Fundamental Investigation of Fuel Transformations in Pulverized Coal Combustion and Gasification Technologies

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ABSTRACT

The goal of this project is to carry out the necessary experiments and analyses to extend leading submodels of coal transformations to the new conditions anticipated in next-generation energy technologies. During the first two projects years, significant progress was made on most of the tasks, as described in detail in the two previous annual reports.

In the current third annual report, we report in detail on the BYU task on the properties and intrinsic reactivities of chars prepared at high-pressure. A flat-flame burner was used in a high pressure laminar flow facility to conduct high temperature, high heating rate coal pyrolysis experiments. Heating rates were approximately 10^5 K/s, which is higher than in conventional drop tube experiments. Char samples from a Pitt No.8 coal and lignite were collected at 1300°C at 1, 6, 10, and 15 atm. Swelling ratios of the lignite were less than 1.0, and only about 1.3 for the Pitt #8 coal. All coals showed slight increases in swelling behavior as pressure increased. The swelling behavior observed for the Pitt #8 coal at each pressure was lower than reported in high pressure drop tube experiments, indicating the effect of heating rate on particle swelling. This heating rate effect was similar to that observed previously at atmospheric pressure. SEM photos revealed that bituminous coal has large physical structure transformations, with popped bubbles due to the high heating rate.

TGA char oxidation reactivities were measured at the same total pressure as the char preparation pressure. The general trend was that the TGA reactivity on a gram per gram available basis decreased for both Pitt #8 and Knife River lignite coal chars with increasing char formation pressure. The Pitt #8 char intrinsic activation energy and oxygen reaction order remained relatively constant with increasing pressure. This new data provides some of the only information available on the morphology, structure, and reactivity of chars prepared in high pressure flames.

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EXECUTIVE SUMMARY

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increasing pressure. This new data provides some of the only information available on the morphology, structure, and reactivity of chars prepared in high pressure flames.

The project is now in a one-year period of no-cost extension, in which the high pressure task at both BYU and Brown will be completed. A final report will be submitted in the Fall of 2004.

1.0. PROJECT BACKGROUND

Increased concern over global warming is currently motivating a major research effort in the U.S. on future energy technologies with low CO_2 emissions. Research is needed to configure and design future coal-fired power-generation technologies with no or minimum impact on atmospheric CO_2 concentrations. A reduction in CO_2 emissions can be accomplished in the near term through increased efficiency with existing systems. Integrated gasification combined cycle (IGCC) systems have been used as the starting point for strategies to reduce CO_2 in the atmosphere, since (a) they are more efficient than conventional systems (50-60% as opposed to the current 34%) *and* (b) they promise to provide a concentrated stream of CO_2 by using steam and pure O_2 as the gasification agents (without N_2 as a diluent). Sequestration processes are currently under development that rely on IGCC, but this technology has not yet been widely demonstrated. In addition to IGCC, systems, combustion systems operating with enhanced oxygen concentration or pressure may also provide concentrated CO_2 streams.

1.1. Role of Model-Based Design.

Within the last several years computational fluid dynamics (CFD) has firmly established itself as an important tool for the design, optimization, and retrofit analysis of full-scale combustion furnaces. CFD tools, when expertly applied, can identify firing configurations that significantly enhance performance and avoid the need for full-scale testing. Computer simulation is even more important for the design and development of next generation energy technologies based on oxygen-enriched combustion and/or gasification. These advanced systems cannot be reliably designed in an evolutionary way, as is often the case with current technologies, since there is no extensive database of operating experience with similar units. Model based design requires fuel-general submodels of coal transformations that are accurate under the combustion and gasification conditions unique to these processes.

1.2. Fuel Transformation Submodels.

Successful furnace simulation requires predictive capabilities for many subprocesses including fuel transformation submodels to predict: (1) pyrolysis and char yield, (2) char oxidation and carbon burnout, (3) nitrogen release, and (3) mineral transformations. One of the

PIs, (T. Fletcher) is the primary architect of the chemical percolation devolatilization (CPD) model (Fletcher et al. 1992), a mechanistic pyrolysis model based on a network description of the chemical structure of the parent coal. The model: (a) is suitable for application in large comprehensive models of coal combustion, and (b) accurately describes key chemical structural features and reaction mechanisms of coal. Another of the Principal Investigators (R. Hurt) been engaged over the last eight years at the Combustion Research Facility at Sandia National Laboratories and at Brown University in the development of advanced submodels for char combustion, with emphasis on carbon burnout prediction. Carbon burnout has become a critical issue in the existing boiler stock as low-NOx burner retrofits have increased carbon carryover and seriously impacted ash utilization markets at many sites in the U.S.. The experimental work has led to the Carbon Burnout Kinetic Model (CBK), a fuel-general kinetics package designed to predict carbon burnout under conditions relevant to current pulverized coal-fired boilers [Hurt et al., 1998]. Special emphasis is given to the late stages of combustion, which exert a strong influence on the burnout process that determines the carbon content of ash and thus ash utilization options [Hurt, 1998].

The fuel submodels listed above have been developed and applied for atmospheric pc-fired combustion systems. In this application they have found practical use in industry codes and have demonstrated some predictive capability, but further validation against field data is needed, as is extension to conditions found in next-generation energy processes. Although many of the condensed phase processes (internal diffusion, thermal annealing) can be directly carried over into models of gasification and O_2-enriched combustion, other reaction processes in the condensed phases require new data to make predictions under these conditions. Specifically new data is needed on: (1) the char formation process at high pressure, (2) char surface kinetics in enhanced oxygen and in the complex gasification environments, (3) nitrogen and inorganic release at high pressure and the concomitant high particle temperatures of enhanced oxygen combustion and oxygen-blown gasification systems, and (4) the development of engineering models that combine char property prediction with simplified surface kinetics for inclusion in practical flame codes.

