated Suspension Model

In light of all the different models described, the next task is to determine which model is best suited for the coal melt during pyrolysis. The Taylor model (Meyer, 1950 and Sherman, 1968) is a potentially good choice for describing the effect of gas bubbles on the coal melt, since it can treat two different fluids -the suspending liquid and the suspended globule. Here as the first approximation, we associate the globules with the gas bubbles and assume them to be spherical and retain their form throughout the course of the experiment ($K=2.5$).

Models for concentrated suspensions of rigid spheres such as those of Frankel and Acrivos (1967) or Hatschek (Hauser, 1939 and Sherman, 1968) can be used to describe the interaction between the liquid metaplast and the solid coal particles. The present work has shown the viscosity of the coal melt to be Newtonian when the shear rate is varied from 2 to 10 s^{-1} . Thus from the perspective of Newtonian vs. non-Newtonian behavior, the Newtonian model by Frankel and Acrivos is applicable in this range of shear rates. The difference in the relative viscosity calculated by the Hatschek and Frankel and Acrivos models is less than 10% when the solid volume fraction (ϕ_s) is greater than 0.5 (assuming the maximum solid concentration (ϕ_{sm}) is 1.0). Since either model seems suitable, both models will be used in this report for illustrative purposes.

The next step is to determine whether the series or parallel model for a suspension/emulsion with two dispersed phases is suitable for describing the effective viscosity of the coal melt. In incorporating the Taylor modeling to Hatschek's or Frankel and Acrivos' concentrated suspension model:

$$\text{factor}(\phi_i) = K \frac{\eta' + 2/5\eta_o}{\eta' + \eta_o} \phi_i \quad (\text{Taylor Model, } K = 2.5) \quad 5.11a$$

and since $\eta_o \gg \eta'$:

$$\text{factor}(\phi_i) = \phi_i \quad (\text{Taylor's Model}) \quad 5.11b$$

$$\text{factor}(\phi_i) = \frac{\sqrt[3]{\phi_i}}{(1 - \sqrt[3]{\phi_i})} \quad (\text{Hatschek Model}) \quad 5.12$$

$$\text{factor}(\phi_i) = 1/8 + 9/8 \frac{2 \sqrt[3]{\phi_i} - 1}{(1 - \sqrt[3]{\phi_i})} \quad (\text{Frankel and Acrivos}) \quad 5.13$$

These factors are substituted into equations 5.6 and 5.7 to determine the relative viscosity of the coal melt. In the series model, there are two alternatives of the new continuous phase. The new continuous phase can either be a gas-liquid emulsion (series model I) or a solid-liquid suspension (series model II). Letting the subscript "g" denote the gas phase and the subscript "s" denote the solid phase :

$$\eta_{rel} = [1 + \text{factor}(\phi_{go})] \cdot [1 + \text{factor}(\phi_s)] \quad (\text{series model I}) \quad 5.14$$

$$\eta_{rel} = [1 + \text{factor}(\phi_{so})] \cdot [1 + \text{factor}(\phi_g)] \quad (\text{series model II}) \quad 5.15$$

$$\eta_{rel} = [1 + \text{factor}(\phi_{go}) + \text{factor}(\phi_{so})] \quad (\text{parallel model}) \quad 5.16$$

A summary of the various viscosity models described above is in Table 5.1. The apparent relative viscosities for suspensions and emulsions calculated from various models are shown in Figures 5.2 and 5.3 for relative gas volume fractions of 0.05 and 0.20.

Figure 5.4 shows the apparent viscosities calculated by the Frankel-Acrivos and Taylor parallel model as a function of solid volume fraction (ϕ_s) and relative gas volume fraction (ϕ_{go}).

5.2.5 Discussion of Results

In general, the models which incorporate Hatchek's concentrated suspension model give slightly lower relative viscosity values than those which incorporate the model of Frankel and Acrivos. The difference is, however, less than about 10%.

The two series models and the parallel model which incorporate the same concentrated suspension model give essentially the same results. Since the exact mechanism by which different phases interact is difficult to determine, each of these three models would seem to be of comparable value for correlating the relative viscosity of a coal melt. The viscosity determined by a concentrated suspension model alone is approximately 20 % lower than that which is determined by a model which considers two dispersed phases (with the relative gas volume fraction of 0.2, Figure 5.3). At a lower relative gas volume fraction (e.g. 0.05), the difference is about 5%. The Taylor models assumes that the surface tension is large enough that the fluid bubbles retain their spherical shape throughout the experiment. These spherical bubbles create "extra" resistance in the suspending liquid and thus increases the effective viscosity of the suspension or emulsion. They act similarly to rigid spheres, but their contribution to the "extra" resistance is less since they are deformable.

Table 5.1: Summary of Viscosity Models for Suspension/Emulsion

<u>Model</u>	<u>Type of System</u>	<u>Range of Predictability</u>
Einstein	Rigid spheres in liquid	ϕ of dispersed phase < 0.05
Frankel & Acrivos	Rigid spheres in liquid	ϕ/ϕ_m of dispersed phase > 0.5 , Newtonian suspensions only
Hatschek	Rigid globules in liquid	ϕ of dispersed phase > 0.5
Taylor	Deformable spheres in liquid	ϕ of dispersed phase < 0.2
Frankel- Acrivos/Taylor	Rigid spheres and deformable spheres in liquid	ϕ of rigid spheres relative to the ϕ 's of liquid and rigid spheres > 0.5 , ϕ of deformable spheres relative to ϕ 's of liquid and deformable spheres < 0.2 , Newtonian suspensions only.
Hatschek/Taylor	Rigid spheres and deformable spheres in liquid	ϕ of rigid spheres relative to the ϕ 's of liquid and rigid spheres > 0.5 , ϕ of deformable spheres relative to ϕ 's of liquid and deformable spheres < 0.2

Figure 5.2: Relative viscosity vs. solid volume fraction for various models. Gas volume fraction = 0.05.

Figure 5.3: Relative viscosity vs. solid volume fraction for various models. Gas volume fraction = 0.20.

