Coal and Biomass Char Reactivity

Investigators: R. E. Mitchell, Associate Professor, Mechanical Engineering Department; P. A. Campbell and L. Ma, Graduate Researchers

Project Overview: There is considerable concern regarding the potential global environmental impact of fossil fuels used for power generation. By increasing the fraction of renewable energy in the national energy supply, some of the impact can be mitigated. Co-firing biomass with coal in traditional coal-fired boilers or using biomass as a reburn fuel in advanced coal-fired boiler configurations represent two options for combined renewable and fossil energy utilization. Gasification of the biomass offers additional options. For example, gasification products can be upgraded, through synthesis, to methanol and even hydrogen, or the products can be burned externally in a boiler for producing hot water or in a gas turbine for generating electricity. The hot gas from the gas turbine can be used to raise steam to be utilized in a steam turbine to enhance overall efficiency (*i.e.*, an integrated gasification combined cycle (IGCC) scheme can be used). Other proposed, but not yet demonstrated, options involve combusting the gasification products with coal in either co-fire or reburn boiler configurations.

The physical characteristics and chemical composition of the biomass influences how it can best be utilized. Upon rapid heating, some biofuels have high gas yields, rendering them suitable for gasification and reburn applications. Other biofuels have high char yields, and are better-suited for co-firing in direct combustion configurations. With the proper choices of biomass, coal, boiler design, and boiler operation, reductions in pollutant and net greenhouse gas emissions can be realized. Identifying the proper choices requires that we gain a better understanding of the behaviors of coals and biomass of various origins when exposed to specified conditions of temperature, pressure, and gas composition. Understanding how the properties of the coals and biomass influence their conversion rates to gaseous products is a necessity. Identifying optimum boiler configurations and operating conditions requires that we develop models capable of predicting accurately boiler performance and pollutant emissions. This requires an understanding of processes that control the physical transformations that fuel particles undergo when exposed to hot, oxidizing environments and the chemical reactions responsible for conversion of the solid material to gaseous species and ash.

Description: In this project, research activities are aimed at providing the information needed to characterize the fundamental chemical and physical processes controlling coal-char and biomass-char conversion to gaseous species in the type environments likely to be established in advanced gasifiers, boilers and furnaces. This requires examining the char conversion process in high-temperature, high-pressure environments so that the rate-controlling processes can be identified and characterized. The research effort will result in a more fundamental understanding of the char gasification and combustion processes.

The effort will result in fundamentals-based sub-models for particle size, apparent density and specific surface area evolution during char conversion and a sub-model for the intrinsic chemical reactivity based on the adsorption of reactive gases and desorption of CO and CO_2. The sub-models will be directly applicable to coal-char and biomass-char gasification and combustion in advanced systems. The models will permit the assessment of selected design configurations and strategies that have the potential to reduce the emissions of greenhouse gases during coal and biomass combustion and gasification. The models will be quite beneficial in determining optimum operating conditions for any selected combustion or gasification scheme.

Status: In our efforts to date, we have formalized our procedure for obtaining the reactivities of coal and biomass chars to oxygen. Chars characteristic of those created at high temperatures and heating rates in real coal-fired boilers and furnaces are produced in a laminar flow reactor in which is established a high-temperature environment (from 1300 to 2000 K) of specified oxygen content (from 3-mol% to 12-mol-% O_2). Partially reacted chars extracted from the flow reactor at selected residence times provide samples for analysis to determine char physical and chemical properties as functions of char conversion.

The extracted char samples are subjected to a variety of tests to determine the conversion rates in the high-temperature flow reactor environments as well as to determine as functions of conversion particle size distributions, apparent densities, specific surface areas, and intrinsic chemical reactivities to oxygen. To provide insight into the impact of heating rate on the properties of the chars produced, chars for analysis are also created in a tube furnace at 1000 K in inert environments. The intrinsic chemical reactivities of these chars are determined.