2.0. PROJECT OBJECTIVE AND APPROACH

The basic project objective is to carry out the necessary experiments and analyses to extend leading submodels of coal transformations to the new conditions anticipated in next-generation energy technologies. The work will use a combination of high-pressure TGA, atmospheric entrained flow reactor experiments, and experiments with a high pressure drop tube furnace to address volatile release, nitrogen release, inorganic release, and char properties and reactivity, with particular emphasis on gasification environments under pressure and enhanced oxygen environments at atmospheric pressure. The CPD and CBK models will be validated against full-scale data on current pc-technologies with industry involvement (McDermott / B&W) and will be extended to the new conditions using the data generated in the experimental portion of the program.

To achieve the above project objective, a multi-university/joint industry team has been assembled, consisting of Brown University (PIs Robert Hurt and Joseph Calo), Brigham Young University (PI Thomas Fletcher), and McDermott's Babcock and Wilcox Power Generation Group (PI Alan Sayre). The research work HAS BEEN divided into the following four tasks, with the participants indicated:

Task 1: Char Formation and Inorganic Release in High-Temperature Pressurized Flows
(Fletcher, BYU)

Task 2: Combustion Kinetics in Environments with Elevated O_2 and CO_2
(R. Hurt, Brown)

Task 3: Gasification Kinetics in Pressurized CO_2
(Calo, Brown; Fletcher, BYU)

Task 4: Validation and Extension of CPD and CBK Fuel Submodels
(Sayre, B&W; Fletcher, BYU; Hurt, Brown)

3.0. DETAILED DISCUSSION OF PROGRESS ON TASK 1: SWELLING PROPERTIES AND INTRINSIC REACTIVITIES OF COAL CHARS PRODUCED AT ELEVATED PRESSURES AND HIGH HEATING RATES

3.1 Introduction

Clean coal technologies are increasingly being considered because of their high efficiencies and minimal environmental impact. Several technologies, such as Integrated Gasification Combined Cycle (IGCC), Pressurized Fluidized Bed Combustion (PFBC) and Pulverized Coal Injection (PCI), have been identified as the most viable alternatives for the clean utilization of coal due to the use of combined cycles [1, 2]. These advanced clean coal technologies have gained increased technological and scientific interest over the last few decades. These technologies use elevated pressure (e.g., 10-15 atm for PFBC, 15-25 atm for IGCC, and less than 5 atm for PCI). Operations at higher pressure will inherently result in an increase in coal throughput, a reduction in pollutant emissions, and an enhancement in the intensity of reaction [3, 4]. These technologies offer higher efficiencies than conventional pulverized-coal power generation and decreased pollution levels. Several challenges remain before widespread acceptance of these technologies, such as cost and reliability.

Entrained flow IGCC systems may be oxygen-blown, providing a hot, high heating rate environment for coal devolatilization. Temperatures for partial combustion in the early part of such an IGCC may be as high as 1371°C [5]. Most existent high-pressure coal combustion data were obtained at lower temperatures (<1100°C); demonstrating the need for pressure-dependent coal reaction data at high-temperatures.

Swelling of a coal during pyrolysis affects particle size and apparent density of the resulting char, which in turn greatly affect the high temperature reaction behavior. At a given particle temperature, a swelling coal particle initially increases diameter during the early stages of pyrolysis, and then shrinks slightly during the later stages of devolatilization [6]. For atmospheric pyrolysis of swelling coals, Gale et al. [7] showed that the swelling ratio and porosity decreased monotonically as the maximum particle heating rates increased from 2_10^4 K/s to 7_10^4 K/s (see Figure 1).

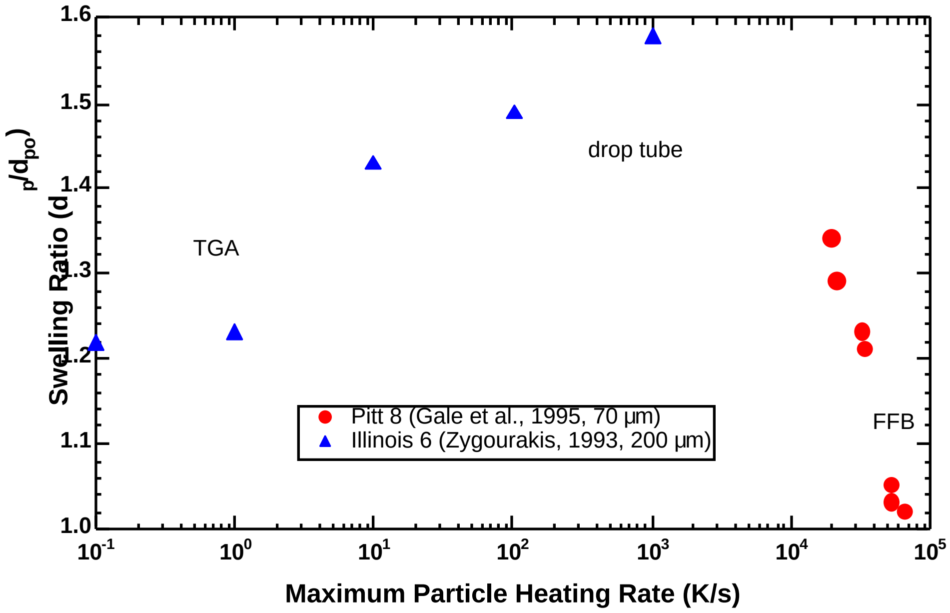

Figure 1: Swelling vs. heating rate at 1 atm [7]

Significant pressurized coal pyrolysis research has been performed in low temperature reactors such as Thermogravimetric Analyzers (TGAs) and wire-mesh reactors. Some research has been performed using medium temperature drop tube reactors [8]. The heating rates of these reactors range from 1 to 10^4 K/sec, which are lower than in entrained-flow industrial applications. Large swelling ratios during pressurized coal pyrolysis have been reported in the literature, suggesting that swelling is enhanced at higher pressures. A coal with almost no swelling at atmospheric pressure swelled significantly under elevated pressures in a drop tube reactor [9]. Wu and coworkers [10] investigated swelling ratios of chars prepared from a pressurized drop-tube furnace (PDTF). The heating rate of the PDTF char was between 10^4 and 10^5 K/s. By comparing PDTF char swelling data with Lee's [9] medium heating rate, there is evidence that a higher heating rate may decrease the swelling ratio, even at elevated pressures.

