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Coal Plasticity at High Heating Rates and Temperatures

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Sarakorn Gerjarusak, William A. Peters, and Jack B. Howard

Energy Laboratory and Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Abstract

The report elaborates upon our earlier discussion (Technical Progress Report No. 9) of heating rate effects on the plasticity of coals from the Argonne premium sample bank. Apparent viscosity vs. time curves are presented for five of these coals. As reported earlier, heating rate had relatively little effect (typically ± 20 K) on the softening temperature of these coals. The results presented here show that as heating rate is increased from 200 to 800 K/s, the plastic period for each of these coals decreases.

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Introduction

A high temperature plastometer with a new cone-shaped shearing disk has been used to measure the apparent viscosity of molten coals as affected by pressure, temperature, time, heating rate, and coal type. Seven coals, from the Argonne National Laboratory premium coal sample bank, have been studied: 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). In this study, all hvb, mvb, and lvb coals show very good plastic behavior, but ND and WY coals did not exhibit any plasticity. In this report, we elaborate upon our earlier discussion (Gerjarusak, et al., 1992) of effects of heating rate on coal plasticity.

Heating Rate Effects

To study the effects of heating rate, the holding temperature and pressure used were 1098 K and 1 atm helium, respectively. As reported in the Ninth Technical Progress Report (Gerjarusak et al., 1992), for each coal, the heating rate has essentially no effect on the softening temperature, T_s - i.e. T_s was typically constant to within $\pm 20\text{K}$ (Figure 1). 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, as proposed by Fong (1986). 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: Softening temperature (temperature when the viscosity of molten coal first reaches 50000 Pa·s) of different coals at various heating rates. Holding temperature of 1098 K and 1 atm helium. ND and WY coals do not exhibit any plasticity.

example, other workers have found that for hvb coals pyridine extractables account for 25-30% of the total mass in the parent coal (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. As shown in Figure 1, different coal types can exhibit different softening temperatures. As we noted earlier (Gerjarusak et al., 1992), this may reflect different metaplast melting points for the different coals, different kinetics of metaplast generation, or both.

Figures 2a- 2e display plots of apparent viscosity vs. time for five different softening coals at three different heating rates. These figures, together with Table 1, 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 ± 1000 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 2a-2e clearly show that the 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. Thus higher heating rates would be expected to shorten the plastic period: (a) by more rapidly bringing the coal to higher temperatures where metaplast depletion is accelerated, while (b) having less effect on the time at which softening begins (Figure 2).

Heating Rates:

Figures 2 a, b, c, d, e, and e: Apparent viscosity of different coals at different heating rates. **Note:** Heating was begun at time = 0.5 s. Holding temperature = 1098 K and pressure = 1 atm helium. Points refer to times at which laboratory data on torque vs. time were used to compute apparent viscosity.

Table 1: Minimum Apparent Viscosity

<u>Coal/Viscosity (Pa•s)</u>	<u>Heating Rates</u>		
	<u>200 K/s</u>	<u>400 K/s</u>	<u>600 K/s</u>
Illinois No. 6 hvb	1766	1759	1753
Pittsburgh No. 8 hvb	1456	1455	1449
Lewiston-Stockton hvb	1680	1694	1650
Upper Freeport mvb	2614	2583	2497
Pocahontas No. 3 lvb	5322	5337	5223

Figures 2a-2e 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. 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 2a-2e may reflect greater resistance of metaplast to depletion by mass transfer (or possibly by secondary reactions), due to its higher molecular weight.

The effects of heating rate on the solidification of coal melts 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 will be used to fit the present resolidification data and test this hypothesis.

Future Work

A multiple independent parallel reaction (MIPR) kinetics model will be used to predict the magnitude and duration of plasticity of different coals. The kinetics parameters of the MIPR model will be fitted from the present data using a nonlinear regression program.

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