Figure 5.4: Relative viscosity vs. solid volume fraction for Frankel-Acrivos and Taylor in parallel model.

The above models correlate suspension viscosity with the volume fraction of a continuous phase with and the volume fraction(s) of one or more dispersed phases. For molten coal one approach is to consider the dispersed phase to consist only of solids, and to estimate the volume fraction of these solids from the volume fraction of the liquid continuum (metaplast) by a material balance. Metaplast concentration must then be known or predictable for the pyrolysis conditions of interest. Direct measurements of metaplast concentrations as affected by pyrolysis conditions are not a prime focus of the present study. Kinetics parameters for predicting metaplast inventories during softening were determined from data on apparent viscosity of molten coal as affected by temperature and time (Section 5.3). Metaplast kinetics models, e.g. the multiple independent parallel reaction (MIPR) model (Anthony et al., 1975), were inputted to viscosity models and parameterized by best fitting predicted viscosities to those determined experimentally.

To account explicitly for effects of suspended solids and of gas bubbles, suspension viscosity models for molten coal require that the relative volume fraction of gas be known throughout the softening period of pyrolysis. In principle this quantity could be determined experimentally or predicted theoretically. Pertinent experiments by Griffin (1989) are noted above, and Oh (1985; et al., 1989) developed a mathematical model that predicts gas volume fractions and bubble size distributions in molten coal. However, either approach would require significant numerical effort to implement. Seeking reduced computational requirements, the present work chose to assume that the apparent viscosity of molten coal can be reasonably modeled in terms of a single liquid continuum phase and one dispersed phase consisting only of solids. In this approximation, gas bubble effects would force the model to underestimate metaplast concentration and overpredict the contribution of the dispersed solids to increase the viscosity of the liquid continuum.

5.3 Metaplast Kinetics Modeling

5.3.1 Introduction

From suspension modeling results, a two phase model has been used to relate metaplast concentration and the apparent viscosity of different coals. In particular, analyzing the plasticity kinetics of coal, the concentrated suspension model of Frankel and Acrivos (1967) has been chosen to relate the viscosity of molten coal to the metaplast concentration:

$$\mu/\mu^* = \frac{9/8}{[(\frac{1-M}{1-M_c})^{-1/3} - 1]} \quad 5.17)$$

where μ^* is the viscosity of the solids-free liquid. From the work of Nazem (1980) who measured the viscosities of carbonaceous mesophase pitch at 623 K to be in the order of 100 Pa·s and assuming that the solids-free metaplast has a similar viscosity, μ^* was chosen to be 200 Pa·s. The quantity M is the intraparticle inventory of softened material (metaplast), having the critical value M_c , at which μ goes to ∞ . At this critical value, the liquid fraction is insufficient to separate the solid particles. The number ranges from .36 to 0.25 for close packing spheres and 0.20 to 0.10 for close packing rods. The solid elements in the coal sample are expected to be more like thin slabs (lamellae) than spheres (Fong et al., 1985). Therefore, to be representative of these ranges, the number for M_c was chosen arbitrarily to be 0.20. In addition, it is seen from Fong's pyridine extractable data that Pittsburgh No. 8 coal only starts to soften when $M > 0.20$ (Fong, 1986). From this equation, one can calculate the transient metaplast inventory, $M(T,t)$, from plasticity data, $\mu(T,t)$, or vice versa.

The multiple independent parallel reaction model is then used to describe the metaplast generation and depletion steps. In the generation step, physical melting of coal is also incorporated. Using a nonlinear least squares regression routine (DUNLSF by IMSL), the activation energy and its variance for each step are fitted to the experimental data. The modeling results are then compared to the experimental results.

5.3.2 Multiple Independent Parallel Reaction Kinetics

With the need for a model which describes the plasticity and metaplast kinetics more realistically, the multiple independent parallel reaction (MIPR) kinetics model will be used in the proposed studies. The MIPR model has been used widely by previous students in combustion at MIT to describe kinetics of weight loss and of tar production during coal pyrolysis (Anthony, 1975, Ko, 1988, and Griffin, 1989). The model is described in detail elsewhere (Anthony, 1975 and Howard, 1981). For the proposed studies, all the reactions involved in the plasticity kinetics and metaplast generation and destruction will be modeled using MIPR. For an irreversible, first-order reaction:

the rate equation and its solution are:

$$dA/dt = -k_A A \quad 5.19)$$

$$A = \exp\left(-\int_0^t k_A dt\right) \quad 5.20)$$

where A is the amount of A at time t and k_A is the rate constant. Using the MIPR model:

$$A = A_1 + A_2 + A_3 + \dots A_n = \sum_0^n A_i \quad 5.21)$$

$$dA_i/dt = -k_{Ai}A \quad , i = 1, 2, 3, \dots, n \quad 5.22)$$

$$A_i = \exp(-\int_0^t k_{Ai} dt) \quad 5.23)$$

$$k_{Ai} = k_{0Ai} \exp(-E_i/RT) \quad 5.24)$$

where i denotes a particular reaction i , k_{0Ai} and E_i are respectively the preexponential factor and activation energy for reaction i . Assuming that all the reactions have the same preexponential factor ($k_{0Ai}=k_{0A}$) and that the number of reactions are large enough to permit the activation energies to be expressed as a continuous distribution, with a probability density function $F(E)$:

$$A = \int_0^\infty \exp\{-k_{0A} \cdot \int_0^t \exp(-E/RT) dt\} \cdot F(E) dE \quad 5.25)$$

Following Anthony et al. (1975) one would choose $F(E)$ to be a Gaussian such that:

$$F(E) = (2\pi\sigma_E^2)^{-1/2} \exp\{-(E_0 - E)^2/2\sigma_E^2\} \quad 5.26)$$

where E_0 and σ_E^2 are respectively the mean activation energy and its variance.