This work focuses on the how char properties change as a function of the total pressure during coal pyrolysis. Because high-temperature and a higher heating rate may have a significant influence on char properties for subsequent coal combustion or gasification, a high-pressure flat flame burner (HPFFB) was developed in this work. The HPFFB can be operated at a temperature of 1300°C at 15 atm pressure, with a heating rate of 10^5 K/sec. Three American coals were processed using HPFFB and the char samples were collected and analyzed.

3.2 Experimental description

3.2.1 Coals Used

Three American coals (Pittsburgh #8 hva bituminous coal, Wydoak Subbituminous coal and Knife River lignite) were used in this work. These coals were sieved and then sealed and stored in a refrigerator prior to use. Characteristics of these coals are presented in Table 1.

TABLE 1
Characteristic of Coals

	Pitt #8	Knife River	Wyodak
Rank	Hva-Bit	Lignite	Sub-Bit
Diameter	~75 μm	<45 μm	45-75 μm
Ash (wt% dry)	8.34	20.38	5.30
Ultimate analysis (wt% daf)			
C	84.58	62.23	65.52
H	5.47	4.23	5.06
N	2.00	0.95	0.90
S	0.49	1.28	0.44
O (by diff.)	7.44	31.3	28.78

3.2.2 High-Pressure Flat-Flame Burner

Elevated pressure char preparation experiments were conducted using a methane-air high-pressure flat flame burner (HPFFB) that is capable of maximum temperatures above 1300ºC at pressures of 1 to15 atm and heating rates of 10^5 K/s. A high-pressure electrically-heated drop tube (HPDT) reactor was previously developed at BYU [11, 12], with pressure capability of up to 25 atm. The gas composition in the HPDT was generally pure N_2, but could be adjusted to include mixtures of O_2, CO_2, and steam. Due to heater limitations, and decreased insulation properties at elevated pressure, the maximum gas temperature attainable at pressures of 10 atm and higher in the HPDT was approximately 1000ºC. This temperature was too low for the pyrolysis and combustion experiments needed for this work. Therefore, a HPFFB was developed and incorporated into the drop tube reactor to provide higher temperatures (and heating rates) at elevated pressures. An automated control system was also added to improve the operation of the HPFFB. A schematic of the HPFFB is shown in Figure 2.