Particle size distributions are measured using a Coulter Multiziser, an instrument that measures the size distributions of particle suspensions using an electroresistive method. Approximately 20,000 particles are monitored for each sample, and the sizes are distributed into 256 channels of the Multisizer, spanning the size range 6.0 to 185 μm. Particle apparent densities are determined using a tap density procedure wherein the weights and volumes occupied by char samples introduced into a graduated cylinder are measured. The outside of the cylinder is tapped until the particles are well-settled before the volumes are recorded. Data are obtained for different amounts of char added to the tube, and then plotted, weight versus volume occupied. The slope of the line plotted is the bulk density of the char in the cylinder, from which the apparent density of the char can be determined employing a packing factor of 0.42, a value determined in previous work by comparing tap density and mercury porosimetry measurements. Specific surface area measurements are made using gas adsorption techniques employing CO_2 as the adsorption gas at 298 K. The adsorption data are analyzed using the well-known approach of Brunauer, Emmett, and Teller [*J. Am. Chem. Soc*. **60**, 309-319, 1938] for (BET) surface areas.

The reactivity tests are performed in a thermogravimetric analyzer (TGA) under chemical kinetics-controlled oxidation conditions. Measured mass loss data during oxidation at specified temperature and oxygen concentration provide the information needed to determine intrinsic reactivity. The measured thermograms (mass loss versus time data) are normalized to determine ash-free conversion (x_c) as a function of time and then differentiated to determine conversion rates as a function of time. The conversion rate data and surface area measurements are combined to determine intrinsic reactivity using the following expression:
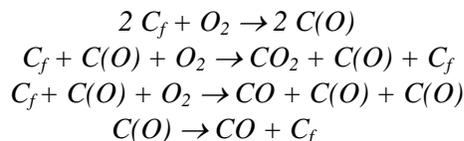
$$R_{ic} = \frac{1}{S_{gc}\,(1-x_c)}\frac{dx_c}{dt}$$

Here, R_{ic} is the intrinsic chemical reactivity of the carbonaceous material and S_{gc} is its specific surface area. The specific surface area is expressed as a function of conversion using the surface area sub-model developed by Bhatia and Perlmutter [*AICHE J*. **26**, 379-386, 1980], which takes into account the opposing effects of pore growth and pore overlap during the merging and coalescence of pores as char gasification proceeds:

$$S_v = S_{v0}(1-x_c)\sqrt{1-\psi\,ln(1-x_c)}$$

In this surface area sub-model, S_v is the surface area per unit particle volume ($S_v = \rho_c S_{gc}$, where ρ_c is the apparent density of the carbonaceous material), and ψ is a structural parameter that is determined from fits to the surface area measurements.

Measured surface areas and mass loss rates in transient and isothermal TGA tests provide the data needed to describe the intrinsic reactivities in terms of temperature and oxygen concentration. The data are used to evaluate the rate coefficients in the chemical reaction mechanism employed to characterize the important reaction pathways in the conversion of carbon to CO and CO_2. Presently, the following four-step heterogeneous reaction mechanism is used:

$$2\ C_f + O_2 \rightarrow 2\ C(O)$$
$$C_f + C(O) + O_2 \rightarrow CO_2 + C(O) + C_f$$
$$C_f + C(O) + O_2 \rightarrow CO + C(O) + C(O)$$
$$C(O) \rightarrow CO + C_f$$

Here, C_f denotes a free carbon site, one available for oxygen chemisorption, and $C(O)$ denotes a carbon site occupied by an adsorbed oxygen atom. It is assumed that each carbon atom represents a potential adsorption site, and that desorption of CO and CO_2 removes a carbon atom from the surface, exposing the underlying carbon atom, rendering it a potential adsorption site. During the course of this project, the reaction mechanism will be modified, as needed, as more data is obtained at different temperatures and oxygen concentrations and for different materials, providing additional insights into the rate-controlling steps during the overall oxidation process.

