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Characteristics and Sources of Intermediate Size Particles in Recovery Boilers

Final Project Report

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Prepared by

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CHARACTERISTICS AND SOURCES OF INTERMEDIATE SIZE PARTICLES IN RECOVERY BOILERS

Final Project Report

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Abstract

As part of the U.S. Department of Energy (DOE) Office of Industrial Technologies (OIT) Industries of the Future (IOF) Forest Products research program, a collaborative investigation was conducted on the sources, characteristics, and deposition of particles intermediate in size between submicron fume and carryover in recovery boilers. Laboratory experiments on suspended-drop combustion of black liquor and on black liquor char bed combustion demonstrated that both processes generate intermediate size particles (ISP), amounting to 0.5-2% of the black liquor dry solids mass (BLS). Measurements in two U.S. recovery boilers show variable loadings of ISP in the upper furnace, typically between 0.6-3 g/Nm³, or 0.3-1.5% of BLS. The measurements show that the ISP mass size distribution increases with size from 5-100 μ m, implying that a substantial amount of ISP inertially deposits on steam tubes. ISP particles are depleted in potassium, chlorine, and sulfur relative to the fuel composition. Comprehensive boiler modeling demonstrates that ISP concentrations are substantially overpredicted when using a previously developed algorithm for ISP generation. Equilibrium calculations suggest that alkali carbonate decomposition occurs at intermediate heights in the furnace and may lead to partial destruction of ISP particles formed lower in the furnace. ISP deposition is predicted to occur in the superheater sections, at temperatures greater than 750 °C, when the particles are at least partially molten.

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Acknowledgments

This project succeeded because of the contributions of a large number of individuals at Sandia, McDermott Technology, Babcock & Wilcox, the Institute of Paper Science & Technology, and Brigham Young University, as well as among our industrial hosts and collaborators at Weyerhaeuser and International Paper. The assistance of the American Forest and Paper Association (AF&PA) and the Department of Energy was also important. Don Hardesty, Sandia manager, assisted with project management during the course of the project. Rick Balthaser of the DOE Albuquerque Operations Office assisted with placement of contracts and disbursement of funding among the project collaborators.

Doug Scott and Dennis Morrison of Sandia assisted with setup and operation of the various measurement systems at International Paper's Courtland boiler. Gian Sclipa assisted with measurements at Weyerhaeuser's Longview boiler and designed and constructed the disk impaction probe. Dan Rader and John Brockmann assisted in the conceptual design of the VIP probe, Dan Chenoweth performed CFD calculations in support of the design of this probe, and Sal Birtola, a contract design technician, implemented the computer design of the probe. Sal also designed the water jackets used with the VIP probe and with the pitot tube/thermocouple probe. Gil Hofacker and student intern Trey Cauley assisted in design and construction of the gas handling system for the VIP probe. Nancy Yang performed SEM on the impaction plate samples.

Bob Roscoe, Bruce Stone, Bill Trout, and Ken Nichols of Weyerhaeuser assisted with project planning, mill coordination, boiler testing, and data interpretation. Peter Ariessohn, of Weyerhaeuser and later with Combustion Specialists Inc. and Enertech Inc., also assisted with project planning, mill coordination, boiler testing, and data interpretation.

Andy Jones, Sheldon Imrie, and Mike Gregory of International Paper assisted with mill coordination and boiler testing.

Steve Lien of the Institute of Paper Science & Technology (IPST) carried out the char bed combustion experiments and participated in reviews of the char bed results. Peter Pfromm and Scott Sinquefield of IPST and Saied Kochesfahani of Borax also participated in some of these discussions.

Elvin Ip of Brigham Young University (BYU) constructed the suspended drop combustion facility and performed the experimental measurements on suspended black liquor drop combustion.

Honghi Tran and the faculty of the Pulp & Paper Centre, University of Toronto, provided cost-share support of this project, through collaborative research on ISP formation during droplet combustion in the UT entrained flow reactor. Dr. Tran and Saied Kochesfahani also participated in periodic phone conferences discussing the project status and future plans.

The efforts of all of these individuals, and any we have failed to mention here, are appreciated and were essential to the successful completion of this project.

Executive Summary

This report documents the results of work performed on a project entitled “Intermediate-Sized, Entrained Particles: Characterization, Formation and Control,” which was funded by the U.S. Department of Energy (DOE), with industrial cost-share, through the auspices of the Forest Products focus area within the Office of Industrial Technologies (OIT) Industries of the Future (IOF) program. Technical evaluation of the proposed work and of the progress during the course of the project occurred through the American Forest and Paper Association (AF&PA) Agenda 2020 Energy Performance Committee.

The purpose of the project was to characterize particles intermediate in size between submicron sodium fume and large carryover particles in pulp mill recovery boilers, determine their dominant sources, and recommend means by which the deposition of these particles onto steam tubes could be minimized. These particles have come to be known as “intermediate size particles” (ISP) and have been assigned the approximate size range of 1-100 μm . The work was a collaborative and multidisciplinary effort involving Sandia National Laboratories (SNL), McDermott Technology Inc. (MTI) and Babcock & Wilcox (B&W), Brigham Young University (BYU), and the Institute of Paper Science & Technology (IPST). The project was nominally divided into four research areas, led by the different research institutions: (1) ISP Formation from Black Liquor Drop Combustion (BYU), (2) ISP Formation from Char Bed Combustion (IPST), (3) ISP Measurements in Recovery Boilers (SNL), and (4) Boiler Modeling Predictions of ISP Formation and Deposition (MTI/B&W). As the lead organization for this project, Sandia also was responsible for overall project management and reporting. Sandia also completed a literature review on ISP formation from black liquor sprays.

ISP formation during black liquor drop combustion was investigated through imaging of devolatilizing and burning black liquor drops and from downstream collection of ejected drop fragments in a pair of cyclones. Softwood liquors and liquors from softwood/hardwood blends were investigated, at solids loadings of 50 wt-% and 70 wt-%. Millimeter-sized drops were suspended on thin wires in a heated furnace or above a flat-flame burner (900 °C, 5-7% O₂). Scanning electron microscopy (SEM) was performed on the collection filters in the cyclones, to characterize the collected ISP. After adjusting the lighting and imaging technique, ISP were observed being ejected from the drops, primarily during the char burning and smelt oxidation phases. Substantial drop-to-drop variability was also found in the apparent production of ISP. ISP mass was determined by weighing the cyclone catch after combustion of 40-50 drops. Strong variation in ISP mass production was found as a function of liquor type, with softwood liquors forming more ISP. In addition, ISP production increased rapidly with increasing dry drop mass and therefore with solids content for a given size wet drop. For an average drop diameter of 2-3 mm, liquors with 70% dry solids produced an average ISP mass of 0.4-1.8% of the initial dry solids. SEM analysis of the cyclone catch showed smooth, spherical particles above 50 μm in diameter, round particles with surface agglomeration from 10-50 μm in diameter, and irregularly shaped particles, often appearing to be super-agglomerates of fume, less than 10 μm in diameter.

ISP formation during char bed combustion was investigated in a newly constructed char bed burning facility at IPST. The new facility contained the char bed in a high-density alumina

crucible that could be heated to 950 °C and used a hot cyclone followed by a gas cooler and a micropore filter to quantify the production of ISP and fume particles during char bed combustion. A video camera, two-color pyrometer, and thermocouples provide information on the bed temperature and distribution of burning on the bed. Standard gas analyzers and a gas flowmeter in the filtered exhaust flow allowed the determination of the instantaneous rate of char combustion. Three different liquors were investigated, oxygen contents in the feed gas were varied from 4-16 vol-%, jet and diffuser feed gas nozzles were used, and the feed gas flowrate was varied over a factor of 3 in a series of 22 experiments. The char was prepared within the crucible by slowly heating 50-55% dry solids (ds) liquor in a nitrogen purge before switching to a reactive feed gas. No influence of liquor type was evident in the results, and the only effect of nozzle type was in the localized burning intensity. The overall burning rate and rate of production of particulates as a function of bed temperature were similar to those previously measured in an earlier reactor design. However, the fume collected in the new reactor exceeded that derived from the interpretation of wet impinger capture in the original reactor, and the ISP concentrations deduced from the cyclone catch were substantially lower than previously deduced (typically amounting to less than 1% of the initial black liquor solids). Considerable particle deposition (0.3 to 2.5% of initial BLS) occurred in the tubing between the reactor and the cyclone and, especially, on the walls of the cyclone and gas cooler (which could only be rinsed as a single unit). If this deposited mass is assumed to be mostly ISP, then the apparent ISP production amounts to 0.1-4% of the initial black liquor solids, and is a significant contributor to the total emitted particle mass. However, SEM analysis of the cyclone catch and of particles captured just downstream of the char bed reactor suggests only a minor contribution of ISP in comparison to the predominant fume. ISP generation in full-size char beds may be enhanced by the aerodynamic shearing action of large, turbulent primary air port jets.

The recent research at Helsinki University of Technology (HUT) on modern, high-solids black liquor sprays was analyzed to evaluate the potential of ISP formation directly from the smallest diameter drops formed in black liquor sprays. The spatial resolution that the HUT researchers were able to obtain in their video imaging was limited to about 1 mm in droplet size. Therefore, no direct measurement information on ISP is available from their data. However, the drop size distribution was found to fit a square-root normal distribution, as was found in previous investigations into black liquor drop size distributions. Using the size distribution parameter determined in the HUT work and a minimum median drop diameter of 4 mm, less than 0.03% of the black liquor mass is predicted to be in drops less than 100 µm in size. Therefore, it appears that direct spray production of ISP particles is inconsequential.

Sampling of ISP particles was performed at two different, representative U.S. recovery boilers – one in the Northwest and one in the Southeast. These sampling campaigns were performed in conjunction with a separate research project focused on development of laser diagnostics for particulate measurements. In both boilers, local ISP mass loading was found to be highly variable in time, in contrast to the fume mass loading. The average ISP mass just above the nose arch was found to be 0.6-3 g/Nm³, or 0.3 to 1.5% of BLS. Both laser-based and (corrected) impaction plate measurements showed that the ISP mass size distribution generally increases with size from 5-100 µm. The ISP concentration was found to drop rapidly from the upper furnace through the convection pass (as a consequence of particle deposition) and the concentration of ISP in the convection pass was found to be sensitive to the action of sootblowers (which appeared to generate ISP-size particles as they removed deposits). SEM

analysis of impaction plate samples revealed that ISP particles larger than $\sim 10\text{ }\mu\text{m}$ tended to be spherical and were often coated with fume (perhaps an artifact of the sampling process). The smallest ISP particles usually appeared to consist of super-agglomerates of submicron fume. SEM energy dispersive x-ray spectroscopy (EDX) was used to analyze the chemical composition of ISP particles. This analysis showed that ISP particles are depleted in potassium and chlorine and, to a lesser extent, sulfur.