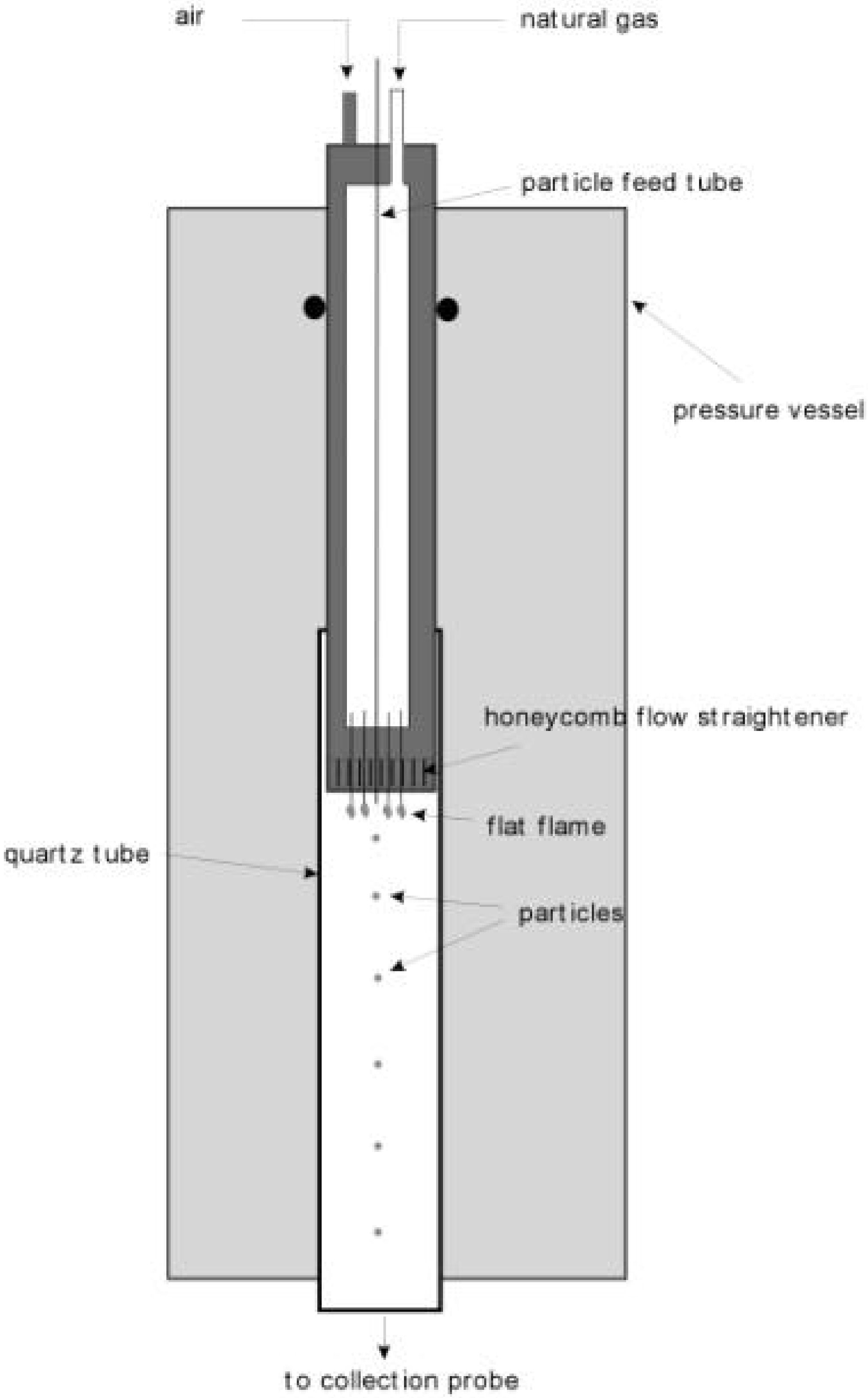

Figure 2: Schematic of high pressure flat-flame burner (HPFFB)

The central component of the HPFFB is a vertical, down-fired flat flame burner that is sealed in a steel pressure vessel. The flat flame reactor uses the hot products of methane combustion to heat the particles, thus more closely approximating the temperature and gas composition of a true pulverized coal combustion environment. The gas flame is thin, permitting complete CH_4 combustion before significant particle heatup. The reaction temperature can be adjusted by changing the equivalence ratio or fuel composition. An electrical heater is used to compensate for heat loss from the reaction tube at high-pressure. The gas temperature profile was measured by inserting a type S thermocouple upwards from the reactor bottom. Flame conditions were adjusted to ensure similar temperatures at different reaction pressures. Residence time can be changed by raising or lowering the burner relative to the collection probe. Maximum particle heating rates in the flat flame reactor were about 10^5 K/s, based on CPD model calculations [13]. Coal particles were injected down the center axis of a 2 inch diameter quartz tube, within which the combustion products from a slightly fuel-lean, high temperature, methane-air flat flame flowed in a laminar fashion.

The steel pressure vessel was pressurized with nitrogen gas, which was allowed to bleed into the reaction gases near the nitrogen quench probe. Pressure inside the furnace was kept constant by a control valve installed at the outlet of the reactor system. A computer-controlled high-pressure feeder injected coal at a speed of 1 g/hr. This feed rate minimized interaction of particles and permitted single particle reaction behavior. Nitrogen was used to entrain coal particles. An O_2 analyzer was used to monitor the composition of the gases exiting the reactor. The methane, air and primary gas were regulated by electronic mass flow controllers. The desired flow rates of these gases were determined (a) by computing the adiabatic flame temperatures, and (b) by comparing the measured temperature profiles and O_2 concentrations at different pressures. The particle collection system includes a water-cooled, gas-quench probe followed by an aerodynamic separation of soot/aerosols from char [11].

Coal was pyrolyzed in the HPFFB at 1300 ºC at pressures of 1, 6, 10 and 15 atm. The flame conditions actually used were slightly fuel-lean (~0.4 mole% O_2 in the post-flame gases) because the methane formed soot at elevated pressures under fuel-rich conditions. Particle residence times in these experiments ranged from 150 to 950 ms.

3.2.3 Kinetic and Physical Properties Determination

Mass release resulting from pyrolysis was determined by the ash tracer technique. The morphologies of the chars were observed by scanning electron microscopy (SEM). Char swelling ratios were measured based on weight loss and tap density data using the relationship [13]:

$$w \;\; /w_{0} = \,)d \;\; /d_{0})(\,p \;\; /p_{0}(^{\varepsilon}$$

Elemental composition was measured using a LECO CHNS instrument.

Char oxidation reactivities were measured in a DMT (Deutsche Montan Technologies, Essen, Germany) high-pressure thermogravimetric analyzer (HPTGA) [14]. Intrinsic char reactivities in the TGA were determined in a manner similar to that of Hecker et al. [14]. Each char sample was oxidized in the HPTGA at low-temperature (615-753 K) and at the same total pressure as its preparation pressure. Sample sizes of 2 to 4 mg were used in a small solid basket. The objective of the TGA study was to explore the effects of char formation pressure on intrinsic char oxidation reactivity.

3.3. Results and discussion

3.3.1 Swelling Ratio

Figure 3 shows measured char mass release and apparent densities of chars as a function of pressure from 1 atm to 15 atm. The heating rate of the HPFFB char in this study was estimated to be about 10^5 K/s. This heating rate is higher than the drop tube reactor because there is no wake from the water-cooled coal injector; the particles in a FFB are convectively heated as they pass through a flame front.