As an example of our capability, scanning electron micrographs (SEMs) of raw and partially reacted almond shell particles are shown in Figure 1 along with mass loss and specific surface area measurements. The raw, unreacted almond shell particles used in the tests were screened to eliminate particles larger than about 1 mm in size. The particles contained 37% ash, by weight. The partially reacted char shown in the SEM was extracted 33 ms after injection into a flow reactor environment containing 8 mol-% oxygen at nominally 1243 K.
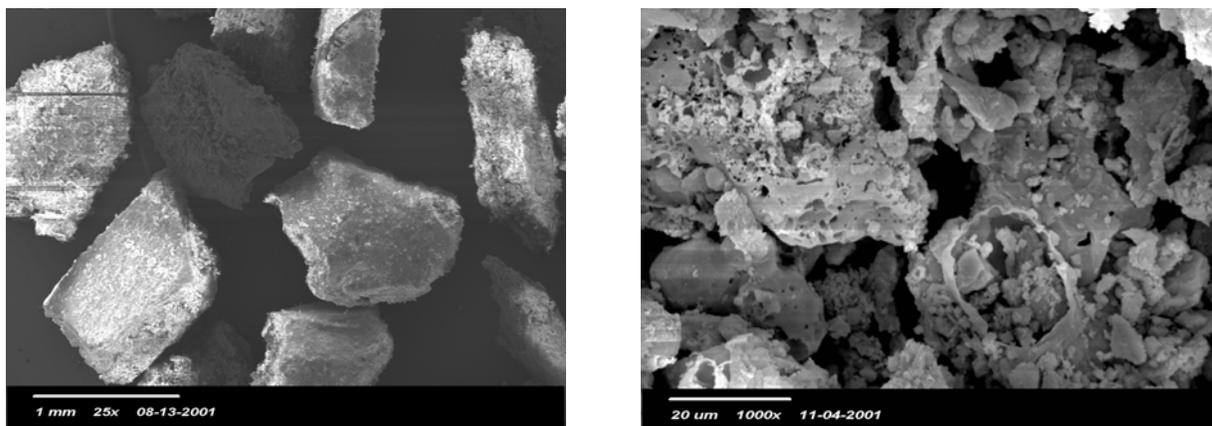
t = 0 ms: m/m$_0$ = 1.0, S$_{gp}$ = 25 m^2/g   t = 33 ms: m/m0 = 0.42, S$_{gp}$ = 20 m^2/g

Figure 1: Scanning electron micrographs of (left) raw almond shell particles and (right) one of its partially reacted chars extracted 33 ms after injection into an environment containing 8 mol-% oxygen at nominally 1243 K.. Note the differences in scale between the SEMs.

Particle size distributions and apparent densities measured for partially reacted chars extracted at 17, 33, 48, 62, and 89 ms from the flow reactor are shown in Figure 2. The panel on the right displays the char particle apparent density as well as the apparent density of the carbonaceous particle material, which was calculated using the measured ash content of each sample. The data indicate that the almond shell particles burn with decreases in both size and apparent density of the carbonaceous material during high-temperature oxidation. As the char

particles burn, the particle apparent densities (carbonaceous material plus ash) increase, approaching that of the ash as the solid, carbonaceous material is gasified.

Measured and calculated intrinsic reactivities for the 33-ms and 89-ms partially reacted almond shell chars exposed to 6 mol-% oxygen at 873 K are shown in Fig. 3. For each sample, the reactivity increases rapidly before reaching a peak at about 15% char conversion. Note that at such low reaction temperatures, the char does not reach a quasi-steady burning rate until relatively late in burnoff, after about 80% of the carbonaceous material has been gasified. The calculated reactivities are in reasonably good agreement with the measured reactivities, indicating that the reaction mechanism and associated rate parameters adequately describe the reaction process during char conversion under kinetically-controlled conditions. Predictions of the mass loss rates in the high-temperature environments established in the laminar flow reactor are also in good agreement with the measurements, suggesting that the kinetic parameters used to describe the rate coefficients of the reactions in the mechanism are reasonable.

