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COAL PLASTICITY AT HIGH HEATING RATES AND TEMPERATURES

First Technical Progress Report

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Abstract

The broad objective of this project is to obtain improved, quantitative understanding of the transient plasticity of bituminous coals under high heating rates and other reaction and pretreatment conditions of scientific and practical interest. To these ends the research plan is to measure the softening and resolidification behavior of two U.S. bituminous coals with a rapid-heating, fast response, high-temperature coal plastometer, previously developed in this laboratory. Specific measurements planned for the project include determinations of apparent viscosity, softening temperature, plastic period, and resolidification time for molten coal: (A) as a function of independent variations in coal type, heating rate, final temperature, gaseous atmosphere (inert, O_2 or H_2), and shear rate; and (B) in exploratory runs where coal is pretreated (preoxidation, pyridine extraction, metaplast cracking agents), before heating. The intra-coal inventory and molecular weight distribution of pyridine extractables will also be measured using a rapid quenching, electrical screen heater coal pyrolysis reactor. The yield of extractables is representative of the intra-coal inventory of plasticing agent (metaplast) remaining after quenching. Coal plasticity kinetics will then be mathematically modeled from metaplast generation and depletion rates, via a correlation between the viscosity of a suspension and the concentration of deformable medium (here metaplast) in that suspension. Work during this reporting period has been concerned with re-commissioning the rapid heating rate plastometer apparatus.

1. Introduction This research is aimed at obtaining better quantitative understanding of coal plasticity under conditions of both practical and scientific interest. Plasticity in bituminous coals occurs upon heating to a critical temperature where certain of their components soften or melt, creating a fluidlike mass often referred to as "softened coal" or "fluid coal". This material is a complex mixture of solid components (mineral matter and the organic constituents or macerals that do not soften) suspended in a fluid mass generated from the softening macerals (mainly vitrinite) in the parent coal. This mixture may also contain growing bubbles of gas produced by the coal pyrolysis. These bubbles cause the softening coal to foam and swell. Resolidification of the softened phase ensues at a temperature and time dictated by the kinetics of the overall coal reaction process. This thermoplastic behavior results in caking and agglomeration of the coal which helps produce the strength and reactivity required in metallurgical coke [1], but also causes bed bogging in fixed or fluidized bed gasifiers [2,3]. Plasticity effects can be more pronounced at elevated pressures and in the presence of hydrogen.

The rheological behavior of coal during its plastic phase influences several fundamental phenomena impacting practical processing: the transport of pyrolysis products out of the coal mass; the transport into the coal of externally introduced reactive gases such as hydrogen and solid additives; swelling of the coal; and bubble dynamics within the coal melt. These processes in turn affect the extent of intraparticle secondary reactions of newly formed pyrolysis volatiles during devolatilization of the coal, and hence can impact the off-gas composition and extent of carbon utilization in gasification and combustion [4,5]. The transient plastic phase may also influence coal liquefaction behavior [6], including hydrogen transfer and conversion reactivity [7-9].

Basic understanding of the transient plastic behavior of coal is thus essential to understanding virtually all thermal conversion or combustion processes that utilize potentially softening coals. Most previous rheological measurements on softening coals have been made under conditions pertinent of the low-temperature stage of metallurgical coke making, i.e. low heating rate (< 0.1 K/s) carbonization of packed bad samples to temperatures below 800 K [10,11]. A commonly used instrument is the Gieseler plastometer, which measures the angular velocity of a bladed stirrer rotated at constant torque through finely powdered coal compacted in a cylindrical crucible and heated at 3 K/min. Quantitative interpretation of the resulting data is difficult since the stirrer creates a spatially complex flow field and attendant widely varying ranges of shear rates. Other plastometers include the Brabender plastograph, the Sapozhnikov platometer, the concentric cylinder viscometer [12], the capillary viscometer of Davies et al. [13], and the high pressure microdilatometer of Khan and Jenkins [14] that provides heating rates of 65 K/min.

