

II.4.4 Characterization of Coal and Biomass Conversion Behaviors in Advanced Energy Systems

Investigators

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Introduction

The goal of this project is to develop models that predict accurately coal and biomass gasification and combustion behaviors in the type environments likely to be established in advanced energy systems. This requires acquiring the information needed to understand and characterize the fundamental chemical and physical processes that govern coal and biomass conversion at high temperatures and pressures. The models can be used to determine operating conditions that optimize thermal efficiency and to examine design strategies for integrating combined cycles for the production of synthesis gas and electric power with minimum impact on the environment.

There is considerable concern regarding the potential global environmental impact of fossil fuels used for power generation. Carbon dioxide emissions are among the concerns. Coal will play a significant role in meeting the world's energy demands for the next fifty to one hundred years even if hydrogen becomes the primary energy carrier. By increasing the fraction of renewable energy in the energy supply, the extent to which carbon dioxide emissions will impact atmospheric properties can be mitigated. Biomass is a renewable fuel, and is considered as being CO₂-neutral with respect to the greenhouse gas balance if the use of fossil fuels in harvesting and transporting the biomass is not considered. Co-firing biomass with coal in traditional coal-fired boilers and furnaces or using biomass-derived gas as a reburn fuel in coal-fired systems represent two options for combined renewable and fossil energy utilization. Configurations that employ both biomass and coal in integrated gasification, combined gas and steam power cycles and hybrid technologies that produce synthesis gas for fuel cells as well as produce electric power in combined gas and steam power cycles offer additional options.

Presently, the United States Department of Energy's Office of Fossil Energy is considering developing hybrid gasifier-combustor energy systems as the core technology for the Department's Vision 21 energy plant of the future [1]. Hybrid technologies are well suited for combined renewable/fossil energy utilization. A number of potential approaches to the co-utilization of coal and biomass have been the subject of demonstration projects, both in Europe and the United States [2]. The selection of any particular co-firing option is likely to be made on the basis of minimum interference with normal operation of the coal-fired facility with minimum impact on its environmental control equipment. The design of efficient coal/biomass co-utilization energy systems with integrated thermal management to minimize waste heat requires an understanding of the processes that control the physical transformations that fuel particles undergo when exposed to hot environments and the chemical reactions responsible for conversion of the solid material to gaseous species and ash. The goal of this project is to provide the needed understanding. Our efforts will result in fundamentals-based sub-models for particle mass loss, size, apparent density, and specific surface area evolution during

conversion of coal and biomass material to gas-phase species during gasification and combustion processes.

Background

In the high-temperature oxidizing environments established in coal-fired boilers and furnaces, the char particles formed subsequent to coal devolatilization burn with decreases in both size and apparent density, and the relative changes in size and density depend upon the extent of char conversion. To capture this effect, models that accurately characterize overall mass loss rates during gasification and combustion at high temperatures must be based on the intrinsic chemical reactivity of the carbonaceous particle material, and parameters that control the mode of burning must depend on char reactivity. Such models have been developed and partially validated in ongoing work in our laboratory [3-6]. A variety of coals, biomass materials and synthetic chars have been tested to determine parameters that describe char reactivity as a function of temperature and reactive gas concentration. In a related study [7], a model for the mode of char particle burning was validated for coal chars and the chars of biomass materials that are relatively friable (and hence, can be pulverized). Almond shells and wood chips fall into this category. Straws do not.

In our experimental approach, chars characteristic of those created at high temperatures and heating rates in actual coal-fired boilers and furnaces are produced in a laminar flow reactor. By properly adjusting the flow rates of the gases (CH_4 , H_2 , O_2 , and N_2) fed to the diffusion-flamelet burner of the flow reactor, gaseous environments can be established inside the reactor that have a specified oxygen content (from trace amounts to 12-mol-% O_2) at specified temperature (from 1300 to 2000 K). Size-classified samples of the materials to be examined (coals, biomass materials, synthetic chars, and chars to be heat-treated) are fed along the centerline of the flow reactor and partially reacted chars are extracted at selected residence times (up to 200 ms) using a solids sampling probe. The extracted samples are analyzed to determine char physical and chemical properties as functions of char conversion. Particle size distributions are measured using a Coulter Multiziser, an instrument that measures the size distributions of particle suspensions using an electroresistive method. Apparent densities of particles are measured using a tap density procedure in which packed-beds of particles in a graduated cylinder are weighed. Specific surface areas of particles are determined from carbon dioxide adsorption measurements employing CO_2/He mixtures at 298 K and 10 atm. Intrinsic char reactivities to oxygen are determined from oxidation tests performed in a pressurized thermogravimetric analyzer (PTGA) under chemical kinetics-controlled reaction conditions. Analytical procedures are discussed in various publications [3-7]. The data are used to validate and to determine parameters in the sub-models developed.