Cumulative size distribution   Particle (■) and char (▼) apparent densities
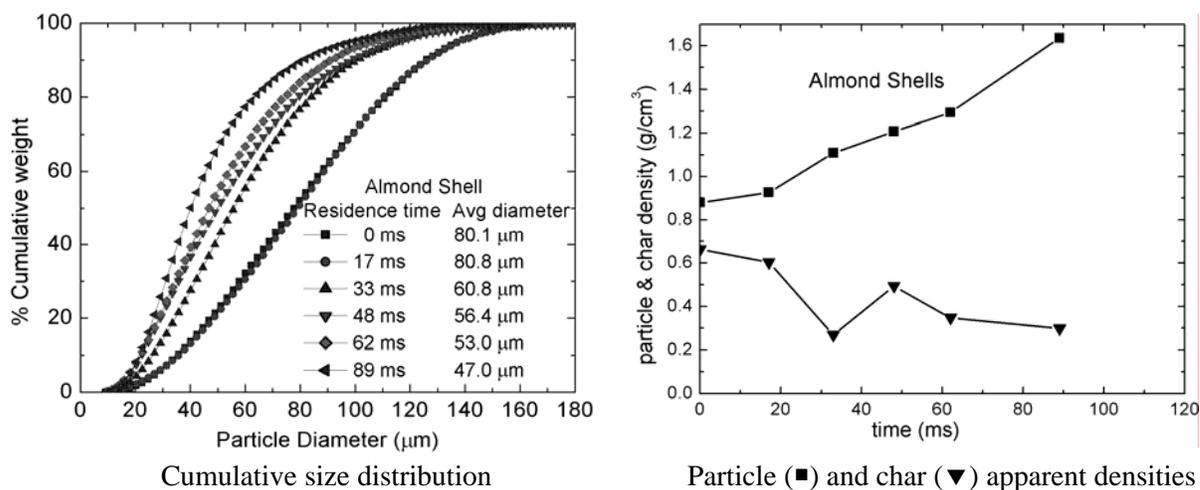
Figure 2. Size and apparent density distributions of almond shell particles burning in 8 mol-% oxygen at nominally 1243 K.

The data shown in Figure 3 indicate that the reactivity of the almond shell chars decrease as they burn in high temperature environments typical of real furnaces and boilers. The 89-ms char has a lower peak reactivity, a lower reactivity at steady-state, and a lower conversion-averaged reactivity than the 33-ms char. This is a consequence of thermal annealing while burning. An important aspect of this work is to characterize this effect of carbon deactivation, which occurs during oxidation at high temperatures.

Continuing Work: To provide insight into the influence of char chemical make-up on rates of oxidation, coals of various ranks and biomass of various origins must be tested. In addition, to provide insight into the impact of ash on the properties of the chars produced, feedstocks having a range of ash contents will have to be tested. An aspect of the first year of this project was to select the materials to be tested during the three-year term of the project.
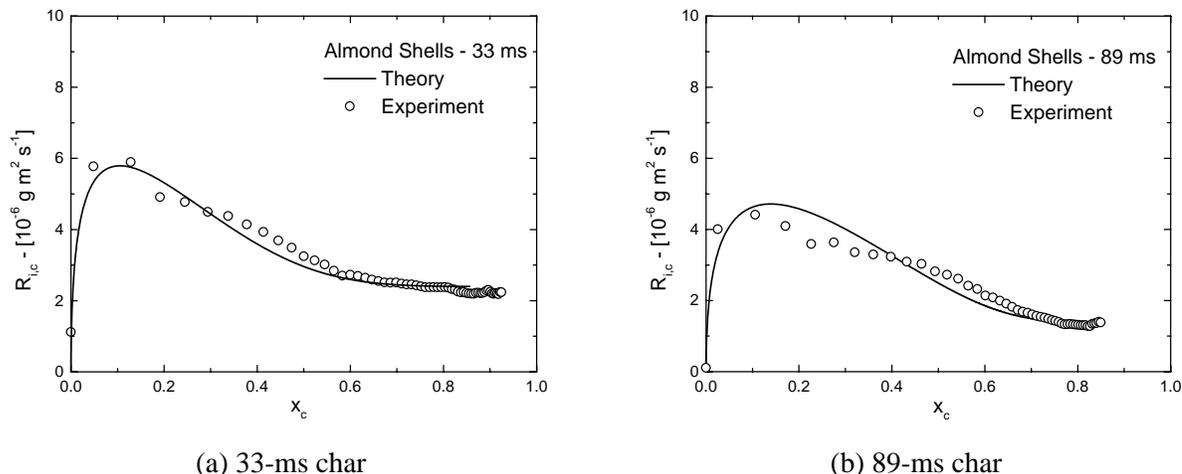
(a) 33-ms char   (b) 89-ms char