Comprehensive modeling was performed for both the Longview and the Courtland boilers using B&W's combustion model, COMO-PR. The model solves steady, three-dimensional, turbulent flow, heat transfer, and black liquor combustion in a recovery boiler. Comparisons of measurements of gas temperature, velocity, and fume concentration in the upper furnace and convection pass showed good agreement with modeling results, once anomalies in the boiler operation data had been rectified. However, ISP concentrations in the upper furnace were substantially overpredicted when using a previously developed algorithm that describes ISP formation from droplet combustion. A possibly significant mechanism for destruction of ISP mass in the middle of the furnace is alkali carbonate decomposition, which is predicted by chemical equilibrium to occur for temperatures greater than $1100\text{ }^{\circ}\text{C}$. Sulfur release during black liquor combustion is also overpredicted in the boiler model, and ISP and carryover particles are predicted to be devoid of chlorine, in contrast to boiler measurements. Deposition by carryover and ISP is predicted to cease for temperatures less than $750\text{ }^{\circ}\text{C}$ (i.e., within the superheater sections), because impacting particles do not stick after they solidify near that temperature.

Overall, significant progress was made during this project in the understanding of the sources of ISP in recovery boilers, their characteristic concentrations, size distribution, and chemistry in typical U.S. recovery boilers, and the locations at which they deposit on steam tubes. In particular, most ISP particles appear to form during the char combustion and smelt oxidation portions of black liquor drop combustion. In the upper furnace, these particles are depleted in potassium and chlorine and generally show a slowly rising mass size distribution from $5\text{-}100\text{ }\mu\text{m}$. They primarily deposit in the superheater section of the boiler. The measured ISP concentrations and size distributions suggest that these particles are important contributors to superheater deposits. Based on the indication of drop combustion as the primary source of ISP and the trends found in ISP production with droplet dry mass, it is expected that ISP production (and deposition) can be reduced through systematic optimization of spray parameters (affecting drop size distribution and trajectories) and of air distribution in the lower furnace (affecting drop residence time and burning intensity). Further research is required to explore the possible reductions in ISP production in this manner.

Background

This report documents the results of work performed on a project entitled “Intermediate-Sized, Entrained Particles: Characterization, Formation and Control,” which was funded by the U.S. Department of Energy (DOE), with industrial cost-share, through the auspices of the Forest Products focus area within the Office of Industrial Technology (OIT) Industries of the Future (IOF) program. This project was recommended for funding in 1999 through the Energy Performance Subcommittee of the American Forest and Paper Association (AF&PA) Agenda 2020 program and, subsequent to project funding in 2000, technical progress was monitored through regular meetings of this same subcommittee.

This project was motivated by the ubiquitous problem of excessive deposit formation in the convection pass of U.S. (and indeed, all North American) kraft pulp mill recovery boilers. These deposits reduce the energy efficiency of these boilers, limit the pulping capacity of many U.S. kraft pulp mills, and often result in boiler pluggage and lost capacity. The fuel that is burned in the Tomlinson furnace is known as strong black liquor, and typically consists of 20 wt-% sodium (on a dry basis) in a mixture of lignin-derived organics, water, and sulfur compounds [Hupa 1997]. The primary functions of recovery boilers in pulp and paper mills are (1) to recover inorganic chemicals from black liquor for recycling through the mill, and (2) to transform chemical energy in the organic portion of black liquor to thermal energy for use in steam or electrical power generation. In the combustion process, inorganic material is released from the fuel, incorporated into the combustion gases as both particles and vapors, and deposited on boiler surfaces. Heat transfer distribution in furnaces depends in large measure on the overall quantity and thermal transport properties of the inorganic material present. Deposit formation in the convection pass represents one of the major operation and design limitations for the boiler.

Traditionally, deposit problems have been associated with two important classes of particles whose existence is readily apparent in the furnace flow: carryover particles and fume [Tran 1997]. Carryover particles are generally considered to be 100 micrometers or greater in characteristic size and originate from black liquor droplets that burn out in flight or from entrainment of particles from the char bed at the bottom of the recovery boiler. They deposit by inertial deposition and predominantly impact the superheater deposits. Fume particles are generally less than 1 micrometer in diameter and form as a condensation aerosol from sodium that is vaporized during black liquor droplet combustion and char bed reactions. Fume is present throughout the convection pass and is believed to deposit primarily from thermophoretic transport across the boundary layer around the tubes.

In recent years, several studies [Verrill et al. 1994; Sinquefield 1998; Sinquefield et al. 1998; Mikkanen et al. 1999; Baxter et al. 2000; Kochesfahani and Tran 2000; Kochesfahani et al. 2000; Lind et al. 2000; Baxter et al. 2001; Lind et al. 2001; Mikkanen et al. 2001; Holve et al. 2001; Shaddix and Holve 2004; Ip et al. 2004] have highlighted the potential importance of particles with sizes 1 to 100 micrometers, between the two well-studied classes, carryover and fume. These particles have come to be known as “intermediate size particles,” or ISP, though they have also been described as “ejecta.” These particles span the particle size range over which thermophoretic particle deposition, turbulent eddy deposition, and inertial particle impaction have varying degrees of importance through the convection pass. Therefore, predicting the

importance of this class of particles to deposit formation in different regions of the boiler is highly dependent on the particle size distribution and molten state (i.e., liquid content) of the particles [Shenassa et al. 2003], in addition to the overall ISP concentration in the flow. The molten state of a fly ash particle, in turn, is controlled by the particle temperature and its chemical composition — in particular the chlorine and potassium content [Tran et al. 2002]. Therefore, to accurately assess the importance of ISP to steam tube fouling and tube bank pluggage, measurements are required of ISP concentrations, size distribution, and chemistry in operating recovery boilers. Also, whereas the concentration of fume particles is largely determined by the furnace temperature and the pulping chemistry, ISP particle sizes and concentration are likely controllable by process variables (such as liquor quality, char bed size and shape, and the furnace air distribution) that can be adjusted without strongly affecting overall recovery boiler performance. To understand and predict the effects of these process variables on ISP loading in the furnace, the chemical and physical mechanisms that result in ISP formation need to be identified.

The project summarized here aimed to characterize ISP in recovery boilers, determine their dominant sources, and recommend means by which the deposition of these particles onto steam tubes could be minimized. The work was a collaborative and multidisciplinary effort involving Sandia National Laboratories (SNL), McDermott Technology Inc. (MTI) and Babcock & Wilcox (B&W), Brigham Young University (BYU), and the Institute of Paper Science & Technology (IPST). The genesis of this project lay in the results from a preceding project entitled “Growth and Property Development of Convection Pass Deposits in Recovery Boilers” [Baxter et al., 2004] that suggested ISP may play a major role in recovery boiler deposits.

The project was nominally divided into four research areas, led by the different research institutions: (1) ISP Formation from Black Liquor Drop Combustion (BYU), (2) ISP Formation from Char Bed Combustion (IPST), (3) ISP Measurements in Recovery Boilers (SNL), and (4) Boiler Modeling Predictions of ISP Formation and Deposition (MTI/B&W). As the lead organization for this project, Sandia also was responsible for overall project management and reporting. Sandia also completed a literature review on ISP formation from black liquor sprays. A summary of both this project and the deposits project was presented at the most recent International Chemical Recovery Conference [Wessel et al. 2004]. Detailed results of both projects are mainly documented in the form of technical publications that are referenced throughout the final reports and the project summary conference paper.

ISP Formation during Black Liquor Drop Combustion

Drop Combustion Methods

ISP formation from black liquor drop combustion was investigated at Brigham Young University (BYU), using the new experimental facility shown in Fig. 1. Millimeter-sized black liquor drops were supported on a 0.001-0.005 inch (25-127 μm) diameter wire or type-K thermocouple wire above a gas-fueled flat flame. Approximate droplet internal temperature was monitored by the thermocouple. A progressive scan CCD camera collected images of the drop drying, devolatilization, and combustion at 60 frames per second. Figures 2 and 3 show a sample video record and thermocouple output for a burning drop. A nitrogen-quench, water-cooled probe, located downstream of the drop, collected particles that were released from the burning black liquor drops. Two successive cyclones, with cut-points of 20 μm and 5 μm , respectively, separated the ISP particles from any fume that was formed and also allowed differentiation between larger and smaller size fractions of ISP. Each cyclone had a glass fiber filter with a pore size of 1.6 μm at the bottom to collect the separated particles. Another filter with a 1 μm pore size was located in the sample flow after the cyclones to collect the smallest particles.

Figure 1. Schematic diagram of suspended drop combustion facility at BYU, with particulate sampling and collection system.

Figure 2. Video camera still photographs of 1 mm dia., 50% ds black liquor drop combustion in 900°C air. From left to right: (1) initial drop suspended on thermocouple wire through a ceramic tube, (2) drying, initial swelling, and first ignition, (3) visible flame around the swelling drop during devolatilization, (4) maximum drop swelling, (5) devolatilization and char burning, (6) char burning and smelt oxidation, (7) final smelt oxidation, (8) end of combustion.

Figure 3. Internal temperature profile of drop combustion sequence shown in Fig. 2 (numbers refer to the eight images shown in Fig. 2).

In total, five liquors were tested, including both softwood and softwood/hardwood blends, as supplied by Weyerhaeuser Corporation. Solids contents of 50% and 70% were investigated for each liquor. Combustion occurred at a gas temperature of ~ 900 °C and an oxygen content of 5-7 vol-%. Typical initial drop diameters were 2-4 mm. The combustion of 10 drops was imaged for each liquor sample. To evaluate the total mass production rate of ISP during black liquor drop burning, 40-50 drops of each liquor sample were burned and the ejected particles were collected and weighed, after completing the entire series of drops. ISP formation from a single drop produces too little mass to reliably measure, so the cumulative samples were used for quantitative results. The ISP particles in the cyclone catches were further analyzed with scanning electron microscopy (SEM). Four samples were cut off from the filters at the base of each cyclone. The morphology of the filters created an extensive charging problem. A low accelerating voltage (10 kV) and carbon paint on gold coating were used to minimize the charging.

Drop Combustion Results

During drop drying and devolatilization, external illumination was necessary in order to view the drop and to be able to see evidence of ISP ejection. On the other hand, once char combustion began, the natural luminosity of the char particle and of any ejected fragments was sufficient for video capture. Some video evidence of surface eruptions with small particle ejection was seen during the drop drying phase, with more violent explosions observed in the lower solids content liquors. Few video records showed ISP formation during the devolatilization phase, while nearly all video records showed ISP formation during the char burning and smelt oxidation phases. The video imaging suggested that high solids liquors form more ISP than low solids liquors. Fig. 4 shows two representative images of ISP formation during char combustion. In general, ISP formation appears to be a surface phenomenon involving small particles shedding from a mostly intact particle, rather than a cataclysmic degradation of the particle in a single event. Also, substantial particle-to-particle variation in ISP formation was evident under nominally identical conditions.