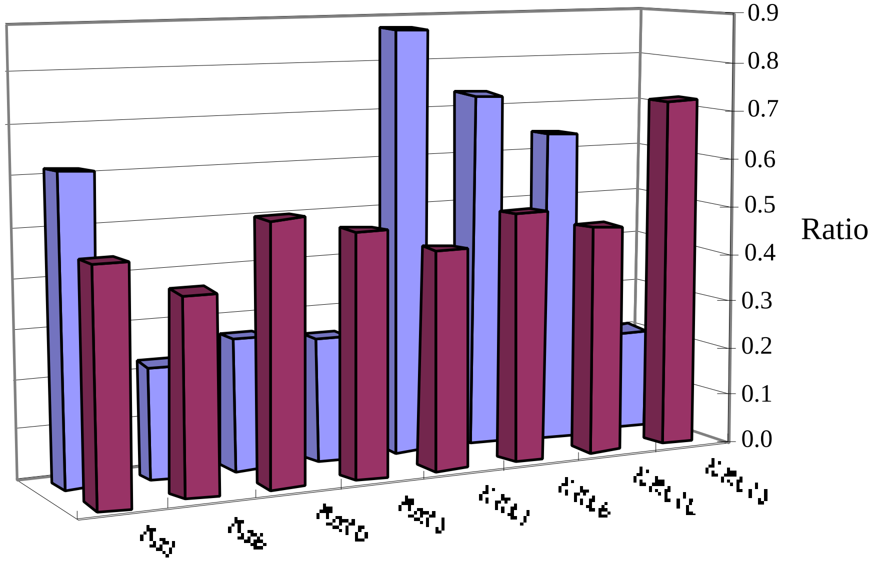

Figure 3: Mass remaining and apparent densities for chars prepared in the HPFFB. Dark bars: m/m_o; light bars: ρ/ρ_o.

The experimental conditions of this experiment are compared with other experiments [9, 10] in Table 2. This high heating rate condition strongly changed the devolatilization characteristics during the early stages of coal pyrolysis, as shown by the comparison of swelling ratios in Figure 4. The swelling ratios for three coals in the HPFFB were much smaller than observed in the PDTF [10] or the high-pressure entrained-flow furnace [9]. The HPFFB char swelling index increases slightly with the increase of char preparation pressure.

TABLE 2

Comparison of Experimental Conditions

	Authors		
	Lee et al.[9]	Wu et al. [10]	Current work
coal	Illinois No.6	Australian Bituminous coal	Two US bituminous coals and one lignite
particle size	62 μm mean particle diameter	63-90 μm	75μm average diameter
apparatus	HEF (high-pressure entrained-flow furnace)	PDTF (pressurized drop-tube furnace)	HPFFB (high-pressure flat flame burner)
heating rate	~10^4 K/s	~10^4-10^5 K/s	> 10^5 K/s
temper.	1189 K	1573 K	1573 K
pressure	0.1-3.8 MPa	0.1-1.5 MPa	0.1-1.5 MPa
atmo-sphere	N_2	N_2 with slightly oxidizing	Combustion product of CH_4/Air

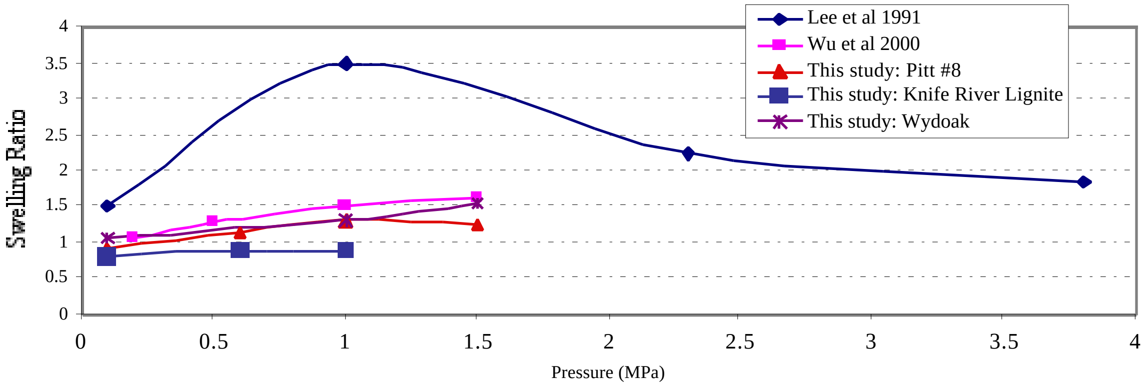

Figure 4: Comparison of swelling ratio in the HPFFB with other studies

However, the swelling ratios at any pressure for the HPFFB chars are smaller than reported in the experiments with lower heating rates. The swelling ratio of Pitt #8 coal increases when pressure increases, reaches a maximum value at 10 atm, and then drops at 15 atm. The Wyodak coal and Knife River also exhibit increasing swelling ratios within the pressure range of 1-15 atm, and indicate that the effect of pressure on the coal swelling ratio is rank dependent. Similar rank dependent results were reported by Lee et al. [9].

Scanning electron micrographs (SEM) of the chars collected in these experiments are shown in Figure 5. The Pitt #8 char particles show evidence of softening, bubble formation, and large blow holes where bubbles have ruptured. The 10 atm particles seem to have smaller blow holes than the 6 atm char, which is consistent with the small increase in swelling behavior shown in Figure 3. The general features of the lignite chars seem to be void of softening behavior.