Figure 3. Intrinsic reactivity of partially reacted almond shell chars exposed to 6 mol-% oxygen at 873 K. Chars were extracted from the laminar flow reactor at 33 and 89 ms after injection of almond shell particles into 8 mol-% O_2 at 1243 K.

The key compounds in biomass materials are cellulose, hemicellulose, and lignin; therefore the materials selected for examination will vary in the contents of these key compounds. Hardwoods generally have high hemicellulose and low lignin contents and softwoods have relatively low hemicellulose and low lignin contents. Besides woods and various straws, materials selected for study will include wastes of such biomass treating industries as the wood-processing industry, the paper and pulp industry, and the food industry. Tests to measure the reactivities of chars produced at high heating rates from cellulose, hemicellulose and lignin will also be performed. The objective of one of the planned studies is to assess the extent to which the reactivity of a biomass char can be predicted based on its fractional contents of cellulose, hemicellulose, and lignin and the reactivities of the high-heating-rate chars produced from these pure compounds.

Since the start of this project, we have begun examination of wood chips, newspaper and glossy paper. Chars of these materials have been produced at high heating rates in the laminar flow reactor and at low heating rates in a tube furnace. The ash-contents of the parent materials ranged from 0.4% (the wood chips) to 24.8% (the glossy paper). The chars have been tested to determine surface areas and intrinsic reactivities. The data have not yet been used to determine kinetic parameters that describe the measured reactivities.

Another aspect of this project involves determining the impact of pressure on the rates of coal-char and biomass-char gasification and combustion. Towards this end, a high-pressure chamber to enclose the laminar flow reactor has been designed and constructed. The chamber will permit high-pressure, high-temperature testing of chars burning under oxidation conditions in which the combined effects of mass transport and chemical reaction control overall char conversion rates. By the end of the first year of this project, the chamber and its associated flow control panel will be installed into the experimental set-up. Pressurized laminar flow reactor tests at pressure up to 50 atm should commence during the first quarter of the second year of this project, as planned. The thermogravimetric analyzer used to measure intrinsic char oxidation rates is already capable of operating at pressures up to 50 atm.

Data to characterize the impact of pressure on coal and biomass devolatilization yields, initial char particle morphology, and oxidation rates will be obtained by performing experiments

over a range of pressures at fixed temperatures. The data will be used to assess the heterogeneous reaction mechanism and other sub-models that have been developed employing data at atmospheric pressure. The sub-models will be modified, as needed, to account for high-pressure effects.

The type of study undertaken with the almond shell biomass is being undertaken with other biomass materials to provide data for analysis in our quest to understand how biomass properties influence char conversion rates and to characterize the physical changes that char particles undergo during gasification. The data will permit the development and validation of the physical and chemical sub-models used in comprehensive models for coal-fired and biomass-fired process units. The comprehensive models can be used to investigate potential design strategies and can help define optimum operating conditions that benefit coal and biomass conversion processes.

Contacts:
R.E. Mitchell: remitche@stanford.edu