Chars for testing are also produced in a tube furnace in nitrogen environments at temperatures up to 1000 °C at low heating rates (less than 50 °C/min). These chars are representative of those formed in grate furnaces, where particles experience a wide range of heating rates in volatiles-rich environments. These chars are also subjected to oxidation tests in the PTGA so that their intrinsic reactivities can be determined.

Figure 1 shows results of a typical oxidation test when wood chips are exposed to 10 mol-% O_2 at 500 °C. After the sample has been put in the PTGA balance pan and the

PTGA is closed, the reaction chamber is purged with nitrogen for 53 min at room temperature to ensure an inert environment. Any CO₂, CO or air, remaining in the reaction chamber is eliminated during this time. After 53 min, the temperature is ramped up to the reaction temperature of 500 °C in 20 min, still in an oxygen-free environment in order to dry the sample. As can be observed from the flat portion of the weight profile from 75 to 90 min, the sample is dry before oxygen is admitted. During this heating and drying of the sample in nitrogen, a small amount of CO and CO₂ is released (desorbed). These carbon oxides are formed from oxygen complexes in the initial char sample.

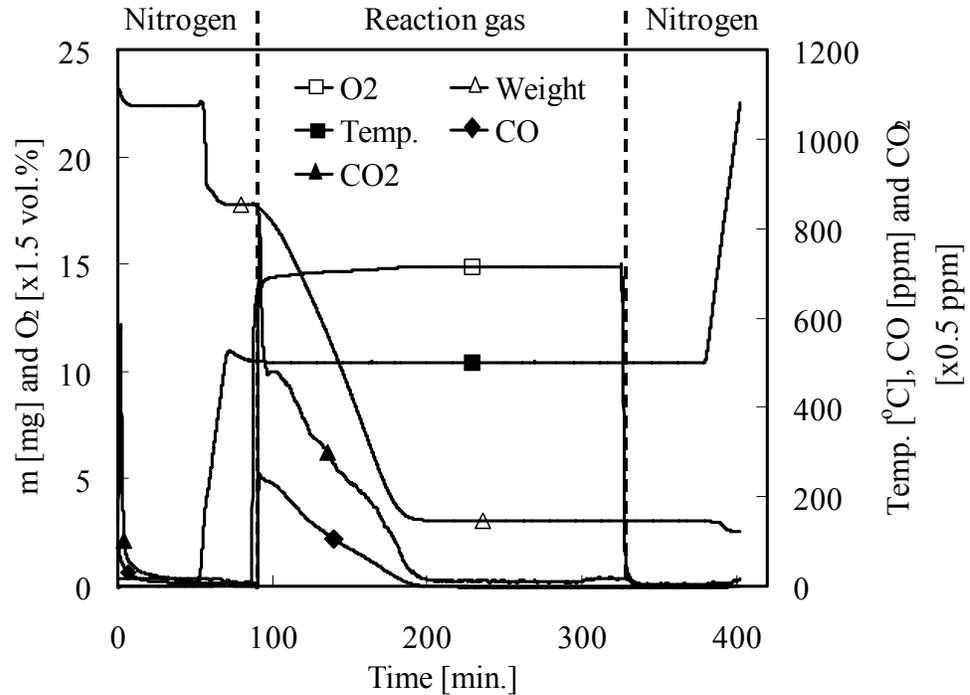


Figure 1: Experimental results from a typical oxidation test in 10 vol-% O₂ at 1 atm.

At 90 min, the reaction gas (10 vol-% O₂ in nitrogen) is turned on. From 90 to 330 min, the sample is kept at a constant temperature (500 °C) and in a uniform and constant gas composition. During the reaction period the oxygen reacts with the carbon in the sample, producing CO and CO₂, which are subsequently released, reducing the mass of the material on the PTGA balance pan. At 330 min the reaction gas is turned off and the sample is once again purged with nitrogen, making sure that the sample is no longer reacting. At 378 min, still in nitrogen, the sample is heated up till 1100 °C in order to remove any adsorbed oxygen complexes remaining on the material in the balance pan. This yields the true sample mass at the end of the test. The oxygen on the sample during this desorption is released as CO and CO₂ if there is still carbon left in the sample.