The rate constant expression at any time t is:

$$\frac{k}{k_{0A}} = \frac{\int_0^{\infty} \exp\{(-k_{0A}) \cdot \int_0^t \exp(-E/RT) dt - (E_0 - E)^2/2\sigma_E^2 - E/RT\} dE}{\int_0^{\infty} \exp\{(-k_{0A}) \cdot \int_0^t \exp(-E/RT) dt - (E_0 - E)^2/2\sigma_E^2\} dE} \quad 5.27a)$$

or when the temperature-time history is linear (constant heating rate = m_h), at any temperature T (Howard et al., 1986):

$$\frac{k}{k_{0A}} = \frac{\int_0^{\infty} \exp\{(-k_{0A}/m_h) \cdot \int_0^T \exp(-E/RT) dT - (E_0 - E)^2/2\sigma_E^2 - E/RT\} dE}{\int_0^{\infty} \exp\{(-k_{0A}/m_h) \cdot \int_0^T \exp(-E/RT) dT - (E_0 - E)^2/2\sigma_E^2\} dE} \quad 5.27b)$$

When the temperature is constant:

$$\frac{k}{k_{0A}} = \frac{\int_0^{\infty} \exp\{-k_{0A}t \cdot \exp(-E/RT) - (E_0 - E)^2/2\sigma_E^2 - E/RT\} dE}{\int_0^{\infty} \exp\{-k_{0A}t \cdot \exp(-E/RT) - (E_0 - E)^2/2\sigma_E^2\} dE} \quad 5.28)$$

Only four parameters ($A(t=0)$, E_0 , σ_E^2 , k_{0A}) are required to correlate the MIPR model to kinetics data for a reaction contributing to plasticity and/or metaplast generation and depletion data.

In addition, the values E_0 and σ_E^2 also shed light on interesting features of the reaction set of interest including its "chemical diversity" as expressed by the range of activation energies for which reactions make significant contributions to the rate process of interest. The variance of $F(E)$ determines the spread around the mean activation energy. A big spread implies that the overall reaction consists of a large number of independent reactions in parallel. A small spread means that the number of independent reactions is few. Further, one can compare the mean activation energy value of the reaction of interest to activation energy values found in other studies of coal devolatilization to gain insights on the possible types of reactions occurring, e.g. cracking.

5.3.3 Description of Metaplast Reaction Kinetics

The following sequence of kinetic steps are used to determine the intraparticle metaplast inventory, $M(T,t)$:

$$M^* = C_r(t) + (M_{mo} - M_m(t)) + M(t) + P(t) \quad 5.30)$$

where M^* is the maximum amount of metaplast that can be formed and $C_r(t)$ is the remaining amount of coal that can react to form metaplast. The quantity $(M_{mo} - M_m(t))$ is the remaining amount of coal that can melt to form metaplast, M_{mo} being the maximum amount of meltable coal and M_m being the amount of metaplast formed by melting. $P(t)$ is the product from the pyrolysis (i.e. light gases, tar, and coke).

The rate of change of metaplast concentration is then:

$$dM/dt = -dC_r/dt + dM_m/dt - dP/dt \quad 5.31)$$

$$dM/dt = r_m + r_g + r_d \quad 5.32)$$

where r_m is the rate of physical melting, r_g is the rate of metaplast generation, and r_d is the rate of metaplast depletion.

For a Gaussian distribution of melting points, the rate of physical melting, r_m , is given to a very good approximation by:

$$dM_m/dt = r_m = \{M_{m0}m_h/(2\pi\sigma_m^2)^{1/2}\} \cdot \exp\{- (T_m-T)^2/2\sigma_m^2\} \quad 5.33)$$

M_{m0} is the amount of meltable components (e.g. pyridine extractables) in the parent coal, m_h is the heating rate at time t , and T_m the mean melting temperature of coal. The quantity r_m is thus described as the product of M_{m0} , m_h , and the melting point probability density function. Since coal is assumed to melt over a narrow range of temperatures, the melting point distribution is estimated to be normal, with a mean $T_m = 600$ K and the variance $\sigma_m^2 = (30K)^2$ (Fong et. al., 1986b). The quantity M_m is found by integrating r_m over time, knowing the temperature-time histories.

Defining M_r as the amount of metaplast formed by the pyrolysis of C_r , the rate of metaplast generation by chemical reaction of the parent coal is given by:

$$-dC_r/dt = r_g = dM_r/dt \quad 5.34)$$

Defining M_{ri} as the amount of M_r formed by an independent reaction i:

$$dM_{ri}/dt = k_{gi}(M_{ri}^* - M_{ri}) \quad 5.35)$$

$$\frac{M_{ri}^* - M_{ri}}{M_{ri}^*} = \exp \left\{ - \int_0^t k_{gi} dt \right\} \quad 5.36)$$

$$\frac{M_r^* - M_r}{M_r^*} = \int_0^\infty \exp \left\{ - \int_0^t k_{gi} dt \right\} \cdot F(E_g) dE_g \quad 5.37)$$

$$F(E_g) = (2\pi\sigma_{Eg}^2)^{-1/2} \exp \{ - (E_{go} - E_g)^2 / 2\sigma_{Eg}^2 \} \quad 5.38)$$

$M_r^* = M^* - M_{mo}$, the maximum amount of metaplast produced by chemical reaction of the parent coal. Using low temperature (< 900 K) transient viscosity data to find $M(t)$, $M_r(t) = M(t) - M_m$, in which M_m was calculated from integrating r_m over time. The generation rate constant (k_g) was found by fitting the parameters M_r^* , the mean activation energy (E_{go}) and its variance (σ_{Eg}^2) to data on $M_r(t)$ for various temperature-time histories. The preexponential factor of k_g was fixed at 10^{13} s^{-1} to simplify the generation of a set of best-fitted kinetics parameters. Otherwise, several sets of best-fitted parameters can be found with markedly different values of k_{go} , each set being a local minimum of the M_r vs. (k_{go} , E_{go} , σ_{Eg} , M_r^*) parameter space.