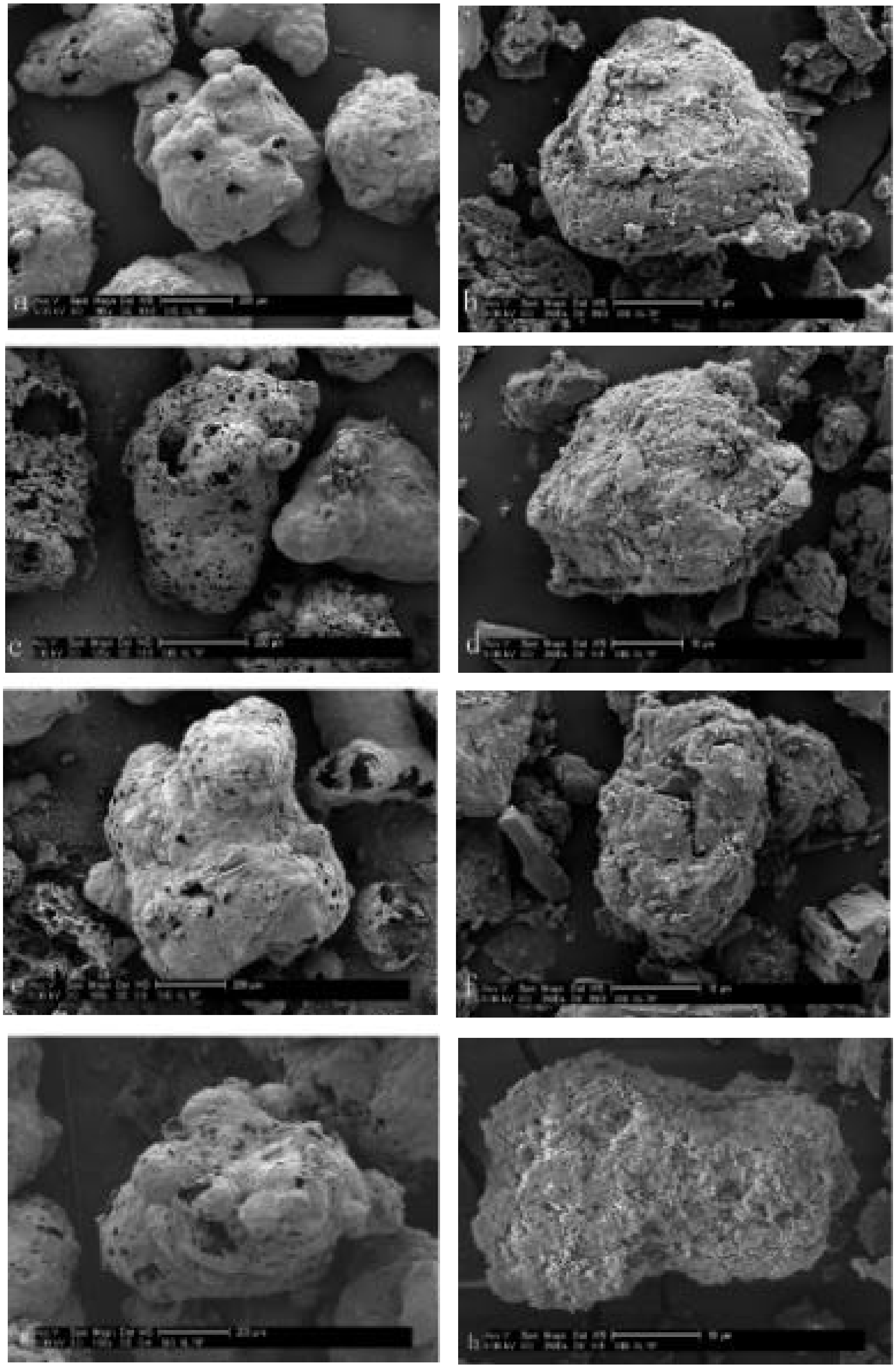

Fig 5. SEM micrograph of char produced from pyrolysis of Pitt #8 coal and Knife River Lignite
(a) Pitt #8 1 atm, (c) Pitt #8 6 atm, (e) Pitt #8 10 atm (g) Pitt #8 15 atm
(b) KRL 1 atm (d) KRL 6 atm (f) KRL 10 atm (h) Pitt #8 15 atm

Both heating rate and pressure affect swelling characteristics during coal pyrolysis. At low heating rates (such as in a TGA, or ~1 K/s), volatiles can diffuse through the pores without causing an internal pressure high enough to cause the particle to swell. At moderate heating rates (such as in a drop tube, or 10^4 K/s), the volatiles formed in the particle interior are formed faster than they can escape through the pores, and swelling occurs if the particle has softened. At high heating rates (approaching 10^5 K/s), the volatiles are formed faster than the swelling process can accommodate, and the bubbles burst. At elevated pressure, higher molecular weight tar precursors do not vaporize, causing more plasticity in softening coals. Hence if conditions are right, enhanced swelling is observed at increased pressures. However, at high heating rates, the surface tension in the bubble walls is overcome and the bubbles burst before significant swelling occurs. For low rank coals and lignites, little softening occurs, and the discharge of moisture and light gases with little tar formation can actually cause particle shrinkage.

The physical structure of the char significantly affects its high temperature oxidation or gasification rate. A comprehensive coal oxidation model needs precise prediction of coal swelling ratio. A correlation of coal swelling ratio with pyrolysis pressure, and carbon content of the parent coal was developed by Benfell[15], which predicts change of the coal swelling ratio with increased pressure from medium heating rate coal pyrolysis(~ 10^4 K/s), but overestimates swelling ratio for high heating rate pyrolysis (~10^5 K/s). Since practical pulverized coal combustion occurs at high temperature (2000K) and heating rate (10^6 K/s), such correlations should include the effects of heating rate.

3.3.2 Intrinsic Combustion Reactivity of Chars

The effect of pressure on the resulting char combustion reactivity is shown in Figure 6 for the Pitt #8 coal and Figure 7 for the Knife River lignite. Pitt # 8 chars were oxidized in the HPTGA at a partial pressure of O_2 of 0.32 atm and a temperature of 715 K. KNL char oxidation conditions were P_{O2} = 0.28 atm and T = 615 K. The temperatures and oxygen concentrations were low enough for each char to avoid mass transfer effects. All of the chars were oxidized at the same total pressure as their respective char preparation pressure (i.e., 1, 6, 10, and 15 atm).