The mass profile between 90 and 330 min is differentiated to determine the overall conversion rate in the environment established in the PTGA. The char particles are assumed to consist of two components: an ash fraction, which is assumed to be non-reactive, and a carbonaceous fraction, which is assumed to react, forming both CO and

CO₂. The specific mass loss rate of the char (R_c) is expressed in terms of the mass loss rate and specific surface area of the carbonaceous portion of the particle material (S_{gc}) as:

$$R_c = -\frac{1}{m_c} \frac{dm_c}{dt} = \frac{1}{1-x_c} \frac{dx_c}{dt} = R_{ic} S_{gc} \quad (1)$$

where m_c is the mass of carbonaceous material in the char at time t ; x_c is the fractional char conversion, daf; S_{gc} is the specific surface area of the carbonaceous material; and R_{ic} is the intrinsic chemical reactivity per unit specific surface area.

The specific surface area model developed by Bhatia and Perlmutter [8] for porous carbons is used to describe the variations in specific surface area of the carbonaceous particle material with conversion under chemically-controlled oxidation conditions:

$$S_{gc} = S_{gc,0} \sqrt{1 - \psi \ln(1 - x_c)} \quad (2)$$

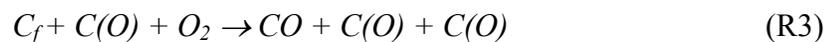
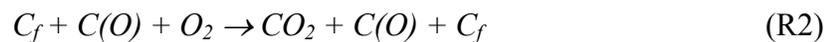
Here, x_c is fractional conversion on a dry, ash-free basis (daf) and ψ is a structural parameter that can be determined from fits to data. Our *in situ* surface area data obtained with coal, biomass, and synthetic chars confirm the validity of this model for constant apparent density burning, as is the case when rates of chemical reaction control overall mass loss rates.

The specific surface area of an ash-laden char particle having an ash fraction X_{ash} after reaction for time t is assumed to obey the relation

$$S_{gp} = X_{ash} S_{ga} + (1 - X_{ash}) S_{gc} \quad (3)$$

S_{gp} is the quantity actually determined from the CO₂-adsorption measurements. The adsorption measurements taken at the beginning of an oxidation test yields $S_{gp,0}$, the initial specific surface area of the char particle. Gas adsorption measurements taken at the end of an oxidation test, after all the carbonaceous material has been burned away yields S_{ga} , the specific surface area of the ash. Equations (1) - (3) permit the determination of char reactivity as a function of char conversion using the measured data.

Reactivities determined in PTGA environments of specified temperature and oxygen content provide the data needed to gain an understanding of the important reaction pathways governing char oxidation. In our approach, the following heterogeneous reaction mechanism is used to characterize the reactivities:



Here, C_f represents a free carbon site, one available for oxygen chemisorption, and $C(O)$ represents a carbon site filled with a chemisorbed O atom. It is assumed that each carbon atom represents a potential adsorption site and that desorption of a chemisorbed oxygen atom removes the associated carbon atom to uncover an underlying carbon site, which becomes available for oxygen adsorption.

To date, Arrhenius parameters that describe the reaction rate coefficients for the above reactions have been determined for several coal, biomass, and synthetic chars. All of the chars examined were produced at high heating rates in the laminar flow reactor. Using the kinetic parameters determined from analysis of the data obtained in the PTGA oxidation tests, mass loss rates in the flow reactor can be predicted accurately using a char combustion model that takes into account oxygen transport to the outer surfaces of particles as well as oxygen diffusion through the pores of particles as the particles burn.

Recent Results

During the past year, we developed the capability to measure O₂, CO, and CO₂ concentrations in the reaction chamber of the PTGA during an oxidation test. The plumbing and instrumentation needed to monitor the gases just above the sample in the balance pan were installed and the software needed to integrate the signals from the gas detectors with the weight measurements was written and compiled to run on the computer that controls the PTGA. Calibration tests were performed as were validation tests with empty balance pans and non-reactive, inert materials. The O₂, CO, and CO₂ profiles shown in Fig. 1 are indicative of our present capability to make simultaneous gas and weight loss measurements during an oxidation test. These measurements permit better characterization of the rates of reactions R2 and R3 in the heterogeneous reaction mechanism. They provide a direct measure of the heterogeneous CO-to-CO₂ product ratio as a function of temperature.