While previous coal plasticity studies are valuable, there remains need for plasticity data and interpretive mathematical models for a wide range of conditions of interest in modern coal utilization including high heating rates (up to 15,000 K/s), elevated temperatures (> 1400 K), for different coal types, with and without the presence of oxidizing (O_2, CO_2) and reducing (H_2, CO) gases. Fong [15] et al. [16-18] made progress to these ends by developing a rapid-heating, fast response plastometer to measure the transient plasticity of softening coal for independent variations in heating rate (40 - 800 K/s), temperature (600 - 1250 K), and pressures of inert or reducing gases from vacuum up to 100 atm. This plastometer was demonstrated by detailed measures of the apparent viscosity of one, highly softening bituminous coal, Pittsburgh No. 8 [15-18]. Also, a mathematical model of coal plasticity kinetics was developed in terms of global intra-coal generation and depletion rates of a material (pyridine extractables) representative of the critical coal softening agent (metaplast) [15-18]. Fong et al. did not study the viscosity of other bituminous coals or investigate effects of oxygen atmospheres, or of oxidative or catalytic pretreatment. Further, their models omitted mechanistic details that could now be added to improve predictive power. Thus while their work is a valuable step forward it leaves unanswered several questions which are the focus of this project.

2. Project Objectives. The broad aim of this research is to provide new, quantitative understanding of the high heating rate plastic behavior of different bituminous coals, especially data and a global model relating transient apparent plasticity to transient intra-coal metaplast inventories. Specific objectives are to:

(1) Determine how the apparent viscosity of softening coals is affected by coal characteristics and by heating rate, final temperature and reactive atmospheres (e.g. oxidizing gases such as O_2; CO_2, reducing gases such as H_2).

(2) Determine if softening coals exhibit non-Newtonian behavior as evidenced by shear rate dependent apparent viscosity.

(3) Determine how coal pretreatment (preoxidation, physical admixture with metaplast cracking agents such as calcium oxide, preextractions with pyridine or other solvents) affect apparent viscosity of softening coal.

(4) Compare transient plasticity to transient intra-particle inventories of pyridine or other extractables.

(5) Develop new, or extend current, kinetics models to correlate and predict coal apparent viscosity as affected by heating rate, temperature, and reaction time and thereby determine the feasibility of reliably predicting the onset/and duration of the softening period and the rates of molten coal solidification.

3. Work During This Reporting Period. Work during this reporting period has been concerned with re-commissioning the rapid heating rate, high temperature coal plastometer system of Fong [15] et al. [16-18], for use in meeting project objectives. Parts of this equipment had been disassembled, and the current project involves a new researcher. It was therefore necessary for that person to become acquainted with this experimental technique (see below) and for the plastometer to be reassembled, before testing and the planned new measurements can proceed.

The experimental approach is conceptually straightforward but care must be exercised in learning and applying this technique. During this reporting period the experimental apparatus for quantifying the plastic behavior of coal was assembled. This apparatus has been described in detail by Fong [15] and Fong et al. [16]. It is a fast-response plastometer (Figure 1), which allows the rapidly changing plasticity of a softening coal to be determined as a function of time at various pyrolysis conditions (i.e. heating rate, temperature, pressure, etc.). The technique is to measure the torque required to rotate at constant speed, and hence constant average shear rate, a thin disc embedded in a thin layer of coal, initially packed as fine particles and confined between two heated metal plates.