The metaplast depletion step would in general be given by:

$$r_d = -k_d M = -dP/dt \quad 5.39)$$

However, a useful simplification becomes possible by inspection of the plots of apparent viscosity vs. time (Figures 1a-e and 2a-e). These figures exhibit a plateau-like region where the minimum apparent viscosity is essentially unchanged with time. This implies that the maximum metaplast concentration, M^* , is observed before any substantial resolidification of the molten coal has begun and hence that the chemical driving force generation of the products:

$$dP/dt = k_d(P^* - P) \quad 5.40)$$

can be reasonably approximated by setting:

$$P^* = M^* = M_r^* + M_{mo} \quad 5.41)$$

Equation 5.30 and 5.41 imply that:

$$P(t) = M^* - M(t) \quad 5.42)$$

The approximations allow the kinetics of metaplast depletion and hence products formation to be modeled without the need to simultaneously solve differential equations for $C(t)$, $M(t)$, and $P(t)$.

In particular here, high temperature (>1000 K) transient viscosity data were used to calculate $M(t)$ and thus $P(t)$ from equation 5.42, again assuming that the metaplast generation step had been completed.

Defining P_i as the amount of P formed by an independent reaction i:

$$dP_i/dt = k_{di}(P_i^* - P_i) \quad 5.43)$$

$$\frac{P_i^* - P_i}{P_i^*} = \exp \left\{ \int_0^t -k_{di} dt \right\} \quad 5.44)$$

$$\frac{P^* - P}{P^*} = \int_0^\infty \exp \left\{ \int_0^t -k_{di} dt \right\} \cdot F(E_d) dE_d \quad 5.45)$$

$$F(E_d) = (2\pi\sigma_{Ed}^2)^{-1/2} \exp \{ - (E_{do} - E_d)^2 / 2\sigma_{Ed}^2 \} \quad 5.46)$$

The depletion rate constant (k_d) were found by fitting the mean activation energy (E_{do}) and its variance (σ_{Ed}^2) to these high temperature data on $P(t)$ for different holding temperatures, estimated from equation 5.42. The preexponential factor of k_d was fixed at 10^{13} s^{-1} , again to generate only one set of kinetics parameters (see discussion of fitting to obtain kinetics parameter of the metaplast generation step).

With each contribution to the metaplast generation and depletion kinetics defined according to equation 5.30, metaplast concentration, $M(t)$, is found by:

$$M(t) = M_r(t) + M_m(t) - P(t) \quad 5.47)$$

The best fitted parameters (M_r^* , E_{go} , σ_{Eg} , E_{do} , and σ_{Ed}) are shown on Table 5.2. The calculated apparent viscosity of different coals is shown in Figures 5.5 a-e for constant heating rate runs and different final holding temperatures and in Figures 5.6 a-e for heating at different rates to the same final temperature.

Table 5.2: MIPR BEST-FITTED KINETICS PARAMETER VALUES^c

COAL	(dmmf)		(Kcal/mole)			
	M _{melt}	M*	E _{go}	σ _{Eg}	E _{do}	σ _{Ed}
IL hvb	.28 ^a	.41	42.7	0.4	59.0	8.0
PT hvb	.30 ^a	.48	43.0	0.4	60.1	7.6
WV hvb	.30 ^b	.45	42.8	0.3	60.0	7.5
UF mvb	.07 ^a	.35	37.7	0.3	63.2	5.5
PO lvb	.01 ^a	.29	38.1	0.3	59.2	4.4

a: data from Snape and Bartle, 1989

b: no data available, estimated to be approximately equal to that of Pittsburgh No. 8 coal.

c: Best-fitted as described in text, beginning with data at 400 K/s and different holding temperatures.
Then, if needed, further refine the fit using the data at 200 K/s and 800 K/s.

$$k_{go} = k_{do} = 10^{13} \text{ s}^{-1}$$

Figure 5.5a: Smooth lines: Apparent viscosity of Illinois No.6 hvb coal at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Holding Temperatures
Pittsburgh No. 8 hvb Coal

Figure 5.5b: Smooth lines: Apparent viscosity of Pittsburgh No.8 hvb coal at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at t = 0.5 s.

Figure 5.5c: Smooth lines: Apparent viscosity of Lewiston-Stockton hvb coal at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Coal Plasticity at Different Holding Temperatures **Upper Freeport mvb Coal**

Figure 5.5d: Smooth lines: Apparent viscosity of Upper Freeport mvb coal at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.5e: Smooth lines: Apparent viscosity of Pocahontas No.3 hvb coal at different holding temperatures predicted from MIPR model described in text; Heating rate = 400 K/s; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.6a: Smooth lines: Apparent viscosity of Illinois No.6 hvb coal at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.6b: Smooth lines: Apparent viscosity of Pittsburgh No.8 hvb coal at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.6c: Smooth lines: Apparent viscosity of Lewiston-Stockton hvb coal at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.6d: Smooth lines: Apparent viscosity of Upper Freeport mvb coal at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

Figure 5.6e: Smooth lines: Apparent viscosity of Pocahontas No.3 lvb coal at different heating rates predicted from MIPR model described in text; Holding temperature = 1098 K; Pressure = 1 atm helium. Symbols: Experimental data. Heating started at $t = 0.5$ s.

5.3.4 Discussion Kinetics Modeling Results

The calculated apparent viscosity of different plastic coals agrees well with the experimental data. The standard error of the estimate (SEE) is calculated for the plastic periods and minimum apparent viscosities for all runs on each coal at 1 atm pressure.

$$SEE = \sum_{j=1}^n \left\{ \frac{(\text{experimental value}_j - \text{predicted value}_j)^2}{n-k} \right\}^{1/2} \quad 5.48)$$

where n is the number of data points and k the number of best fitted parameters used in the model. The average standard error of estimate (ASEE), for the plastic periods and for the minimum apparent viscosity, is found by averaging the SEE's for all five coals. In previous work, a SEE was calculated for a set of data on tar yields where each measured tar yield corresponded to a specific and complete temperature-time history (Ko, 1988). However, for each temperature-time history in this work a set of many viscosity data points is obtained. It was therefore concluded that SEE's should be computed, not for the entire set of individual viscosity readings associated with each temperature-time history, but rather for two parameters characteristic of the composite viscosity vs. time behavior for each temperature-time history. These two parameters are the minimum apparent viscosity and the plastic period. The resulting SEE's and corresponding ASEE's are listed in Table 5.3. The ASEE's for the plastic period and the minimum apparent viscosity are 0.13 s and 317 Pa·s, respectively. These values are comparable to the measurement resolution of the plastometer (0.1 s and ± 300 Pa·s). It is therefore concluded that the model does a good job of fitting the overall plastic behavior of this set of five coals, as affected by temperature-time history.