Figure 4. Video camera still photographs of ISP particles being ejected from burning black liquor drop (50% ds).

The total ISP collected in the cyclones was found to vary substantially with liquor type, with the softwood liquors consistently forming more ISP for both 50% and 70% ds liquor series. A smaller effect is seen as a function of dry solids content, with higher dry solids yielding more ISP, even when normalized to initial BLS. For an average drop diameter of 2-3 mm, liquors with 70% ds produced an average ISP mass of 0.4-1.8% BLS. A limited survey of ISP production for somewhat smaller drops showed a substantial decrease in ISP production as the initial drop mass decreases.

The particle mass collected in the large, coarse cyclone dominated over the mass collected in the small, fine cyclone. Fig. 5 shows SEM images of ISP particles collected in the coarse cyclone. These particles were primarily spherical. The most numerous particles in the coarse cyclone catch appeared to be those with a diameter of 10-20 μm . These particles had small amounts of particle agglomerations on the surface. Particles collected in the fine cyclone were usually smaller than 5 μm and irregularly shaped. A number of the particles (in either cyclone catch) with diameters smaller than 10 μm appeared to be super-agglomerates of fume. An example is shown in Fig. 5. Few isolated fume particles were found in the catch of either the coarse or the fine cyclone. No differences were observed in the characteristics of the ISP particles produced from the different liquors or liquor solids content.

Figure 5. SEM photomicrographs of ISP collected in the coarse cyclone: clockwise from top left, a 100 μm particle (500X), a 20 μm particle (2500X), a 15 μm particle (4500X), and a 10 μm particle (4500X).

ISP Formation during Char Bed Combustion

Char Bed Combustion Methods

For this project, a new char bed burning facility was designed and built at the Institute of Paper Science and Technology (IPST). The facility that was used previously [Kochesfahani et al., 2000; Lien & Verrill, 2004] had undergone severe corrosion and had insufficient external heating to fully simulate the high-temperature, reducing atmosphere expected in recovery boilers at the surface of the char bed. A schematic of the new facility is shown as Figure 6. An electrical furnace allows char forming and preheating to 950 °C. The reactor shell is fabricated from stainless steel and the char and smelt are contained in a high-density alumina crucible. The gas supply is mixed and heated in a separate gas pre-heater before entering the reactor. The gas is delivered through a nozzle or diffuser-type head several centimeters above the initial surface of the char bed.

The char is prepared within the alumina crucible by metering 400-800 ml of 50-55 wt-% dry solids black liquor into the unheated crucible and then slowly heating it for three hours to 900°C under a nitrogen purge. At the end of this char formation process, the gas to the reactor is changed to an oxygen-nitrogen mixture and char combustion commences. During the run, char surface temperature is measured by a two-color pyrometer and two thermocouples located near the burning surface. Combustion progress is monitored with a video camera. The outlet gas composition (O_2 , CO_2 and CO) is measured with standard instrumentation to determine the rate of char combustion.

The new char bed burning system is designed to directly collect and measure the ISP formed during combustion, whereas the old system dissolved the evolved particles in a series of wet impingers and used the chemical analysis of the impinger solutions to infer the ISP concentration [Kochesfahani et al., 2000].

Figure 6. Schematic diagram of char bed combustion facility at IPST consisting of two major components: a char bed reactor (right) and a particulate collection system.

The new reactor exhaust gas flows to a hot cyclone with a bottom size cutoff of 5 μm , proceeds through a gas cooler, and then flows through a micropore filter. The arrangement of cyclone and gas cooler is shown in Figure 7. A wet impinger is plumbed in parallel to the filter to collect any overburden of fume produced during the char combustion experiments.

Figure 7. Arrangement of char burning reactor (right), exit gas cyclone (center), and gas cooler (left).

Because of the large amount of fume generated, the filter cannot be used for the entire burn. Instead, it is used for a period of 60 to 480 seconds, until the pressure drop across the filter exceeds 25 kPa (3.6 psi). The total fume generated by this method is then calculated by adjusting for the ratio of total carbon burned compared to the carbon released during the filtration period. The filtration period typically corresponds to one-third of the burning time. Scanning electron microscopy (SEM) was used to study the material collected on the filter and the cyclone for some of the tests.

Char Bed Combustion Results

A total of twenty-two tests were performed. The test plan specified three different oxygen contents in the feed gas (4, 8, and 16%) and three different gas flow rates (50, 100 and 150 slpm). Two different gas injection methods were utilized; for the first twelve tests the jet nozzle impinged directly on the char bed surface, and for the next ten tests the diffuser nozzle produced a well mixed gas phase above the bed without flow directly normal to the char surface. From comparison of burning rates and observation of combustion videos, there does not seem to be a large difference in the results obtained with the two different nozzles. With the jet nozzle the combustion appears to be more localized, with a hot fast-burning region where the jet impinges on the bed. The diffuser nozzle produces a more uniform burning surface, but overall the burning rates, temperatures and particulate formation rates are similar with either nozzle.

The temperature of the char bed surface is essentially controlled by the rate of char bed burning. The heaters for the reactor bring the char to an initial temperature between 800 and 900°C before the combustion starts. With the introduction of oxygen and the initiation of char bed burning, additional heat is generated from the exothermic combustion reactions. The maximum temperature measured during the steady-state burning period was typically 2% higher than the average surface temperature calculated from the average of the two thermocouple and pyrometer measurements [Lien & Verrill, 2004].

Char combustion creates CO₂, CO, and NO_x. These compounds all increase rapidly at the start of the burn and then more slowly during the test. Based on review of the temperature and gas composition data for each experiment, a time period is selected which best represents steady state conditions. Knowing the inlet gas flow rate and the concentration of CO and CO₂ in the outlet gas, it is a straightforward calculation to determine the average burning rate in moles of carbon per second during this steady-state period.

The burning rates obtained in the new char bed reactor agree very well with the data generated in the old apparatus [Kochesfahani et al., 2000; Lien & Verrill, 2004]. In Figure 8, both the old data and the new data are plotted and follow the same trend and lie within the same range on the graph. For this comparison, char surface temperature is the average of thermocouple and pyrometer measurements during the steady-state burning period. The cross-sectional area of the char surface exposed to the combustion gas was 79-91 cm² for the original reactor and 81-86 cm² for the new reactor. The two data sets also agree if the char burning rate is normalized by these areas. Video images reveal that the actual surface area varied in time, because of the changing three-dimensional shape of the char surface exposed to the combustion gas. This variability may explain the wide range of burning rates, 11±4 m-mol C/sec, at about 1100°C in the new reactor.

Figure 8. Char surface temperature vs. burning rate for combined data of Kochesfahani et al. [2000] and Lien and Verrill [2004] in original reactor (collectively referred to as “Old Data”) and present work in new reactor (referred to as “New Data”).

Measurement of Particulate during Char Bed Burning

Fume formation is calculated from the rate of deposition on the micropore filter, as integrated over the steady-state burn period, and the total material collected in the cyclone is taken as ISP. For each test, an overall mass balance was performed on the reactor. The total mass recovery ranged from 84% to 101% of the initial char. By this method, the estimated total particulate generated during the tests ranged from 0.8% to 8.7% of the initial black liquor solids (BLS). This is similar to the range of values obtained during the earlier work when the total was 0.3% up to 8.1% of BLS [Lien & Verrill, 2004]. Total particulate generation by the original experimental apparatus is compared with measurements made in the new apparatus in Figure 9.

Estimating Contributions of Fume and Intermediate Size Particles

Two different methods were attempted to estimate the amount of fume and ISP generated during each char burn in the new reactor. The first method was based on the dry material collected by the cyclone and fume filter. The second method includes the material deposited on the walls of the piping leading to the cyclone and fume filter (see Fig. 7), this was recovered by rinsing these parts after each test and analyzing the rinse solution.

Figure 9. Total particulate formation vs. temperature for combined data of Kochesfahani et al. [2000] and Lien & Verrill [2004] in original reactor (collectively referred to as “Old”) and present work in new reactor (referred to as “New”).

In Figure 10, fume and ISP estimated by dry collection methods are plotted against the char surface temperature. Even though measurement of total particulate was similar to results obtained with the original reactor, the split between the fume and ISP was much different. In the earlier work the ISP ranged from 0.04% to 6.0% of initial black liquor solids with an average of 2.4%. In the tests using the new reactor, the ISP ranged from 0.02% to 1.3% with an average of only 0.16% of BLS. It is not clear why the amount of fume drops off at 1000°C and then begins to increase again at 1100°C, but the higher temperatures correspond to higher inlet oxygen levels. Since the volatilization of the sodium and other inorganic species increases with temperature, it would be expected that the fume formation would increase steadily with temperature.

Only one test showed ISP production that was greater than 1% of the initial black liquor solids mass. After this test, the reactor was disassembled and it was noticed that a deposit had formed on the thermocouples at the outlet of the reactor before the cyclone. This higher level of apparent ISP is probably due to material from this deposit breaking off and collecting in the cyclone.

It is possible that the dry collection method underestimates the ISP and overestimates the fume. The filter sample is collected early in the run and extrapolated over the entire run. There may be a significant drop in the fume formation rate over the run, which means that the amount of fume is overstated. Similarly, the dry sample of ISP is only the material collected in the bottom of the cyclone. Since a significant portion of the ISP may adhere to the walls of the cyclone, there may actually be more ISP material. For the last series of tests the material in the short section of outlet pipe before the cyclone was collected and added to the cyclone catch. This increased the solid amount by a factor of 2, although the total ISP material was still quit low.

Figure 10. Partitioning of particulate captured during char bed combustion experiments using the new reactor in which the categories of particulate were determined by filtration during a portion of the total burn time (fume) and by total dry cyclone catch (ISP).

To include possible deposition of ISP in the gas piping leading up to the cyclone, the outlet sections of the reactor were disassembled and rinsed out to recover any material deposited in these pieces. These samples are used in a second method to determine the amount of fume and ISP. In this method the fume is calculated as the total fume collected in the filter (not a rate) and the material dissolved in the impinger. With the use of a single impinger, this measurement tends to underestimate the fume (Kochesfahani et al. [2000] found that three successive impingers were necessary to collect the vast majority of the fume). The ISP is based on the dry material in the cyclone (and in the outlet pipe for the last five tests) and the solids in the solution rinsed out of the cyclone and the cooler assembly.

In Fig. 11, the particulate from the modified method is plotted against char surface temperature. As in Fig. 10, there is an apparent discontinuity in the trends of particulate generation with temperature at around 1000°C. With this method, the split between the estimated fume and ISP was much more even than the dry collection method. The fume ranged from 0.6% to 5.6% of the initial black liquor solids with an average value of 2.0%, whereas the ISP ranged from 0.1% to 3.9% of BLS with an average of 1.5%. In the earlier work, the ISP ranged from 0.04% to 6.0% of BLS with an average of 2.9%.