As part of our effort 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, three cellulosic-based biomass materials were tested to determine the reactivity of their chars to oxygen. The materials selected (wood chips (WC), newspaper (NP), and glossy paper (GP)) had similar chemical compositions on an ash-free basis, but differed in their ash-content. Proximate and ultimate analyses are shown in Table I.

Table I: Proximate and ultimate analyses and specific surface areas of biomass materials and their chars.

	Proximate Analysis			Ultimate Analysis (daf)					Surface Area	
	VM (wt%)	Fix-C (wt%)	Ash (wt%)	C (wt%)	H (wt%)	O ^a (wt%)	N (wt%)	S (wt%)	S _{gp,0} (m ² /g)	S _{gc,0} (m ² /g)
Parent										
WC	86.3	13.3	0.4	47.7	6.2	46.0	0.1	<0.02		
NP	85.9	10.7	3.5	46.3	6.0	47.6	0.1	<0.02		
GP	70.6	4.5	24.8	41.9	5.3	52.7	0.1	<0.02		
Char										
WC	7.6	90.2	2.2	98.58	0.4	0	1.0	0.02	389	398
NP	9.4	79.1	11.5	98.1	0.8	0	1.0	0.1	360	407
GP	21.4	16.8	61.8	73.6	1.7	23	1.1	0.6	140	366

^a Obtained by mass balance

Note the relatively high ash content of the glossy paper. It is likely that the clays and other additives used as filling material to obtain a glossy finish contributed to the non-combustible components of the paper. The compositions of the ashes were somewhat similar, SiO₂ and CaO accounting for about 60% of the weight of the ash of each parent

material. About 35% of the weight of the ash of the glossy paper was unidentified, and is believed to be associated with additives used in processing the paper.

Chars were produced by devolatilizing the biomass materials in nitrogen at low heating rates in a tube furnace maintained at 900 °C. The proximate and ultimate analyses of the low-heating-rate chars are also shown in Table I. Note that the chars still contain some volatile matter. The volatile matter content determined for the glossy paper char is unusually high and so is the value reported for its oxygen content. Since the oxygen content is determined by difference, it is likely that the value reported for the oxygen weight fraction of the glossy paper char includes constituents of the additives used in the finishing process. [The standard ultimate analysis procedure assumes that the organic portion of the material examined only contains C, H, O, N, S, and Cl elements.] Also presented in the table are the specific surface areas determined for the char particles. Note that the specific surface areas of the carbonaceous portions of the chars are similar.

Intrinsic chemical reactivities determined for the chars of the three cellulosic-based biomass materials when exposed to 10 mol-% oxygen at 500 °C are presented in Fig. 2. One of the newspaper chars was heat treated by injecting the char produced in the tube furnace into the laminar flow reactor when an environment containing trace levels of oxygen at 1550 K was established. This char is labeled NP-HT; its reactivity is also shown in the figure.