Table 5.3: Standard Error of Estimate for MIPR Kinetics Model^a

<u>Coal</u>	<u>SSE(Plastic Period), s</u>	<u>SSE(Min Viscosity), Pa·s</u>
Illinois No. 6 hvb	0.14	203
Pittsburgh No. 8 hvb	0.14	279
Lewiston-Stockton hvb	0.07	395
Upper Freeport mvb	0.21	424
Pocahontas No. 3 lvb	0.07	283
Average (ASEE)	0.13	317

a: see equation 5.48 in text.

In general, the model predictions fit the experimental results well, except for predicting that at lower heating rates (200 and 400 K/s), the apparent viscosity begins to increase at a later time than that observed. At lower heating rates, the experimentally observed viscosity during resolidification increases slowly at approximately 1000 K, then increases very rapidly when the holding temperature of 1098 K is attained. This earlier rise in viscosity is hypothesized to be caused by secondary reactions, which the model does not address, degrading the plasticizing power of the metaplast by forming higher molecular weight liquid which is more viscous.

The activation energy values of the metaplast chemical generation step for hvb are higher than those for mvb and lvb coals. There are two processes for forming metaplast: physical melting and chemical reaction. While metaplast generation for mvb and lvb coals is mostly due to chemical bond breakings, for hvb coals it is mostly due to melting. If two coals have comparable plastic behaviors, the one with a lower metaplast formation from physical melting maintains a comparable metaplast inventory by having a higher metaplast formation from chemical reactions. Lower activation energy values (i.e. higher chemical reaction rates) would then be expected for mvb and lvb coals to compensate for the lower inventories of meltable components in these coals. The standard deviation values of E_g are very small, supporting the interpretation that chemical generation of metaplast occurs by a small number of, or even one, pathway. Thus the sometimes observed phenomenon of higher product yield at higher heating rate, attributed by some interpretations to competing chemical pathways with different activation energies, is expected to be of little importance here. By modeling the metaplast generation kinetics as a single reaction, the modeling results are essentially the same. However, the SEE's and ASEE's improve by 18%, since the number of fitted parameters (k) decreases from 5 to 4, with the removal of σ_{E_g} from the parameter space.

The activation energy values of the depletion step for all coals are about the same except for the mvb coal which is slightly higher. Since Upper Freeport mvb coal solidifies at much later time than other coals, its depletion step's activation energy is higher (implying a lower rate of depletion kinetics). The standard deviation of E_d , σ_{Ed} , decreases with increasing rank, ranging from 4.4 kcal/mole for Pocahontas No. 3 lvb coal to 8.0 kcal/mole for Illinois No. 6 hvb coal (Table 5.2). A tendency toward greater uniformity in the molecular structure of the parent coal structures with increasing rank is supported by these σ_{Ed} results. Higher rank coals have a more uniform molecular structure, and therefore their liquid metaplast should be made up of more similar molecules. These similar molecules react by more similar pathways, thus the lower σ_d , indicating that there are fewer independent reactions contributing to metaplast depletion. Hvb coals have higher σ_d values, implying that the depletion reactions may involve a larger number of different reactions.

5.4 Coal-Type Specific Parameter Modeling

For plastic coals, relationships between simple indices of coal type and observed plasticity would be beneficial. From the present data, there is no evidence for a continuous increase (or decrease) in plasticity with increasing coal rank. This section will concentrate on the investigation of the relationships between maximum plasticity (and thus maximum metaplast concentration) and simple indices of coal type for different coals.

5.4.1 Different Indices of Coal Type

One of the simplest indices of coal type for different coals is their elemental content. Coal consists of inorganic materials (e.g. 5-20 wt%) and organic materials, i.e. macerals,

made up of largely C, O, H, N, S, and mineral matter. In general, as the rank increases, the carbon content of a coal increases, while its oxygen content decreases. The balance of the mass consists mainly of hydrogen, nitrogen, and, in high sulfur coals such as Illinois No. 6 hvb, organic sulfur. Carbon and hydrogen NMR studies also allow for more refined classifications of coal elements such as fraction of aromatic carbon (carbon aromaticity, C_{fa}) and fraction of hydrogen attached to aromatic carbon (proton aromaticity, H_{fa}). Ultimate analyses and structural data for the coals studied here are shown in Table 5.4.

Plot of maximum plasticity at 1 atm pressure of helium and at vacuum vs. %C for different coals is shown in Figure 5.7. Hvb coals are shown to be very plastic. Although mvb and lvb coals are less plastic than hvb coals, they still exhibit a strong plastic behavior. However, the %C content does not correlate well with plasticity.

Labile Bridges

Labile bridges are mostly aliphatic, with some alicyclic and heteroatomic functionalities. They are the bridges which link the larger aromatic clusters or molecules together. The initial fraction of labile bridges are important since they are the key reaction centers. When a labile bridge is heated, its dissociation can produce reactive fragments which may further dissociate to produce smaller aromatic fragments or condense to form char and release noncondensable gases (Niksa and Kerstein, 1991). Scissions of labile bridges can therefore create smaller aromatic molecules including liquid metaplast. Thus, coals with higher fractions of labile bridges should exhibit greater plasticity. Figure 5.8a shows a plot of maximum plasticity vs. fraction of aliphatic carbon content ($1-C_{fa}$). In general, hvb coals with higher aliphatic carbon fraction (and thus higher labile bridge fractions) exhibit greater plasticity than mvb and lvb coals with lower aliphatic carbon fraction.