Although these results are more in line with the earlier work of Kochesfahani et al. [2000], it is likely that this method is overestimating the ISP and underestimating the fume. In this method the ISP includes the rinse solution from the cooler, which is after the cyclone and probably contains mostly fume. Also, the deposits on the piping before the cyclone may have a significant fume component. Inclusion of this particle mass under the heading of ISP reduces the calculated fume by the same amount.

Based on the amount of particulate formed and the gas flow rate in the new char bed reactor, the amount of fume is estimated to range from 2 to 16 g/Nm³ and the concentration of ISP from 0.035 to 0.82 g/Nm³. These values are in reasonably good agreement with the values recently determined in two North American recovery boilers, where the fume concentration ranged from 5 to 10 g/Nm³ and the concentration of ISP was typically between 1 and 2 g/Nm³ [Wessel et al., 2004; and as reported later in this report].

Figure 11. Partitioning of particulate captured during char bed combustion experiments using the new reactor in which the categories of particulate were determined by filtration during an interval of the run (fume) and rinsing the reactor exhaust piping and cyclone (ISP).

Visual Inspection of Particulate

Samples of the dry particulate material collected in both the cyclone and in the filters were analyzed by SEM. A total of 39 images were collected from ten different solid samples. There were seven samples from the filters for seven different tests. Samples of three different cyclone samples were also inspected. The material collected by the filters appears to be composed entirely of fume. The material is scraped from the filter and comes off as large flakes. These flakes are composed of roughly spherical particles which range in size from 0.3 to 1.0 μm . These particles are partially sintered together to form a continuous structure; a typical image of the material from the filter is shown in Figure 12.

Figure 12. SEM image of material collected on filter during char bed burning test in new reactor (7.55 mmol C/s burning rate, 161 slpm gas flow, 7.86 vol% O₂ at inlet, 965°C average temperature).

The cyclone catch shows more variation in the microscopic structure. The material from one test was made up of individual particles up to 1000 μm in size. On a smaller scale the SEM images show that these particles are agglomerations of a variety of particle shapes and sizes (Figure 13). Spherical particles ranging in size from 0.5 to 3.0 μm may be formed from sintered fume particles. The other particles are blade-like -- less than 1 μm thick, about 1.0 μm wide, and at least 5.0 μm long.

In most experiments the filter was located after the cyclone, so large particles were removed before the filter. In some of the later tests the filter was installed directly at the outlet without the cyclone, so that any ISP should be captured directly on the filter. The appearance of this type of filter sample is shown in Fig. 14. The vast majority of the material is composed of sintered fume particles. Based on comparison with images from the downstream filter in earlier tests (Fig. 12), the fume has sintered to a greater extent. Since the gas temperature at this location is higher, it is not surprising that the filter samples collected directly out of the reactor are more sintered. Small amounts of blade or ribbon-shaped pieces similar to those seen in the cyclone catch (Fig. 13) are present in some of the reactor exit samples. Most interestingly, only a few larger spherical particles (~10 μm) were observed that likely resulted from fragmentation mechanisms during the char bed burning experiments. This latter fact suggests that the amount of ISP generated during char combustion in the new reactor was quite low.

Figure 13. SEM image of material collected in cyclone during char bed burning test in new reactor (7.35 mmol C/s burning rate, 162 slpm gas flow, 8.20 vol% O₂ at inlet, 982°C average temperature).

Figure 14. SEM image of material collected on filter close-coupled to reactor exit (4.42 mmol C/s burning rate, 90 slpm gas flow, 7.94 vol% O₂ at inlet, 928°C average temperature).

Recommended Equipment Modifications

This work confirms that intermediate sized particles can originate from combustion processes occurring on the char bed of recovery boilers, but the relative contribution of this source of material on overall ISP levels remains unclear. Additional experimental work is needed to either measure particle size distribution at the exit of the char burning reactor (e.g., by the *in situ* laser particle counting technique described by Shaddix and Holve [2004]) or by modification of the collection system to allow isolation of the larger ISP from submicron fume.

The experience gained during this work suggests several limitations of the equipment configuration:

- significant sintering occurred in the hot cyclone;
- significant deposition of particles occurred in the cyclone and gas cooler;
- direct connection of gas cooler to cyclone (Fig. 7) made recovery of material by rinsing cyclone walls difficult.

A redesign of the gas cooler and cyclone arrangement is shown in Fig. 15 that would provide the following advantages:

- no change to flow direction until after gas cooler, minimizing deposition of larger particulate on pipe walls before reaching the cyclone section;
- gas cooler before cyclone reduces sintering of material collected in cyclone;
- dilution nitrogen introduced after gas cooler increases gas velocity and improves ISP collection efficiency in cyclone;
- pipe unions allow easy removal of cyclone for rinsing to determine total amount of collected material.

Figure 15. Recommended modification to char bed burning reactor exit configuration for better differentiation of ISP from fume in particulate measurements.

Conclusions

A new experimental apparatus was used to measure particulate generation during black liquor char bed burning. The trend in the measured char burning rate as a function of surface temperature was found to be in good agreement with previous work [Kochesfahani et al., 2000, Lien & Verrill, 2004], despite the considerable differences in the gas flow geometry.

The total amount of collected particulates was also similar in these earlier studies, varying from 1-9% of the initial black liquor solids and generally showing an increase with increasing bed temperature (burning rate). The fume measured by collection on a filter in the new reactor exceeds that derived from the interpretation of the wet impinger capture in the original reactor, and the ISP concentrations deduced from the new reactor are lower than previously suggested. In fact, the actual cyclone catch was very small for the char combustion experiments conducted in the new reactor, typically amounting to less than 1% of the initial black liquor solids. Considerable particle deposition (0.3 to 2.5% of the initial BLS) occurred in the short length of tubing between the reactor and the cyclone and, especially, on the walls of the cyclone and the gas cooler (that could only be rinsed off as a single unit). If this deposited mass is assumed to be mostly ISP, then the apparent ISP production amounts to 0.1-4% of the initial black liquor solids, and is a significant contributor to the total emitted particle mass. However, SEM analysis of the cyclone catch, as well as of the particles captured on a filter placed in the flow just downstream of the char bed reactor, suggests only a minor contribution of ISP in comparison to the predominant fume. Unfortunately, the true ISP mass from char bed burning in the new reactor could not be determined with certainty.

ISP Formation from Black Liquor Sprays

The potential formation of ISP particles from the liquor spray process in recovery boilers is not being investigated directly in this project, but is a potentially important source of ISP that needs to be accounted for in order to perform accurate modeling of ISP formation in boilers. A research group at the Helsinki University of Technology (HUT) has been investigating the spray properties of modern, high-solids black liquor using an endoscope to collect backlit video images of spray breakup both in an actual recovery boiler and alongside the boiler in a spray booth. Drop size determinations have been performed using stroboscopic backlighting at a distance of four meters from the nozzle, but only in the spray booth. Based on the similarities in the overall spray breakup process evidenced in the furnace and in the spray booth, it is reasoned that the final drop size distributions should be similar in the two environments. Ari Kankkunen from HUT presented an update on these measurements and their interpretation at the Black Liquor Colloquium held in Park City, Utah, in May 2003. In discussions initiated at the Colloquium and continued afterward, it became clear that the spatial resolution that the HUT researchers were able to obtain in their video imaging was limited to about 1 mm in droplet size. Therefore, no direct measurement information on ISPs is available from their data. In general, the high-solids liquor shows a strong resistance to breakup of the spray ligands and therefore tends to form large, irregularly shaped drops (as imaged at the maximum available displacement from the nozzle, 4 m).

However, the mean spray velocity, disintegration of the liquid sheet, and mean drop size were found to be strongly affected by the liquor “flashing” phenomenon, when firing the liquor at 16–18 °C above the atmospheric boiling point [Kankkunen and Miikkulainen, 2003]. In all cases, the drop size distribution was found to fit a square-root normal distribution, as indeed has been consistently found in previous investigations into black liquor drop size distributions. The calculated drop size distribution for the range of volume median drop diameters found by Miikkulainen and Kankkunen under typical liquor conditions for 27 mm and 28 mm diameter splashplate nozzles is shown in Fig. 16. On the basis of this size distribution function and a realistic minimum median drop diameter of 4 mm, less than 0.03% of the liquor mass is contained in drops less than 100 μm in size and less than 2% of the liquor mass is contained in drops less than 1 mm in size. As shown in the next section, ISP concentrations measured in recovery boilers typically correspond to 0.5–1% BLS, so the results from the Finnish study argue against significant ISP formation directly from the combustion of small spray drops. It should be noted, however, that smaller median drop diameters and larger size distribution standard deviations have been found when using smaller diameter nozzles and for liquors with lower solids content, implying a greater rate of formation of small drops. Until accurate measurements are made in the small drop size range or accurate, detailed spray modeling is performed with sufficient size resolution, the actual magnitude of this source of ISP particles will remain uncertain.

Figure 16. Calculated black liquor spray drop size distributions for a square-root normal distribution, spanning the range of volume median drop diameters (in 1 mm increments) measured by Miikkulainen and Kankkunen. The standard deviation used was that recommended by these authors.

ISP Measurements in Recovery Boilers

Recovery boiler measurement campaigns in this project focused on performing new, accurate measurements of ISP in full-scale recovery boilers operating under normal conditions. Two boilers were chosen for characterization: the Longview, Washington, boiler operated by Weyerhaeuser Company, and the Courtland, Alabama, boiler #3 operated by the International Paper Corporation. These boilers were chosen for sampling based on a number of factors, including representation of Northwest and Southeast U.S. pulp regions, availability of access ports for large (3.75" OD) water-cooled sampling probes (especially near the entrance to the superheaters), and characteristic age and firing practice of the boiler. The Longview boiler is a two-drum boiler built by B&W in 1975. During the period of particulate sampling of this boiler, it was firing $\sim 5.0 \times 10^6$ lbs virgin ds/day. In contrast, the Courtland boiler was firing $\sim 3.9 \times 10^6$ lbs virgin ds/day. Taking into account the slightly larger cross-sectional area of the Courtland furnace and the heating values of the black liquor solids at the two mills, the heat input per plan area was 0.78×10^6 Btu/ft²-hr (2.46 MW/m²) at Courtland and 0.98×10^6 Btu/ft²-hr (3.09 MW/m²) at Longview. Therefore, the Longview boiler was operating under a $\sim 25\%$ higher liquor load than the Courtland boiler.

The boiler measurements in this project were made in conjunction with a separate project focused on development of laser diagnostics for particulate measurements [Shaddix and Holve, 2004]. In this project, a novel extractive sampling probe was developed for ISP (described below). Unfortunately, during the limited sampling time with this probe (at the Courtland boiler), the probe did not perform as expected and primarily captured fume particles. Therefore, primary quantification of the concentration and size distribution of ISP fell to the light scattering technique developed under the diagnostics project, as supported by analysis of short-exposure impaction plate samples. Measurement of the chemical composition of ISP was achieved through SEM analysis of the impaction plate samples, using energy dispersive x-ray spectroscopy (EDX), which yields the relative atomic composition of the material. Additional details regarding the sampling techniques are provided below.