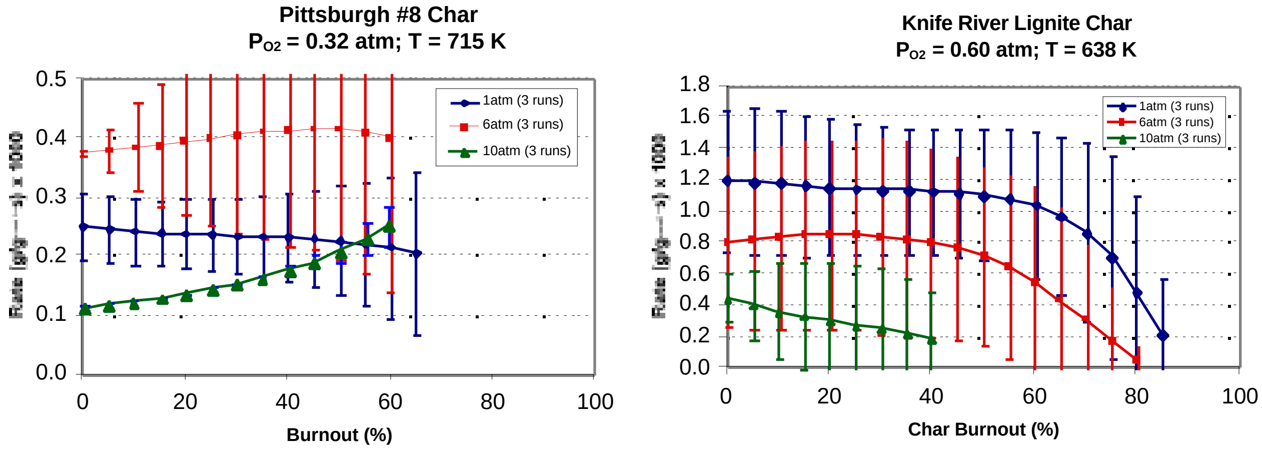

Figure 6a: Left, TGA reactivity data for Pitt # 8 char (Po_2 = 0.32 atm; T = 715 K)
6b: Right TGA reactivity data for Knife River lignite char (Po_2=0.28 atm; T=615 K)

There seems to be some uncertainty in how to interpret TGA data from char oxidation tests to represent and compare reactivity. Previous researchers have used average reactivity over a certain range of char burnout, maximum reactivity, initial char reactivity, or the reactivity at 20% burnout [8, 14, 16, 17]. In the results presented here, the entire TGA reactivity curve as a function of burnout is presented. Reactivity was computed on a "gram reacted per gram available", dry ash-free basis. At the end of each TGA test, the sample was burned completely at higher temperatures and O_2 levels in order to determine the ash content for that sample. The sample and basket were then weighed on a separate balance to improve the accuracy of the reactivity data. Each TGA test was repeated three times. The average reactivity value and standard deviation value were computed from the repeat samples at intervals of 5% in the char burnout, and error bars were set at ± 2 standard deviations.

Initial reactivities vary in an unpredictable manner due possibly to movement of the sample basket or slow degassing of a small amount of pyrolysis products. Therefore, reactivities are compared at TGA char burnouts between 20% and 60%. As seen in Figure 6a, each Pitt #8 char reactivity is relatively constant for burnouts from 30 to 60% for each given pressure. This region of constant char reactivity is consistent with results presented by Hecker et al. (2003), where chars produced at atmospheric pressure in a FFB were examined in a HPTGA. Hecker's results also indicate no change in reactivity for the same starting char as total pressure is increased. In contrast, Figure 6a shows that after 60% burnout, the 6 atm HPFFB char is observed to decrease in reactivity faster than the 1 atm FFB char. At this degree of char burnout, activated sites may have been mostly consumed and initial pore structure destroyed, causing char reactivity changes. The reactivity of the 10 atm Pitt #8 char is about 50% lower than the reactivities at the lower pressures. This decrease in reactivity with pressure differs from results reported previously in the literature [8].

A series of TGA tests were applied to 1, 5, 10, and 15 atm Pitt #8 chars to determine reaction orders and activation energies, following the basic TGA test procedure of Hecker et al. [14], the reactivities at a char burnout level of 10%, and an n-th order model. Activation energies were determined from standard Arrhenius plots (ln[rate] vs 1/T at constant oxygen partial pressure). Oxygen reaction orders were determined from a power law model by determining slopes of ln[rate] vs ln[P_{O2}]. The total pressure during these TGA tests was kept the same as the char formation pressure, so as to emulate a continuous combustion process. TGA conditions used here were temperatures from 693 to 753 K and oxygen partial pressures from 0.2 to 0.8 atm. The low temperatures ensure that intrinsic rates were measured. Resulting O_2 mole fractions were 20 to 50% for the 1 atm test, and lower than 13% for the 6, 10, and 15 atm tests. Low O_2 mole fractions are preferred to minimize char heatup from reaction. The reaction orders and activation energies determined from these experiments are shown in Table 3, along with N_2 BET surface areas. Except for the 6 atm data point, the activation energy stays roughly constant with total pressure, and the oxygen order stays relatively constant at roughly 0.74, in agreement with Hecker's results [14].

Table 3
Pitt #8 Kinetic Data

Total Pressure (atm)	Activation Energy (kcal/mol)	Oxygen Order	N_2 Area m^2/g
1	29.2	0.78	40
6	18.9	0.64	88
10	32.4	0.74	93
15	30.9	0.73	77

The effect of pressure on resultant char reactivity has been studied under a variety of reaction conditions [8, 16, 18-22]. Different pyrolysis atmospheres and temperature were used; char reactivities included oxidation rates as well as H_2O, and CO_2 gasification rates. Among them, three references [18, 19, 22] used high temperature (700-930°C) in their reactivity tests, and hence are not used for direct comparison. Roberts et al. [8] pyrolyzed three Australian coals at 5, 10, and 15 atm. Char oxidation reactivities were measured at 10 or 15 atm at 723K in 50% O_2. One char initial reaction rate increased with pressure increase and two other chars had no clear trend. However, the reactivities after normalization by the char CO_2 surface areas were the same. Cai and coworkers [16] found that both Pitt #8 and Linby char combustion reactivities decreased with hydropyrolysis pressure from low to medium pressure(20-30 bar), then increased with hydropyrolysis pressure. Lee et al. [21] found that Illinois char reactivity generally decreased with increasing char formation pressure, but that this decrease was not as significant for residence times longer than 1 s. Lee found no correlation between the micropore surface area (CO_2) of chars and reactivity.