ND: Beulah-Zap Lignite
 WY: Wyodak Subbituminous
 IL: Illinois No. 6 hvb
 PT: Pittsburgh No. 8 hvb
 WV: Lewiston-Stockton hvb
 UF: Upper Freeport mvb
 PO: Pocahontas No. 3 lvb

Figure 5.7: Maximum plasticity (minimum viscosity) of different coals at vacuum and 1 atm helium. Heating rate of 400 K/s and holding temperature of 1098 K. ND and WY coals do not exhibit any plasticity.

5.8a: Maximum Plasticity vs. Aliphatic Carbon Fraction

5.8b: Maximum Plasticity vs. %O

5.8c: Maximum Plasticity vs. %H

Figure 5.8 : Plasticity vs. different indices of coal type at vacuum and 1 atm helium. Heating rate: 400 K/s and Holding temperature: 1098 K. Smooth lines: free drawn trend lines. Symbols: experimental data. ND and WY coals do not exhibit any plasticity.

Oxygen Content

Oxygen also plays an important role in coal devolatilization. Oxygen promotes cross-linking of labile bridges which suppresses formation of liquid fragments or metaplast (Niksa and Kerstein, 1991). Coals with higher oxygen content might therefore be expected to exhibit lower plasticity. Figure 5.8b shows a plot of maximum plasticity vs. %O content of a coal. Here, hvb coals with higher oxygen content still exhibit significant plasticity, more than mvb and lvb coals with lower oxygen content. This is probably because the magnitude of plasticity is coupled with other indices of coal type (e.g. labile bridge content and hydrogen content), and the effects of oxygen content on coal plasticity is not clear cut in Figure 5.8b. In discussing possible explanations for coal type effects on pyrolysis, Suuberg et al. (1979) noted that reactions of two hydroxyl groups can result in water and an etheric oxygen bridge between two moieties in the coal structure. Thus phenolic groups are expected to inhibit plasticity by participating in cross-linking of metaplast or its precursors, and by consuming hydrogen which could otherwise stabilize radicals. Thus a possible relation of OH content of the coals and decreased plasticity was investigated. However, decreasing plasticity was not found to be correlated with increasing OH content. Therefore it was decided to concentrate only on the contribution of total oxygen content to plasticity in the formulation of a coal specific parameter to correlate the magnitude of plasticity of different coals.

Hydrogen Content

Hydrogen is important because it can stabilize radicals. The abstractable hydrogen is hydrogen which is not attached to aromatic carbons. Its inventory depends on Hf_a and the total amount of hydrogen in the parent coal. Abstractable hydrogen stabilizes aromatic molecules, and is thus believed to promote plasticity. Coals with higher content of non

aromatic hydrogen would therefore be expected to exhibit higher plasticity (Ko et al., 1988 and Niksa, 1991). Figure 5.8c shows a plot of maximum plasticity vs. %H content. In general, hvb coals with higher hydrogen content exhibit greater plasticity, i.e. lower apparent viscosity, than mvb and lvb coals with lower hydrogen content.

5.4.2 Formulation of A Parameter to Correlate Plasticity with Coal-type

Ko (1988) and Ko et al. (1989) correlated maximum tar yield in rapid pyrolysis of powdered coal (diameter < 100 μ m) with a coal-type parameter X_{tar} :

$$X_{tar} = \frac{(\text{no. of labile bridges})(\text{amt. of abstractable H})}{(\text{no. of cross-linked bridges})} \quad 5.49)$$

from the assumption of that tar generation proceeds via the global mechanism:

Here, the importance of labile bridges, oxygen, and hydrogen is recognized in determining the three factors used to determine X_{tar} . The number of labile bridges is assumed to be proportional to the aliphatic carbon content of the raw coal. The amount of the abstractable hydrogen is assumed to be proportional to the amount of elemental hydrogen in the raw coal. The number of cross-linked bridges is assumed to be proportional to amount of the elemental oxygen and organic sulfur in the raw coal. The analysis of Ko et al. provided a good linear correlation between maximum tar yield at various pressures and X_{tar} . (Ko, 1988 and Ko et al., 1989)

In light of Ko's previous correlation and the strong relationship between metaplast and tar, it seems plausible to try to correlate maximum plasticity with a coal-type parameter. This coal-type parameter should incorporate the importance of labile bridges, oxygen, and hydrogen content. First, the coal-type parameter for plasticity was formulated as:

$$X_P = \frac{(\text{no. of labile bridges})(\text{total amount of hydrogen})}{(\text{total amount of oxygen})} \quad 5.51)$$

with:

$$\text{no. of labile bridges} = ((1 - C_{f_2}) \cdot [C \text{ wt\% dmmf}])^{1.8} \quad 5.52)$$

taken from Ko's X_{tar} formulation (Ko, 1988) and:

$$\text{amount of hydrogen} = [H \text{ wt\% dmmf}] / 1.0079 \quad 5.53)$$

$$\text{amount of oxygen} = [O \text{ wt\% dmmf}] / 15.994 \quad 5.54)$$

A plot of maximum plasticity vs. X_P is shown in Figure 5.9a. A linear correlation between plasticity and X_P is quite good at vacuum and better at 1 atm He pressure. However, knowing that not all hydrogen participates in stabilizing free radicals, it seems logical to replace the amount of hydrogen in equation 5.47 by the amount of abstractable hydrogen. Here, the amount of abstractable hydrogen is formulated as the amount of hydrogen which is attached only to aliphatic carbon atoms minus a correction suggested by Ko (1988) to account for experimental observations that OH group may compete for the abstractable hydrogen:

$$\begin{aligned} \text{amount of abs hydrogen} &= (1 - H_{f_2}) \cdot [H \text{ wt\% dmmf}] / 1.0079 \\ &\quad - [OH \text{ wt\% dmmf}] / 17.002 \quad 5.55) \end{aligned}$$

$$[\text{OH wt\% dmmf}] = 33.2 - 35[\text{C}] \quad (\text{Ko, 1988}) \quad 5.56)$$