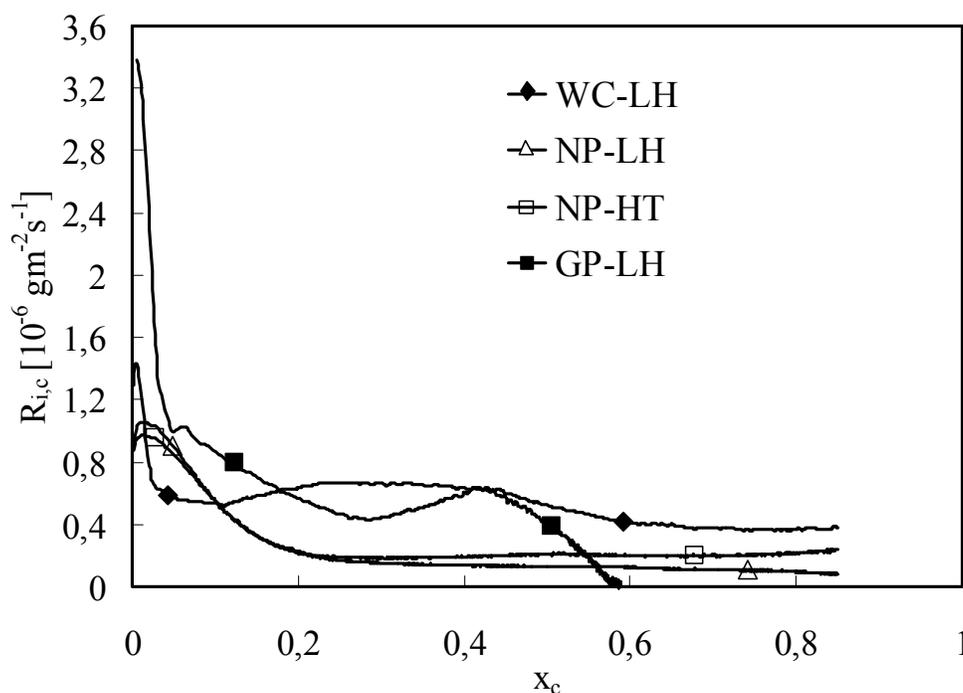


Figure 2: Intrinsic reactivity ($R_{i,c}$) as a function of char conversion (x_c).

The results reveal that the reactivities of the cellulosic-based chars selected for study vary with conversion. All the chars have peak reactivity at low conversions ($x_c < 0.03$, daf). At the onset of oxidation, these low-heating-rate-produced chars exhibit a rapid increase in reactivity followed by a rapid decrease. At ash-free conversions greater than about 0.15, char reactivities are factors ranging from 3 to 6 below the peak values, and

remain at these relatively low levels until the final stages of burning. Note that subjecting the newspaper char to a higher temperature had a relatively minor effect on its reactivity. The heat-treated char does not, however, exhibit as sharp a peak as its parent char at the onset of oxidation. It should be noted that all of the coal and biomass chars that we have previously examined were produced at high heating rates and none of the chars exhibited such sharp initial peaks in reactivity as observed with these chars that were produced under low heating rate conditions.

The reactivity profiles of the chars produced at low heating rates are possibly the consequence of the carbonaceous material consisting of two components, one that is more reactive than the other. The initial peak in reactivity is due to the highly reactive portion of the char, which is quickly consumed once the char is exposed to oxygen at high temperatures. It may be that the more reactive portion of the carbonaceous material is associated with the volatile matter content of the char. Low heating rates provide opportunities for primary devolatilization products to undergo secondary reactions and reattach to the carbonaceous matrix as they diffuse through devolatilizing particles. Such reattached fragments are likely to be measured as volatile matter during a proximate analysis. The glossy paper char has the highest peak reactivity; it also has the greatest amount of volatile matter, as indicated by the proximate analysis. The peak reactivities of the wood chip and newspaper chars are comparable; so are the volatile matter contents of their chars. Additional tests are planned to determine if this is indeed the case. In order to predict the types of reactivity profiles exhibited by these low-heating-rate chars, it is necessary to modify our heterogeneous reaction mechanism to include two types of carbon sites, one type being more reactive than the other. Such modifications are being considered.

The data obtained with the glossy paper chars indicate a possible impact of the ash in the char on inhibiting char oxidation rates near burnout. Note that the reactivity profile for the glossy paper char falls to nearly zero at about 58% conversion, daf. The char particles at this extent of conversion are ash-rich, containing more than 75% ash by weight. It is likely that the ash plays a role in limiting the reactivity of the char by, for example, encapsulating the carbonaceous material, rendering it more difficult for oxygen to reach the carbonaceous surfaces where it can be adsorbed. By the time the wood chip and newspaper chars are 75% ash by weight, char conversion is over 95%, daf. Any ash inhibition effects are minor for these low-ash materials. Studies are underway to shed insight into the possible inhibiting effect of ash, an important effect for biomass materials having high ash contents.

Future Plans

Studies to determine the relationship between coal and biomass properties and model parameters are ongoing as are studies to characterize the impact of the ash-content of particles on char reactivity. A particular goal of our current research is to characterize the impact of total pressure on coal- and biomass-char reactivity. To this end, coal and biomass materials are being subjected to oxidation tests at high pressures. Our heterogeneous reaction mechanism will be modified to reflect our latest understanding of rates of the key chemical reactions controlling the conversion of the carbonaceous solid material to gas-phase species. The objective of one of our 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, the principle building blocks of biomass materials. Towards meeting this goal, cellulose-rich, hemicellulose-rich, and lignin-rich biomass materials are being identified and will be tested to determine the reactivity of their chars to oxygen.

The work being performed will allow us to characterize accurately the chemical and physical changes that coal and biomass particles undergo during combustion and gasification processes. The studies undertaken will help us to understand how coal and biomass properties influence char conversion rates in high-temperature, high-pressure environments. The data obtained will permit the development and validation of the physical and chemical sub-models needed 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 yield high coal and biomass conversion efficiencies with minimum impact on the environment.

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