Virtual Impaction Probe

The "Virtual Impaction Probe," or VIP probe, was developed specifically in this project for measuring ISP while alleviating the difficulties of particle deposition within the sampling probe and the observance of highly agglomerated fume particles in the ISP catch (which are likely an artifact of the sampling process). Previous attempts at sampling ISP experienced these difficulties [Mikkanen et al., 1999, 2001; Baxter et al., 2001]. The relatively large size of ISP particles, when combined with the high flow velocities in the furnace, make it difficult to successfully extract ISP particles from the flow. In addition, the high concentration of fume particles results in rapid deposition on probe surfaces and ISP particles as the extracted flow cools.

A schematic of the VIP probe is shown together with an engineering drawing in Fig. 17. In the schematic, the probe itself is oriented horizontally, perpendicular to the boiler side wall. The probe's coannular design makes it simpler than a bent probe to manufacture and to fit within a given size sampling port. The plate that is connected with spacers off the end of the probe serves to give the probe a nominally isokinetic sampling profile for any flow oriented tangential to the boiler wall (i.e., there is no alignment needed relative to the mean flow vector). In addition, the open flow space between the endplate and the main probe allows large carryover particles to inertially propagate past the entrance to the probe and to re-enter the main boiler flow. The angled inlet to the probe acts to "focus" the larger ISP particles, directing them towards the center of the probe. The subsequent rapid flow expansion and redirection into the outer annulus of the probe serves as a virtual impactor, pulling away most of the small fume particles from the larger ISP particles, whose inertia carries them into the central sampling tube. Within the central sampling tube, sintered metal sidewalls are used that are purged with nitrogen gas, decreasing the likelihood of fume agglomeration within the central tube and keeping the ISP particles from settling onto the probe wall. Shortly down this central tube, a filter collects the ISP particles for off-line analysis of total mass, size distribution, and particle morphology. To effectively design this probe, taking into account the flow characteristics in the upper furnace and the desired size split in the virtual impactor, calculations were performed using the CFX computational fluid dynamics (cfd) package with particle tracking capabilities. Based on the dimensions and flowrates used in the model of the probe and an assumed ambient flow at 850 deg C with a velocity of 9 m/s, the predicted capture efficiency of different sized particles is shown in Fig. 18.

Figure 17. Schematic (left) and 3-D engineering drawing (right) of the end of the "Virtual Impaction Probe." The long vertical arrows show the predominant direction of gas flow in the boiler. The dots represent ISP particles. In both figures, the green plate at the end of the probe is the endplate. The bright green band in the engineering drawing shows the location of the filter holder for collecting sampled ISP.

Figure 18. Calculated particle capture efficiencies for the modeled ISP sampling probe, when sampling into an 850 deg C flow at 9 m/s and pulling 47 cfm along the outer annulus of the probe and 3 cfm (+ diluent gas) along the centerline.

Laser Particle Counting

A custom-designed *in situ* laser particle counting system was developed for measuring ISP concentrations and size distributions in recovery boilers by Process Metrix LLC, as part of a separately funded project [Shaddix and Holve, 2004]. This technique relies on the application of Lorentz-Mie scattering theory to deduce the size of the particle, based on the magnitude of the near-forward laser scattering signal. This approach minimizes sensitivity of the measurement to non-spherical particle shapes. Particle velocities are determined using a time-of-flight calculation of the particle passage through the measurement volume. Variations in the particle trajectories through the laser beam require that the collected intensity signals be analyzed statistically to yield the overall concentration and particle size distribution, through a mathematical deconvolution procedure. The requirement that the preponderance of scattering events involve a single particle limits the number density of particles that can be effectively measured with this technique, depending on the laser focus width (and therefore the maximum particle size to be measured). The strong decrease in particle scattering strength with decreasing particle size also sets a minimum particle size that can be measured (for a given laser beam and detector configuration). To increase the overall size range that can be measured with this technique, a dual laser beam configuration can be used, with one laser's focus much tighter than the other.

The uncertainty in the laser particle counting measurement was evaluated by two means. First, comparing the scattering signal strength through optical reticles before and after each sampling campaign gave an average deviation of 6% from the nominal diameter (equating to an 18% deviation in volume or mass). Second, mass balance tests were performed with Portland cement in a room temperature flow cell as well as in an elevated temperature flow reactor. The overall mass balance for these tests was 84%, with a variance of $\pm 17\%$. This level of error and variance in the laser particle counting mass measurements is consistent with the reticle results and estimates of particle size calibration and density errors. The variance in these mass balance tests was due primarily to $\pm 5\%$ laser diode power variation and the use of non-spherical cement particles.

Impaction Plate Sampling

To collect individual ISP particles for SEM analysis and for comparisons with particle counting measurements of ISP, a 10-foot long probe was constructed onto which a 1.85-inch diameter stainless steel sampling plate could be mounted for insertion into the boiler (see Fig. 19). Through trial-and-error, it was determined that the optimum sampling time varied from 10 seconds in the upper furnace and superheater banks to 30 seconds at the generator bank and economizer. Exposure for longer periods of time resulted in overlapping particle impactions and, in the upper furnace, partially melted deposits. The collected impaction samples were examined using both optical microscopy and, for a few samples, scanning electron microscopy (SEM). Manual particle counting and sizing was performed on some of the collected images from the optical microscopy and the Image Pro Plus commercial software package was used to determine size distributions from the SEM images. Energy dispersive x-ray spectroscopy (EDX) was performed in concert with SEM for different size ISP particles on samples collected in the upper furnace. The EDX technique measures the relative atomic composition of the material interrogated by the focused x-ray beam. Because this beam only penetrates a few micrometers in depth into the material, care had to be taken to only consider those deposited ISP particles that did not have fume particles coating the surface. The Courtland boiler samples had a number of such particles deposited, whereas identification of fume-free particles was difficult for the samples from the Longview boiler. Consequently, only the EDX results from the Courtland boiler showed variations in particle chemistry relative to fume.

Quantitative analysis of ISP particle size distribution concentration from the impaction samples was complicated by impaction efficiencies that vary from zero for the smallest ISP to nearly one for the larger ISP, and by uncertainty in the sticking coefficient of the particles onto the plate surface. Interrogation of a number of impaction plates suggested that once a layer of fume has coated the steel plate, the sticking coefficient is nearly one, at least for particles in the ISP size range. This conclusion is based on the observation of relatively few locations where the fume deposit was diminished or removed completely upon impaction and rebound of a particle. A literature review was conducted for impaction efficiency onto round, flat plates. Surprisingly, no directly applicable analysis was identified. However, a number of studies have been conducted of impaction onto long flat ribbons, as are used in some particulate capture devices. A classic study of this type [Langmuir and Blodgett, 1946] provides the most easily usable information, in the form of impaction efficiency curves as a function of the inertial separation number. Applying “typical” flow conditions at the thermoprobe port during the sampling at Longview ($T = 850\text{ }^{\circ}\text{C}$, $v = 9\text{ m/s}$) and an assumed particle density of 2.6 g/cm^3 (appropriate for nonporous Na_2SO_4), the impaction efficiency drops to zero for particles less than $14\text{ }\mu\text{m}$ in diameter. The complete curve of impaction efficiency versus particle size is shown in Fig. 20. Of course, considerable variability is evident in the flow velocity and temperature in this region of the boiler, and high-resolution SEM images suggest that the smaller size portion of ISP particles is composed of fume particle aggregates, with some open space within the aggregates. Hence, at least for some particles and/or size ranges, the impaction curve should be shifted to the right, as indicated in Fig. 20 for the case of an apparent particle density of 1.5 g/cm^3 and a velocity of 6 m/s .

Figure 19. Photographs of the stainless steel sampling plate at the end of a 10-foot long probe used to collect particle samples from the boiler flow. The photo on the left shows the clean, unexposed probe next to a ruler marked in inches. The photo on the right shows the probe and plate after exposure to the upper furnace flow at Courtland.

Figure 20. Calculated inertial separation number and resultant impact efficiency onto the impaction disk as a function of particle size. The efficiency curve with filled circles is for baseline flow and particle conditions, whereas the curve with open squares is for a low impaction condition.

Fume Mass Probe

At Longview, no direct measurements of fume mass were performed during the ISP sampling campaign. An indirect measurement was provided by the constant attenuation level of the 670 nm laser light as it crossed the flow-through sampling slot in the laser particle counting probe. Detailed size distribution and fume mass measurements from the Longview boiler were previously obtained in December 1999 [Baxter et al., 2001]. At Courtland, a water-cooled, nitrogen-purged bent-nosed probe previously used for particulate sampling at Longview [Baxter et al., 2001] was used to measure the fume mass concentration. Based on previous experience, it was recognized that the water cooling in this probe was insufficient to allow it to be inserted and maintained at a significant depth into the upper furnace. Also, previous experience had demonstrated that a significant fraction of the sampled particle mass would deposit onto the probe walls. Therefore, sampling occurred with an insertion depth of 1-2 ft and distilled water was used to perform a thorough wash-out of the inner probe tube and filter holder after collection of each filter sample. An ion chromatography analysis of the probe wash was combined with the measured filter weight to determine the total sampled particle mass. To specifically discriminate against sampling ISP particles, the measurements were performed near the top of the upper furnace, where ISP concentrations are relatively low (as verified by impaction plate samples), and the probe sampling flowrate was purposefully set to be strongly non-isokinetic.

Thermocouple and Pitot Tube Probe

For sampling at Longview, separate, uncooled thermocouple and pitot tube probes were used to assess the mean temperatures and flow velocities at any given sampling port. Because the probes were uncooled and therefore tended to droop after prolonged exposure to the high-temperature flow, these measurements did not provide reliable information as a function of insertion depth or sampling time. At Courtland, a water-cooled pitot tube probe, with an accompanying thermocouple, was used to simultaneously record the flow velocity and temperature at a given insertion depth (1 m and 2 m insertion depths were used). Datasets were captured with the pitot tube turned in 45 degree increments to establish the flowfield variation and turbulence levels throughout the plane direction parallel to the boiler wall.

Longview Sampling Results

Sampling campaigns were conducted at the Longview boiler in November 2000 and May 2001. Four separate sampling ports were utilized: (a) the thermoprobe port just above the nose arch and before the entrance to the superheaters, (b) an enlarged inspection port in the mid-superheater, (c) an enlarged inspection port just before the entrance to the boiler bank, and (d) a man-door just before the entrance to the economizer (see Fig. 21). All of these ports were located on the right side of the boiler. Measurements were obtained at insertion depths of one and two meters into the boiler flow.

Figure 21. Diagram showing location of four sampling ports used at Weyerhaeuser's Longview boiler.