Ko (1988) assumed that abstractable hydrogen should be proportional to aliphatic hydrogen. In formulating a relation for estimating abstractable hydrogen from coal elemental composition, he assumed that aliphatic hydrogen concentration in the coal was proportional to total hydrogen concentration in the coal. For the present set of coals, data are available on the actual fraction of aromatic hydrogen in the coals of interest. Therefore we can directly calculate the fraction of aliphatic hydrogen as $1 - H_{f_a}$. The revised X_p is formulated as:

$$X_p(\text{corrected}) = \frac{(\text{no. of labile bridges})(\text{amount of abstractable hydrogen})}{(\text{total amount of oxygen})} \quad 5.57)$$

A plot of maximum plasticity vs. a revised X_p , corrected to better account for the abstractable hydrogen ($X_p(\text{corrected})$) is shown in Figure 5.9b. The linear fit between maximum plasticity and $X_p(\text{corrected})$ is better than that of the uncorrected X_p , especially in correlating data under vacuum.

5.4.3 Discussion of Coal-Type Specific Parameter Modeling

The present correlations represent an attempt to explain coal-type effects on coal plasticity. Here it has proved fruitful to formulate a coal-type parameter for apparent viscosity analogous to that for tar yields devised by Ko (1988). The effects of labile bridges, oxygen, and hydrogen in the specific coal are incorporated into the present coal type parameter in reflection of their hypothesized effects on metaplast and hence on coal plasticity. Although rich in labile bridges and hydrogen, lignites and subbituminous coals have abundant oxygen which promotes cross-linking, causing the formation of liquid fragments or metaplast to be suppressed, leading to a lack of plastic behavior in these

5.9a: Maximum Plasticity vs. X_p 5.9b: Maximum Plasticity vs. $X_p(\text{corrected})$

Figure 5.9: Plasticity vs. coal-specific parameters at vacuum and 1 atm helium. Heating rate of 400 K/s and holding temperature of 1098 K.

coals. The primary volatile products of their pyrolysis are noncondensable gases. With much lower oxygen content than that of low rank coals, Hvb coals are also rich in labile bridges and hydrogen which leads to very good plastic behavior. High rank coals have lower plasticity than hvb coals because they have considerably less labile bridges.

A coal-type parameter for correlating plasticity is intended to be used as a rough guide, or at least to predict trends in plasticity for a coal when experimental data are not available on the plasticity of that coal. One is able to use the correlation knowing only the ultimate analysis and a few structural data for the given coal.

6 Conclusions and Recommendations

Conclusions

- 1) By varying the shear rates of the plastometer and observing the apparent viscosity, molten Pittsburgh No. 8 hvb coal was found to be Newtonian for shear rates from 2 to 10 s^{-1} .
- 2) At higher temperature (i.e. 1098 K), pressure effects are important at vacuum where the plastic period decreases and minimum apparent viscosity increases when compared to those at 1 atm of inert gas. Increasing inert gas pressure from 1 atm up to 50 atm does not significantly change coal plasticity. It is hypothesized that higher pressure inhibits mass transport of metaplast to tar vapors, but also enhances metaplast repolymerization into coke and char.
- 3) The plastic period decreases with increasing holding temperature. It is hypothesized that higher temperature increases mass transport of liquid metaplast to tar vapors and metaplast repolymerization to coke and char.
- 4) Heating rate has essentially no effect on the individual softening temperature of each plastic coal, thus implying that metaplast generation, by physical melting (as would be expected) or by chemical bond breaking, or both, is not strongly affected by heating rate.
- 5) The plastic period decreases with increasing heating rate. It is hypothesized that higher heating rate increases mass transport of liquid metaplast to tar vapors. In addition, higher temperature is reached faster, resulting in enhanced metaplast repolymerization to coke and char.

6) Coal type strongly affects the magnitude and duration of plasticity. Hvb coals are most plastic. Mvb and lvb coals exhibit comparable plasticity to hvb coals, though the maximum plasticity and duration of the plastic period are less. Low rank coals such as subbituminous and lignite do not exhibit any plasticity under the present heating conditions.

7) The number density and volume fraction of bubbles in molten coal are not consistent with those usually associated with foams. During high heating rate pyrolysis of coal (heating rate $> 10^3$ K/s), the bubble number density is high, but the volume fraction of bubbles in the molten coal is too small to be foam-like. During low heating rate pyrolysis of coal (heating rate $< 10^2$ K/s), the volume fraction is high, but the number density of bubbles in the molten coal is too low to be considered foam-like.

8) The apparent viscosity of molten coal can be reasonably modeled by approximating the melt as a two phase suspension of a solid in a liquid. Although the contribution to the apparent viscosity of the coal melt by gas bubbles is not negligible, it is not significant enough for this research to use a three phase suspension model, considering the difficulty of determining the time-dependent gas volume fraction either experimentally or theoretically.

9) The transient coal plastic behavior is well predicted using a kinetics model that assumes metaplast is generated by physical melting and by chemical reactions, and depleted by chemical reactions. The model assumes that the chemical reaction steps can be mathematically described by multiple independent parallel reaction kinetics (MIPR). The model has five fitted parameters: the maximum amount of metaplast that can be generated (M^*), the mean activation energy and its variance for the chemical generation reactions (E_g and σ_{E_g}), and the mean activation energy and its variance of the chemical depletion

chemical (E_d and σ_{Ed}). All of these parameters have been determined by best fitting the model to experimental data on viscosity vs. temperature-time histories.

11) The MIPR model's standard errors of estimate (SEE's) have been determined for the minimum apparent viscosity and the plastic period of each coal. The average of the SEE's for the minimum apparent viscosity and the plastic period of all five plastic coals have been found to be approximately the same to the viscosity and time resolutions of the plastometer which are 300 Pa·s and 0.1 s, respectively.