Generally, at low to medium pressures (1-40 atm), most of these studies showed that char reactivity decreased as char formation pressure increased. One study found that char reactivity increased with pressure increase. The effect of pressure on pyrolysis would be to decrease the tar yield, and hence increase the hydrogen content in the char, which in turn would translate to higher reactivities. Increased hydrogen contents in the char at increasing pressure are generally observed. However, high-pressure also increases the fluidity of the char, making the char surface more ordered, which relates to lower reactivity. This resolidification process can also be affected by residence time, causing lower char reactivity [21]. Char surface area may also contribute to reactivity change with pressure, but further experiments are needed to resolve the inconsistency within different studies.

Figure 6b shows that the lignite reactivities also decrease monotonically with increasing pressure. This is an interesting result, since the lignite char does not soften and resolidify during pyrolysis, and also since the effect of pressure on lignite pyrolysis yields are thought to be minimal. Explanations for this behavior are left for further studies.

3.4. Conclusions

A flat-flame burner was used in a high pressure laminar flow facility to conduct high temperature, high heating rate coal pyrolysis experiments. Heating rates were approximately 10^5 K/s, which is higher than in conventional drop tube experiments. Char samples from a Pitt No.8 coal and lignite were collected at 1300°C at 1, 6, 10, and 15 atm. Swelling ratios of the lignite were less than 1.0, and only about 1.3 for the Pitt #8 coal. All coals showed slight increases in swelling behavior as pressure increased. The swelling behavior observed for the Pitt #8 coal at each pressure was lower than reported in high pressure drop tube experiments, indicating the effect of heating rate on particle swelling. This heating rate effect was similar to that observed previously at atmospheric pressure. SEM photos revealed that bituminous coal has large physical structure transformations, with popped bubbles due to the high heating rate. TGA char oxidation reactivities were measured at the same total pressure as the char preparation pressure. The general trend was that the TGA reactivity on a gram per gram available basis decreased for both Pitt #8 and Knife River lignite coal chars with increasing char formation pressure. The Pitt #8 char intrinsic activation energy and oxygen reaction order remained relatively constant with increasing pressure.

3.5 References

1. Smoot, L.D., *Progress in Energy and Combustion Science* 24 (5) (1998) 409-501.
2. Smoot, L.D. and P.J. Smith, *Coal combustion and gasification.* Plenum Press, New York, 1985, p. x, xvi, 443.
3. Takematsu, T. and C. Maude, *Coal Gasification for IGCC Power Generation*. London, 1991.
4. Harris, D.J. and J.H. Patterson, *Aust. Inst. Of Energy J.* 13 (1995) 22.
5. DOE, *The Wabash River Coal Gasification Repowering Project*, The U.S. Department of Energy Wabash River Coal Gasifiaction Project, 2000.
6. Gale, T., "*Effects of Pyrolysis Conditions on Coal Char Properties*", Ph.D. Thesis, Brigham Young University, 1994.
7. Gale, T.K., C.H. Bartholomew, and T.H. Fletcher, *Combustion and Flame* 100 (1-2) (1995) 94-100.
8. Roberts, D.G., D.J. Harris, and T.F. Wall, *Energy & Fuels* 17 (4) (2003) 887-895.
9. Lee, C.W., A.W. Scaroni, and R.G. Jenkins, *Fuel* 70 (8) (1991) 957-965.
10. Wu, H., G. Bryant, K. Benfell, and W. Terry, *Energy & Fuels* 14 (2000) 282-290.
11. Monson, C.R., G.J. Germane, A.U. Blackham, and L.D. Smoot, *Combustion and Flame* 100 (4) (1995) 669-683.
12. Mathias, J.A., "*High Pressure Oxidation Rates for Large Particles*", M.S. Thesis, Brigham Young University, 1996.
13. Fletcher, T.H., *Fuel* 72 (11) (1993) 1485-1495.
14. Hecker, W.C., M.P. Madsen, R.S. Michael, J.W. Allen, R.J. Sawaya, and T.H. Fletcher, *Energy and Fuels* 17 (2) (2003) 427-432.
15. Niksa, S., G.-s. Liu, and R.H. Hurt, *Progress in Energy and Combustion Science* 29 (5) (2003) 381-477.
16. Cai, H.Y., A.J. Guell, I.N. Chatzakis, J.Y. Lim, D.R. Dugwell, and R. Kandiyoti, *Fuel* 75 (1996) 15-24.
17. Roberts, D.G. and D.J. Harris, *Energy & Fuels* 14 (2) (2000) 483-489.
18. Sha, X.Z., Y.G. Chen, J. Cao, Y.M. Yang, and D.Q. Ren, *Fuel* 69 (5) (1990) 656-659.

19. Kajitani, S. and N. Suzuki, *12th International Conference on Coal Science*, 12 (2003) 10C4
20. Van Heek, K.H. and H.-J. Muhlen, *Fundamental issues in control of carbon gasification reactivity*. Kluwer Academic Publishers, 1991, p. 1.
21. Lee, C.W., R.G. Jenkins, and H.H. Schobert, *Energy and Fuels* 6 (1992) 40-47.
22. Chitsora, C.T., H.-J. Muhlen, K.H.v. Heek, and H. Juntgen, *Fuel Process. Technol.* 15 (1987) 17-29.