Impaction plate samples showed much higher concentrations of ISP and carryover particles in the superheater region than further back in the convection pass. Particles in the ISP particle size range (from a few μm up to $100\ \mu\text{m}$), tended to deposit as spherical particles, except for a trend of the larger particles in the superheater region appearing as ellipsoids (presumably because they still were partially molten when they struck the impaction plate). The smallest ISP particles ($< 10\ \mu\text{m}$) most often appeared to consist of super-agglomerates of submicron fume (see Figs. 22-23).

Figure 22. Optical microscopy of impaction plate samples from a 10-s exposure in front of the superheater at the Longview boiler. The magnification of the images is 7.5X on the left and 30X on the right, with the corresponding length scales indicated. Dark regions indicate where impaction of a carryover particle has removed the coating of fume from the steel plate.

Figure 23. SEM photomicrographs of ISP particles captured on an impaction plate during a 10-s exposure in front of the superheater at the Longview boiler. The magnification of the images increases left to right from 100X to 500X to 5000X, with the corresponding length scales indicated. Background fume particles are discernable at the higher two magnifications.

The laser particle counting measurement of ISP particles at Longview showed strong temporal variations in the overall particle concentration (particularly at the large particle end of the ISP distribution) when sampling through the thermoprobe port at the entrance to the superheater. Particularly strong temporal variations and higher overall ISP concentrations were evident at the ports in the convection pass when the sootblowers were active (see Fig. 24), suggesting that the action of the sootblowers in removing deposits also creates particles in the ISP size range. To better explore this phenomenon in front of the superheaters, where there was particular interest in characterizing the ISP (for deposit modeling purposes), an extensive set of measurements was performed with the sootblower cycle operating as usual and another set was performed with all of the sootblowers turned off. Whereas even at this location it was observed that the ISP particle loading is sensitive to local operation of sootblowers, the average ISP loading in front of the superheaters was found to be insensitive to the operation of the sootblowing cycle.

Figure 24. Size-integrated mass loading of ISP particles, in 5-minute averages, as a function of sampling position in the Longview recovery boiler.

It is also apparent from Fig. 24 that the mass loading of ISP decreases rapidly through the convection pass (as a consequence of particle deposition). The mean concentration of ISP measured at the entrance to the superheater was $\sim 1 \text{ g/Nm}^3$ (i.e., 1 gram of ISP mass per cubic meter of gas at “normal” conditions of 1 atm and 20 °C). The earlier sampling campaign at Longview [Baxter et al., 2001] consistently measured a fume concentration of 10 g/Nm^3 . The measured laser extinction when performing the particle counting measurements corresponds to a fume concentration of $5\text{-}10 \text{ g/Nm}^3$, depending on the assumptions one makes. Therefore, the average ISP mass loading in the upper furnace was $\sim 10\%$ that of fume.

Analysis of impaction plate samples from the Longview boiler showed good agreement with the laser-based measurements of size distribution and total particle concentrations, at least for particles greater than $30 \mu\text{m}$ in size, once the impaction data had been corrected for the size-dependent impaction efficiency. This comparison is shown in Fig. 25. As shown previously (Fig. 20), the calculated impaction efficiency drops rapidly to zero for particles smaller than $30 \mu\text{m}$, although smaller particles than this were observed on the impaction plates (indicative of the importance of other deposition mechanisms for particles in this size range).

Figure 25. Comparison of laser counting data for mass size distribution of ISP particles at the thermoprobe port of the Longview boiler (labeled “PPC data”) with particle analysis from SEM images of impaction plate sample. The filled symbols show the results of applying a deposition efficiency correction to the impaction data, based on the calculations shown in Fig. 20.

Courtland Sampling Results

Sampling at the Courtland boiler was conducted in August 2002. Except for the fume mass measurement (near the top of the furnace), measurements at Courtland were limited to two man-doors along the front wall at the maintenance beam level (just above the nose arch). The laser particle counting diagnostic included two different laser beams at Courtland, allowing measurements to be made in the same 5-100 μm detection window used at Longview as well as a 1.2-2.1 μm detection window. Measurements were obtained at insertion depths of one and two meters into the boiler flow. Complete air duct profiling and liquor and fly ash chemical analyses were also performed during the Courtland measurement campaign, to assist in setting up B&W's comprehensive boiler model.

Optical microscopy images of an impaction plate sample collected from Courtland are shown in Fig. 26. In comparing to the images of the impaction plate samples from Longview, the same mix of carryover particles and ISP is seen. In general, the impaction plate samples from Courtland showed a higher density of ISP particles than the samples collected from the thermoprobe port at Longview. This is consistent with the laser particle counting results (presented below).

SEM-EDX analysis of selected, fume-free ISP and small carryover particles showed a strong sensitivity of particle chemistry to particle size, as shown in Fig. 27. In particular, the evolution from fume particles, where the more volatile inorganics (esp. chlorine and potassium) are strongly enriched, to ISP particles, where the more volatile inorganics are preferentially volatilized (and therefore depleted, relative to the black liquor source), is striking. At still larger particle sizes, the degree of depletion is diminished. The sulfur content is also decreased in ISP and carryover relative to fume, indicating substantially greater carbonate content in these particles.

Figure 26. Optical microscopy of impaction plate samples from a 10-s exposure at the maintenance beam level at the Courtland boiler. The magnification of the images is 10X on the left and 30X on the right. The appropriate length scale for the 30X image is shown in Fig. 22.

Figure 27. SEM-EDX analysis of impaction sample particle chemistry as a function of particle size. The data at 1 μm is for fume particles.

The fume mass extraction probe measured a fume mass loading of 7.3-8.0 g/Nm^3 near the top of the upper furnace. In these samples, 46-47% of the measured mass was on the sample filter and the remainder of the mass deposited on the inner walls of the probe and filter holder.

During the use of the VIP probe, an unexpectedly rapid build-up of particles occurred on the sample filter. Visual inspection suggested that most of the collected mass was in fact fume particles, as opposed to ISP. Subsequent analysis with optical and electron microscopy confirmed that the ISP particle concentration collected on the filters was insignificant in comparison to fume (see Fig. 28). Analysis of the pressure and temperature readouts from the critical flow orifice flow control system that monitored the suction flow down the center of the probe (into the filter, which was located just a few inches down the probe) showed that ~75% of the nitrogen purge gas that was being introduced into the central region of the probe was actually being pulled forward toward the sample end of the probe and then out through the annular suction flow (see Fig. 17). After correcting for this, the estimated particulate concentration (representing fume and particles < 50 μm) was found to be 9.0–10.5 g/Nm^3 . These values are consistent with the fume and ISP concentrations measured (with better accuracy) by the fume sampling probe and the laser particle counting probe, respectively.

Figure 28. SEM photomicrographs of particulate collected on a silver filter along the center of the VIP probe. Photo on left shows a few small ISP particles scattered on matrix of fume. Photo on right shows fume particles.

The laser particle-counter measurements at the maintenance beam level of the Courtland boiler showed many of the same characteristics as at the Longview boiler, including a strong temporal variation. As shown in Fig. 29, the data from the Longview boiler suggest a size distribution peak between 10-20 μm , but the data from Courtland do not show this. Rather, the Courtland data show that the ISP particle mass loading increases with increasing size to at least 100 μm . Also, the small laser beam data show that the falloff from the fume mass peak continues out to 2 μm before the ISP particle distribution begins. The size-integrated ISP concentrations from Courtland span a nearly identical range as was found for the upper furnace of the Longview boiler and have a mean of $\sim 2 \text{ g/Nm}^3$. The temporal variation of the total ISP mass concentration at Courtland is shown in Fig. 30. This variation was compared to the sootblower record and to strain gauge readouts of the accumulated deposit mass in the superheater, but no consistent trends were observed. In contrast to the strong variation in ISP particle mass as a function of time, the particle mass from 1.2-2.1 μm measured by the small laser beam is almost constant in time, having a value of $0.8 \pm 0.15 \text{ g/Nm}^3$. This trend supports the conclusion that the particles in this size range represent the large-particle end of the fume particle distribution, and are not formed in the same manner as the larger ISP particles.

The measured ISP particle concentrations can be converted to the equivalent percentage of black liquor dry solids loading, for comparison with the results from the drop combustion and char bed combustion studies, if the assumption is made that the concentration of ISP particles is relatively uniform across the flow cross-section of the boiler (at least at the thermoprobe and maintenance beam measurement locations). To make the conversion from ISP mass loading per unit flow volume to total ISP mass relative to the fired mass, information is needed about the molecular weight of the flue gas (or really, of the gas in the upper furnace) and the mass of flue gas produced per mass of black liquor consumed. Using the typical recovery boiler flow parameters for a 70 wt-% solids liquor that were reported by Adams [1997], a particle mass concentration of 1.0 g/ Nm^3 corresponds to 0.50 wt-% BLS (as fired). Based on the mass balance for the Courtland boiler calculated from the operations data (reported below), 1.0 g/ Nm^3 corresponds to 0.45 wt-% BLS (as fired) or 0.48 wt-% BLS (virgin). Therefore, the ISP mass data from Courtland and Longview show typical values between 0.3-1.5% BLS.

Figure 29. Mass size distribution of entrained particles as determined with the dual-laser particle counting diagnostic during 5-minute data collection periods at the Courtland recovery boiler. The thick line is the median dataset from the Longview thermoprobe port.

Figure 30. Time record of total mass concentration of ISP particles during successive 5-minute data collection periods at the Courtland recovery boiler, as determined by the laser particle counting diagnostic.

Recovery Boiler Modeling

Methodology

Comprehensive modeling was performed for both the Longview and the Courtland boilers using B&W's combustion model, COMO-PR. The model solves steady, three-dimensional, turbulent flow, heat transfer, and black liquor combustion in a recovery boiler. The model predicts:

- combustion of black liquor spray and char deposits on the furnace walls and char bed
- release of sodium, sulfur, potassium and chlorine
- quantity and composition of inorganic material (including carryover, ISP, and submicron fume) leaving the furnace
- distribution of gas velocity, temperature and chemical composition in the furnace and convection pass
- distribution of convection and radiation heat transfer to the furnace walls and convection surfaces (tube banks)
- particle deposition and adhesion and deposit thermal properties

Sub-models for particle formation and deposition were implemented in the comprehensive model, and these modeling capabilities were previously described and demonstrated [Wessel et al., 1998; Wessel & Verrill, 1998; Verrill & Wessel, 1998; Wessel & Baxter, 2003; Baxter et al., 2004]. No additional algorithms for particle formation were developed during this project.

Particle Formation Sub-models

Of the particle formation processes in a recovery boiler, carryover formation is perhaps best understood and most accurately modeled. However, additional work is needed to characterize the inorganic reactions needed to predict carryover composition, liquid content, and sticky temperature. Fume formation is not as well understood due to the complexity of vaporization-condensation, aerosol dynamics, and sulfur scavenging from the flue gas. Sub-models for fume formation are perhaps capable of predicting the quantity of fume, but have greater difficulty predicting fume composition and chemical reactions.

ISP formation is the least understood of the three classes of particulate, although significant progress has been made in this project in measuring ISP concentrations in operating recovery boilers [Wessel et al., 2004] and measuring the quantity of ISP formation during black liquor combustion of droplets [Baxter et al., 2004b] and during char bed combustion [Lien & Verrill, 2004]. Sub-models for ISP formation have not been formulated, with the exception of a pre-existing model for physical ejection [Verrill & Wessel, 1998]. However, there are significant differences in experimental technique and quantitative results for ISP formation during droplet combustion between earlier measurements [Verrill et al., 1994] and more recent measurements [Baxter et al., 2004b], which brings the accuracy of the pre-existing sub-model into question. However, fundamental understanding gained by experimental work to-date may be sufficient to quantify the sources of ISP and to propose mechanisms for ISP formation in a recovery boiler, but it is not sufficient to develop sub-models to describe these processes.

Inorganic transformations may have a large effect on the quantity and composition of ISP from the time they are initially formed, to the point where they have been measured in the upper furnace and convection pass. The large surface area-to-volume ratio of ISP enhances heat and mass transfer with surrounding gases, promoting the occurrence of chemical reactions. For example, sulfide oxidation and carbonate decomposition are competing exothermic and endothermic reactions, respectively, and may regulate the temperature of ISP and carryover. Particle temperature has a significant effect on the rate of chloride vaporization, for which mass transfer is also enhanced by the large surface area.

As part of this project, carbonate decomposition was investigated as a possible mechanism for ISP destruction in the recovery furnace. Sodium and potassium carbonate decomposes by a combination of the following global reactions starting at about 1100°C, based on multiphase chemical equilibrium calculations:

where M = Na or K. Gas temperatures greater than 1100°C exist over a significant volume of the lower furnace. ISP is also expected to reach these temperatures due to the enhanced ability of small particles to exchange heat with the gas. If ISP is formed during combustion in the lower furnace, then potentially all of the carbonate (composing 40 to 60% of the weight of the initial inorganic material) could be destroyed before it reaches the convection pass of the boiler. The kinetic rates for these reactions have not been measured, to our knowledge, so the kinetic limited rate of decomposition of carbonate cannot be predicted.

Finally, the formation processes of all three classes of particulate are highly interdependent. Inorganic transformations and chemical reactions of carryover and ISP are potentially a significant source of alkali vapors, which lead to fume formation. Particle-to-particle interactions, such as aerosol agglomeration and fume deposition on the surface of ISP and carryover particles, may affect the size, sticky temperature and deposition behavior of these particles. These processes are not adequately described by existing sub-models.

Longview Operating Data

The Weyerhaeuser Longview (WA) recovery boiler is a B&W boiler, with an original design capacity of 3.6 million lb/day virgin dry solids, and furnace cross section of 36' 2" wide by 31' 10" deep. The convection pass consists of a boiler screen that extends out from the furnace arch, small pendant steam superheater, cross-flow generating bank (two-drum design), and a cross-flow economizer with baffles. In December 1999, Sandia National Laboratories conducted a series of measurements to characterize ash particles in the recovery boiler [Baxter et al., 2001; 2004c]. Samples of gas entrained particulate were extracted from the furnace and convection pass to characterize the particle size and concentration. In addition to particle sampling, the tests included measurement of gas composition, gas velocity, and temperature in various locations of the boiler.

Extensive boiler operating data were collected for the Longview boiler for several months prior to the measurement campaign, and for several days in association with the campaign. Table 1

gives a summary of average operating conditions recorded from the digital control system (DCS) and Table 2 gives the chemical compositions of the virgin and as-fired black liquor. When performing mass and energy balances on the boiler, several inconsistencies were identified in the DCS readings. After several iterations, the most consistent and justifiable correction to the DCS data seemed to be on the basis of the measured boiler feedwater flow. With this correction, the boiler was assumed to be operating at a load of 4.8 million lb/day virgin solids, whereas the measured liquor flow indicated a load of 4.5 million lb/day and a correction based on the measured steam flow yielded a firing rate of 5.4 million lb/day. These differences are substantial, and lead to differences in the modeled temperature and velocity distributions in the boiler.

Table 1. Average and Corrected Recovery Boiler Operating Conditions

	Average DCS Balance Summary Data	Average DCS Dec. 7-13, 1999 Boiler Testing	Corrected Based on Measured Steam Flow	Corrected Based on Measured Feedwater Flow ²
Steam Temp. (°F)	678 °F	692	678	678
Steam Flow (1000 lb/h)	755	760	755	679
Blow Down (1000 lb/h)	33	29	33	33
Feed Water (1000 lb/h)	712	707	788	712
Firing Rate (lb/day virgin)		4.49×10^6	5.40×10^6	4.83×10^6
Liquor Flow (gpm)	411	398	489	437
Solids (%)	73.2	73.1	72.6	72.6
Temperature (°F)	259	259	259	259
Air Flow (1000 lb/h)	912	868	954	821
Excess O ₂ (mol %, wet)	2.4	2.2	2.72	2.2

² Conditions used in the comprehensive model (Rev 1)

Table 2. Longview Black Liquor Analyses

Sample		Virgin ¹	As Fired ²	As Fired ³
Solids	% wt BL	70.80	72.60	72.20
HHV	Btu/lb BLS	5621	5143.2	5270
C	% wt BLS	33.23	30.41	31.28
H	% wt BLS	3.08	2.82	2.67
N	% wt BLS	0.07	0.06	0.07
S	% wt BLS	5.12	6.46	5.60
Na	% wt BLS	19.75	20.60	22.23
K	% wt BLS	1.68	1.89	1.59
Cl	% wt BLS	0.67	0.90	0.73
Inerts	% wt BLS	0.00	0.00	0.00
O (by diff)	% wt BLS	36.40	36.86	35.83
		100.00	100.00	100.00

1) Average of virgin BL analyses from 3/98 through 6/99.

2) Calculated from virgin BL assuming 8.5% ash recycle

3) Average of as-fired BL analyses from 12/10/99 and 12/14/99

Longview Modeling Results

Figures 31 and 32 show predicted gas velocity and temperature distributions for the center plane of the Longview furnace and convection pass. Higher velocities are predicted near the front and rear walls of the furnace, with the highest velocity near the tip of the furnace arch. No recirculation is present above the small arch in this boiler. Consequently, flow and temperature distributions are fairly uniform through the screen, pendant superheater, and generating bank. The flow cascades through the baffles of the economizer and exits through the economizer gas outlet. Predicted gas temperatures are in reasonable agreement (46°C higher) with DCS measurements of 363°C at the generating bank outlet, and are in good agreement (6°C lower) with DCS measurements of 194 °C at the economizer outlet.

Figure 33 shows predicted gas temperature distributions for horizontal planes at the inspection doors where measurements were taken. Figure 34 compares measured and predicted gas temperatures as a function of distance from the front wall. Predicted gas temperatures in the upper furnace were consistently higher (by about 150 °C) than measured values at inspection doors on the front wall (floors 6, 7, and 8). Measured values may be low because they were made with a large, bare thermocouple, without any shielding or correction for radiation exchange with the furnace walls. Another cause for the disparity may be the uncertainty in the liquor firing rate. Both measurements and modeling predictions show that the gas temperature is higher on the left side of the furnace, and the temperature imbalance decreases with furnace elevation (Figure 33).

Model predictions for fume and ISP concentrations are based on pre-existing algorithms for particle formation [Wessel & Verrill, 1998]. Predicted fume concentrations in the upper furnace and convection pass are in good agreement with measured values (from 10-11 g/Nm³) [Baxter et al., 2001]. Predicted ISP concentrations are in the range of 7-8 g/Nm³, whereas extractive probe measurements in 1999 suggested ISP mass loadings around 1 g/Nm³, similar to the concentrations measured in the subsequent laser-based measurements.

Figure 31. Predicted center-plane distributions of gas velocity for Longview boiler, per operating conditions of Dec. 1999.

Figure 32. Predicted center-plane distributions of gas temperature for Longview boiler, per operating conditions of Dec. 1999.

Figure 33. Predicted gas temperature distribution at horizontal planes through the centerline of inspection doors at three elevations, for Longview recovery boiler, per operating conditions of Dec. 1999. Thermocouple measurement locations are indicated by crosses.

Figure 34. Comparison of measured and predicted gas temperatures for Longview recovery boiler, per operating conditions of Dec. 1999.

Table 3 shows the predicted composition of carryover, ISP, and fume, and measured composition of the electrostatic precipitator (EP) dust. Carryover and ISP are depleted in potassium and chlorine, while fume is enriched in these elements, consistent with data from SEM-EDX of particle deposition coupons collected in 2001 (reported elsewhere in this report). However, the predicted fume composition is lower in chloride and carbonate, and higher in sulfate than that measured in the EP dust, and the complete depletion of chlorine predicted for carryover and ISP contrasts with the SEM-EDX measurements, which give Cl enrichment factors of 0.7-0.9 for these particles. The model predicts SO₂ and HCl emissions of 0 ppm and 158 ppm, respectively. Therefore, about 70% of the chlorine that leaves the boiler model is still in the flue gas, and the remainder is captured in the ash. DCS measurements show SO₂ was negligible (2.3 ppm) and the EP dust analysis reveals that more chlorine was captured in the ash. The differences are attributed to uncertainties in predicted sulfur release during black liquor combustion. With less sulfur release, model predictions for chloride and carbonate in the ash should be in closer agreement with the data.

Figure 35 shows the predicted overall particle deposition rate, peaking at about 2 kg/h-m² in the superheater and decreasing to 0.05 kg/h-m² in the generating bank and economizer. Deposition by carryover and ISP does not extend beyond the gas temperature contour of about 750°C, because impacting particles do not stick after they solidify near that temperature. Fume deposition extends throughout the convection pass, and is higher in regions of high gas velocity around bends of the economizer baffles.

Table 3. Measured and Predicted Particle Composition for Longview Boiler

Constituent (wt %)	Carryover (predicted)	ISP (predicted)	Fume (predicted)	EP Dust (measured)
Sulfate (SO ₄)	29.64	58.2	64.8	46.4
Sulfide (S ⁻)	0.31	0.0	0.0	0.0
Carbonate (CO ₃)	30.69	7.4	0.1	12.1
Sodium (Na)	36.61	32.3	29.6	29.1
Potassium (K)	2.69	2.1	4.1	3.6
Chlorine (Cl)	0.07	0.0	1.5	3.0
K Enrichment (mol/mol)	0.81 0.04	0.71 0.00	1.48 1.09	1.33 2.32
Cl Enrichment (mol/mol)

Figure 35. Predicted center-plane mass deposition rate for Longview boiler, per operating conditions of Dec. 1999.

Courtland Operating Data

The International Paper Courtland (AL) recovery boiler is a B&W boiler, with a design capacity of 4.0 million lb/day virgin dry solids, and furnace cross section of 32' 11" wide by 36' 5" deep. The convection pass consists of pendant primary and secondary steam superheater banks, boiler screen, longitudinal-flow generating bank (single drum design), and two longitudinal flow economizer banks. In August 2002, Sandia National Laboratories conducted measurements for several days to characterize ash particles, primarily sampling through two maintenance beam doors near the furnace arch (as described in detail elsewhere in this report). Samples of gas aerosol (fume) were extracted to characterize the dust loading and laser diagnostics and impaction samples were used to characterize the particle size and concentration. In addition to particle sampling, the tests included measurement of gas velocity and temperature.

Boiler operating data were gathered for the Courtland recovery boiler during the August 2002 measurement campaign. However, as with the Longview boiler, inconsistencies between measurements of air, liquor, and steam flow had to be resolved to estimate the operating conditions at the time of the test. The best-estimate boiler load was 3.9 million lb/day virgin solids, based on measured steam flow. The complete operating conditions are summarized in Table 4. The black liquor and electrostatic precipitator (EP) ash composition from Courtland is shown in Table 5.

Table 4. Courtland Recovery Boiler Operating Conditions, August 2002 Test

Firing Rate	
Virgin DS Flow Rate	3.88×10 ⁶ lb/day (1,761 t/day)
As-Fired DS Flow Rate	4.15×10 ⁶ lb/day (1,884 t/day)
Liquor Delivery	4 B&W Splash Plate Nozzles
Nozzle Arrangement	One nozzle centered on each wall
BL Solids Content	70.6%
BL Temperature	260°F (127°C)
Nozzle Pressure	17 psig (117 kPa)
Air Delivery	B&W 3-level Air system
Total Air Flow	740,000 lb/hr (335,600 kg/hr)
Air Flow Distribution	Pri 38.3%, Sec 35.4%, Ter 26.3%
Boiler Steam	Single-Drum Design
Steam Flow Rate	530,000 lb/hr (240,400 kg/hr)
Steam Temperature	900°F (482°C)
Steam Pressure	1270 psig (8.756 MPa)

Table 5. Courtland Black Liquor and EP Ash Analyses

	Virgin Liquor	As-Fired Liquor
Chemical analysis (wt % d.s.)		
Total sulfur	6.69	7.10
Sulfate sulfur	4.54	4.64
Carbon	31.8	31.7
Hydrogen	3.8	3.6
Nitrogen	0.11	0.13
Sodium	21.5	21.5
Potassium	1.89	1.89
Chloride	0.42	0.44
Dry solids (%)	70.5	70.6
HHV (Btu/lb d.s.)	5480	5340
EP Ash		
Chemical analysis (wt %)		
Sodium	27.8	
Potassium	4.05	
Chloride	1.54	
Sulfate	58.8	
Carbonate	2.9	

Courtland Modeling Results

Modeling results for the Courtland boiler were subject to the uncertainties in boiler operating conditions (particularly air flow and liquor spray distribution). Char bed combustion predictions were sensitive to liquor spray conditions (velocity and droplet size) which were difficult to estimate with black liquor flashing at the nozzles. With an initial set of assumptions for black liquor spray, the model predicted blackout conditions and excessive accumulation on parts of the bed, leading to incomplete combustion and insufficient heat release in the lower furnace (for which there was no evidence during the measurement campaign). With slightly different assumptions for the extent of black liquor flashing (vapor formation inside the nozzle and the effect on spray velocity), char bed combustion improved and predictions were in better agreement with measured values. These latter results are described in this report.

Figures 36 and 37 show predicted gas velocity and temperature distributions at the center plane of the Courtland furnace. Higher velocities are predicted near the front wall of the furnace, as the flow accelerates upward past the furnace arch. Flow and temperature distributions are influenced by a large recirculation zone above the arch; however, they become more uniform as the gas crosses the last bank of superheater tubes and screen tubes, near the entrance of the generating bank. The flow accelerates around several sharp turns as it snakes through the longitudinal sections of the generating bank and economizer. The predicted gas temperature at the economizer outlet was 31°C lower than the DCS measurement of 195°C.

Figure 38 compares measured and predicted velocity, temperature, and particle concentrations at a horizontal plane at the center of the maintenance beam doors. Predicted gas temperature and velocity (left side of figure) are in reasonably good agreement with measured values. The scarcity of measurement locations and separate timing of these measurements makes it difficult to verify the distribution in temperature and velocity in this boiler. Predicted fume concentration was consistently lower than measurements, whereas predicted ISP concentration was much higher.

Detailed model predictions of ash and flue gas composition are not presented due to unresolved disparities between measured and predicted values. The model predicts SO₂ emission of 645 ppm and HCl emission of 84 ppm in the flue gas (wet basis). Field measurements showed SO₂ emission was negligible (0.3 ppm) and chlorine was captured in the ash. These disparities are attributed to low bed temperatures, under predicted fume concentration, and uncertainties in predicted sulfur release.

Figure 39 shows the predicted overall particle deposition rate, peaking at about 1kg/h-m² in the superheater and decreasing to 0.03 kg/h-m² in the generating bank and economizer. Deposition by carryover and ISP does not extend beyond the gas temperature contour of about 750°C, because impacting particles do not stick after they solidify. Fume deposition extends throughout the convection pass, and is higher in regions of high gas velocity around bends of the generating bank and economizer baffles.

Figure 36. Predicted center-plane distributions of gas velocity for the Courtland boiler, per operating conditions of Aug. 2002.

Figure 37. Predicted center-plane distributions of gas temperature for the Courtland boiler, per operating conditions of Aug. 2002.

Figure 38. Comparison of measured and predicted conditions at the horizontal plane through the centerline of the maintenance beam doors for Courtland boiler, per operating conditions of Aug. 2002.

Figure 39. Predicted center-plane mass deposition rate for Courtland boiler, per operating conditions of Aug. 2002.

Conclusions

Comprehensive modeling results for Courtland and Longview recovery boilers exhibited similar trends and disparities between measured and predicted values of ISP and fume particle concentrations. Existing algorithms significantly overpredict ISP concentration (near the furnace exit), moderately underpredict fume concentration in some cases, and have difficulties predicting associated sulfur capture and chlorine enrichment in the ash. Although experimental investigations have successfully quantified ISP formation rates and concentrations in the boiler, rational sub-models cannot be developed without a better understanding of the mechanisms of ISP formation. The destruction of ISP (conversion to fume) in the furnace may also play a significant role, but the chemical kinetics for some key reactions have not been measured.

Comprehensive modeling of particle formation and deposition was useful as a forensic tool for explaining experimental observations and evaluating potential ISP formation mechanisms. However, modeling has not yet been developed to the level of sophistication needed to predict the behavior of convection pass deposits accurately. Although ash deposition predictions are insightful, they cannot be analyzed or interpreted with any confidence until rational sub-models for ISP formation and destruction are developed. Sub-models are also needed to describe experimentally observed fume deposition rates, deposit properties, and potential interaction with ISP particles. Field data gathered on this project will be valuable for testing new algorithms, for validating modeling results, and for improving our understanding of particle formation and deposition processes.

Conclusions

This project focused on gaining an understanding of the sources, characteristics, and deposition of particles intermediate in size between submicron fume and carryover in recovery boilers

Laboratory experiments on suspended drop combustion of black liquor demonstrated substantial generation of intermediate size particles (1-100 μm), with most of the mass ejection appearing to occur during the char burning and smelt oxidation phases. Substantial drop-to-drop variations in ISP formation were observed. Cyclone collection of the accumulated ISP mass, following successive combustion of 40-50 drops, yielded an ISP mass production rate of 0.4-1.8% of the initial dry solids (for liquors with 70 wt-% dry solids).

Cyclone collection of ISP above a laboratory char bed combustion rig yielded very small amounts of particle mass, most of which appeared to be agglomerated fume. The total amount of particulate that accumulated on the walls of the transfer tubing and the cyclone was significant, however, amounting to 0.3-2.5% of black liquor solids. Direct filter capture of particles exiting the char bed burner suggested that fume particles predominate. Therefore, it appears that ISP particle generation from burning char beds is minor, at least in the absence of the strong air jet shearing action that occurs in full-scale recovery boilers. Similarly, the recent drop size measurements conducted by the Helsinki University of Technology on modern, high-solids black liquor sprays suggest that direct spray production of ISP is inconsequential.

Laser-based and impaction plate measurements of ISP in two representative U.S. recovery boilers showed the ISP mass to be highly variable in time (in contrast to fume mass) and to average about 0.5 to 1% of black liquor solids. The ISP mass size distribution generally increases with size from 3-100 μm . The amount of ISP decreases rapidly from the upper furnace through the convection pass (evidence of particle deposition), though sootblowing appears to generate ISP (from the dissolution of steam tube deposits) within the convection pass. Scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDX) showed that ISP particles are depleted in potassium and chlorine, and, to a lesser extent, sulfur.

Comprehensive boiler modeling was performed on the two sampled recovery boilers. Comparisons of measurements of gas temperature, velocity, and fume concentration in the upper furnace showed good agreement with modeling results, once anomalies in the boiler operation data had been rectified. ISP concentrations in the upper furnace were substantially overpredicted when using a previously developed mechanism to describe ISP formation from droplet combustion. Chlorine depletion in ISP is predicted to be absolute.

Further research is required to develop robust, accurate rate equations for ISP production from black liquor drop combustion and char bed combustion (to the extent it is a significant source). Improved control of ISP production is likely possible (based on the observed variances in ISP production during drop combustion and in the recovery boilers) and is likely achievable through optimization of spray parameters and the air distribution in the lower furnace.

Technology Transfer

The results of this project were disseminated to the pulp and paper industry in a number of ways during the course of this project:

- Interim results of this project were presented on two occasions at the University of Toronto, Pulp & Paper Center, Annual Research Review Meeting, Toronto, Ontario, Canada in November 2001 and 2002. Participants of these meetings included consortium members from several pulp and paper companies, equipment suppliers, and industry consultants. These meetings provided valuable feedback from industry which helped guide the direction of this project.
- The status and results of this project were also presented annually to the American Forest and Paper Association (AF&PA) Agenda 2020 Energy Performance Committee.
- Additional presentations on this project were made at the following technical conferences:
 - United Engineering Foundation conference on Behavior of Inorganic Material in Recovery Boilers, held in Bar Harbor, ME, June 2000
 - International Chemical Recovery Conference, held in Whistler, BC, June 2001
 - Black Liquor Colloquium, held in Park City, UT, May 2003
 - TAPPI Paper Summit 2004, held in Atlanta, GA, May 2004
 - International Chemical Recovery Conference, held in Charleston, SC, June 2004
- Results of this project are documented in several technical publications, authored by the principal investigators or their colleagues. These papers are referenced throughout this report and included in the List of References.

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