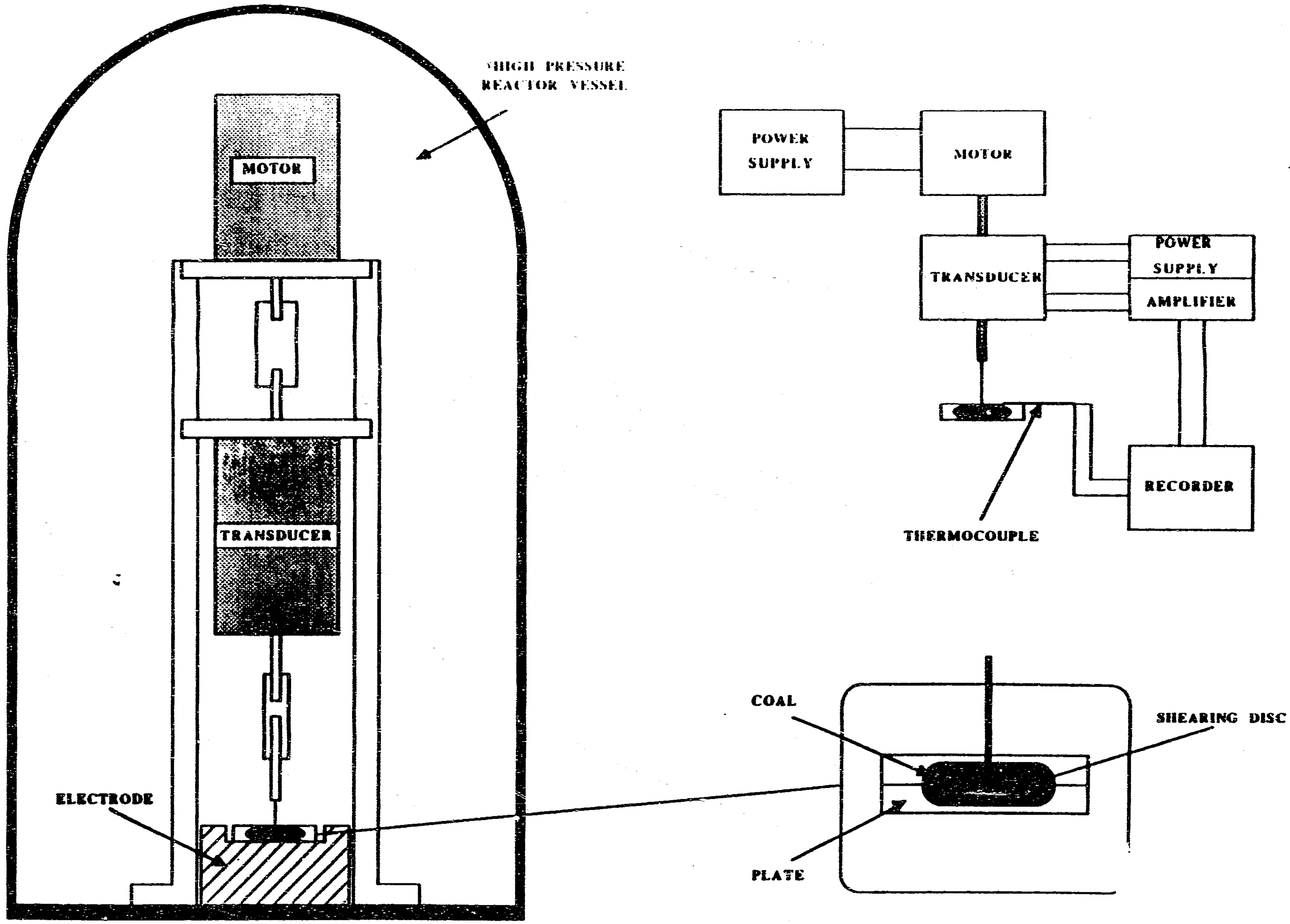

Figure 1 : Schematic of the coal plastometer

The torque is measured with a transducer (Figure 1) one end of which is connected to the shearing disc, while the other is coupled to a 12 V DC gearmotor driven by a speed controller. The shearing disc rotates inside a "cavity" formed between two metal plates and filled with ground coal (Figure 1). The plates are mounted to two electrodes and they are heated with electrical current supplied by a set of 12 V lead automobile batteries. The time-temperature profile is preselected and controlled with carbon rheostats and digital timers [15-17]. Upon heating, the coal softens and the changes in the viscosity result in changes in the torque which are detected by the fast-response transducer, the signal of which is amplified and finally recorded by an electronic recorder capable of acquiring data at a maximum rate of 1 point per msec.

4. Future Plans

At present, the plastometer has been assembled and mounted inside a pressurizable pyrolysis vessel (Figure 1). Future work will test the plastometer by comparing torque vs time curves measured at high heating rates for a high molecular weight polymeric material with previous experimental results obtained by Fong [15]. Experimental studies of effects of coal characteristics and of pretreatment, reactive atmospheres, and shear rate on coal plasticity at high heating rates will then be undertaken.

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