11) Coal plasticity is moderately well correlated with simple indices of coal type such as the elemental C, O, and H contents and well correlated linearly with a coal specific parameter defined in terms of simple indices of coal type such as labile bridge fraction and H and O contents. These indices are combined to calculate a coal specific parameter $X_p(\text{corrected})$:

$$X_p(\text{corrected}) = \frac{(\text{no. of labile bridges})(\text{total amount of abstractable hydrogen})}{(\text{total amount of oxygen})}$$

which has a good predictive ability for coal maximum plasticity as affected by coal type at vacuum and at 1 atm pressure..

Recommendations

1) The Newtonian behavior of molten should be further investigated. The range of shear rates for this study should be increased, and the measurements should be conducted for other coals. Currently, the maximum shear rate of the plastometer is approximately 11 s^{-1} due to a limit set by the gear motor's maximum angular speed and the size of the current

apparatus. The possibility of incorporating a higher performance gear motor to the current plastometer setting should be investigated.

2) The effects of pressure on plasticity should be further investigated, particularly at lower temperatures. With a trade-off between mass transport of metaplast to tar and repolymerization of tar to coke and char, there should be an optimum pressure (and temperature) for maximum plasticity.

3) The effects of reactive gases such as H_2 and O_2 should be investigated. Hydrogen is hypothesized to enhance plasticity, and oxygen is hypothesized to diminish plasticity. Plasticity data obtained under these reactive gas atmospheres will shed light on these hypotheses.

4) The effects of coal pretreatment such as alkylation and preoxidation should be investigated. These pretreatments are hypothesized to affect plasticity by altering the metaplast generation and depletion reaction processes.

5) The plastometer can be used to investigate the rheological behavior of other thermoplastic materials such as thermal softening polymers at high heating rates and temperatures.

6) High heating rate studies of lower rank coals should be performed to potentially induce plasticity for systematic measurement in an apparatus similar to the current plastometer, but modified to provide higher heating rates.

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Appendix 1. Sample Viscosity Calculation

The apparent viscosity, η , is obtained by applying the equation for a concentric cone-and-plate viscometer in which the disk rotates between two stationary plates:

$$\eta = \frac{3T_m/4\pi R^3}{\gamma_R}$$

where T_m is the measured torque, $\gamma_R = \Omega/\theta$ is the shear rate of the cone-shaped disk of radius R and cone angle θ , and Ω is the angular speed of the disk.

In the actual experiments, the voltage drop (V_d) across the torquemeter was measured. Here, the maximum reading of $5 \text{ V} = 10 \text{ oz}\cdot\text{in} = 7.06 \cdot 10^{-2} \text{ N}\cdot\text{m}$. Therefore, the voltage drop is converted to torque by:

$$T_m = V_d \cdot \frac{1.41 \cdot 10^{-2} \text{ N}\cdot\text{m}}{1 \text{ V}}$$

Knowing the average torque due to friction (T_f) = $3.18 \cdot 10^{-4} \text{ N}\cdot\text{m}$:

$$\eta_{\text{calc}} = \frac{3(T_m - T_f)/4\pi R^3}{\gamma_R} = \frac{3(T_m - 3.18 \cdot 10^{-4} \text{ N}\cdot\text{m})/4\pi R^3}{\gamma_R}$$

Using this expression to calculate the viscosity of the viscosity standard, $\eta_{\text{calc}} = 5.58 \cdot 10^3 \text{ Pa}\cdot\text{s}$ ($= \text{kg}\cdot\text{m}^{-1}\text{s}^{-1}$). With $\eta_{\text{actual}} = 5.22 \cdot 10^3 \text{ Pa}\cdot\text{s}$:

$$\text{apparatus constant} = a = \frac{\eta_{\text{actual}}}{\eta_{\text{calc}}} = 0.935$$

Therefore, the expression used to calculate the viscosity throughout this work is:

$$\eta_{\text{actual}} = 0.935 \cdot \frac{3(T_m - 3.18 \cdot 10^{-4} \text{ N} \cdot \text{m}) / 4\pi R^3}{\gamma_R}$$

$R = 3.75 \cdot 10^{-3} \text{ m}$; $\theta = 2^\circ$; and for most runs $\Omega = 0.67 \text{ rpm}$

$$\gamma_R = \Omega / \theta = \frac{(0.67 \text{ rpm}) \cdot (360^\circ)}{(1 \text{ min} / 60 \text{ s}) \cdot 2^\circ} = 2.01 \text{ s}^{-1}$$

Therefore:

$$\eta_{\text{actual}} = 0.935 \cdot \frac{3(T_m - 3.18 \cdot 10^{-4} \text{ N} \cdot \text{m}) / 4\pi (3.75 \cdot 10^{-3} \text{ m})^3}{2.01 \text{ s}^{-1}}$$

Appendix 2. Thermal Lag of Coal Sample Calculation

Defining T_0 as the initial temperature of coal before heating; T_1 as the temperature of the shearing chamber; and T as the temperature of the coal sample, for unsteady-state heat conduction in a slab of finite thickness, the temperature at the center of the center of the slab is:

$$\frac{T - T_0}{T_1 - T_0} \equiv 0.95$$

when $\alpha/b^2 \equiv 1.5$. With the thermal diffusivity of coal (α) $\equiv 1.5 \cdot 10^{-7} \text{ m}^2/\text{s}$ and the coal layer of thickness $2b \equiv 0.13 \cdot 10^{-3} \text{ m}$, the time (t) required to obtain $\frac{T - T_0}{T_1 - T_0} \equiv 0.95$ is:

$$t \equiv 1.5 \cdot \frac{(0.65 \cdot 10^{-4} \text{ m})^2}{1.5 \cdot 10^{-7} \text{ m}^2/\text{s}} \equiv 0.042 \text{ s}$$

At the heating rate of 1000 K/s , the thermal lag is approximately $1000 \text{ K/s} \cdot 0.042 \text{ s} \equiv 42 \text{ K}$: