Investigation of Fuel Chemistry and Bed Performance in a Fluidized Bed Black Liquor Steam Reformer

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EXECUTIVE SUMMARY (ABSTRACT)

The University of Utah project "Investigation of Fuel Chemistry and Bed Performance in a Fluidized Bed Black Liquor Steam Reformer" (DOE award number DE-FC26-02NT41490) was developed in response to a solicitation for projects to provide technical support for black liquor and biomass gasification. The primary focus of the project is to provide support for a DOE-sponsored demonstration of MTCL's black liquor steam reforming technology at Georgia-Pacific's paper mill in Big Island, Virginia. A more overarching goal is to improve the understanding of phenomena that take place during low temperature black liquor gasification. This is achieved through five complementary technical tasks: (1) construction of a fluidized bed black liquor gasification test system, (2) investigation of bed performance, (3) evaluation of product gas quality, (4) black liquor conversion analysis and modeling and (5) computational modeling of the Big Island gasifier.

Several experimental devices have been constructed under this program. The largest of these is a 10-inch diameter pressurized fluidized bed steam reformer having four bundles of 20 heaters and designed to simulate conditions within a full-scale reformer. This system is housed at the University of Utah's off-campus Industrial Combustion and Gasification Research Facility, and includes all necessary auxiliary equipment (steam generating boiler and feedwater conditioning system, steam superheater, syngas afterburner, flue gas cooler and computerized control system). A smaller nitrogen-fed fluidized bed system has been constructed at Brigham Young University for the purpose of studying bed agglomeration behavior and conditions that cause such agglomeration. An even smaller 2-inch nitrogen fluidized bed in the laboratories at the University of Utah allows investigation of mechanisms of particle growth, particularly coating and particle clustering by black liquor. Other experimental devices include a single-droplet reactor for study of liquor pyrolysis behavior and a Plexiglas cold flow model of the University of Utah steam reformer that allows visualization and measurement of gas and solid flow characteristics.

Several computational models have been developed under this program. One developed at the University of Utah is a relatively simple, Microsoft Excel-based model that predicts gas velocities and compositions throughout the reactor and considers only the four major gas species: H_2O , CO_2 , H_2 and CO . The value of this model lies in its simple interface and instantaneous updating when input parameters are changed. It is also easily configured to handle different reactor geometries and liquor properties. A more advanced model developed by Reaction Engineering International considers three phases within the bed (dense, bubble and wake) and takes backmixing of solids into account. Bubble hydrodynamics (size, velocity, splitting and coalescence) are also taken into consideration. The model calculates mass and energy balances of the system and uses drying and devolatilization rates and reaction kinetics to determine the local chemistry of the system, overall conversion and gas composition throughout the bed and freeboard. A third model focuses specifically on heat transfer and associated temperatures in and around the tube bundles of a full-scale reformer. This model takes as input results from 3-D hydrodynamics simulations created at NETL using MFIX, and can predict particle temperatures as well as heater tube internal and surface temperatures.

Conversion of black liquor in a steam reformer occurs in stages: drying, pyrolysis and heterogeneous steam reforming. The product gas leaving the reformer is primarily a mixture of steam, H_2 , CO_2 , CO and methane. The water-gas shift reaction is apparently strongly catalyzed by alkali species in the bed solids, resulting in high concentrations of hydrogen as carbon monoxide reacts with steam to form hydrogen and

carbon dioxide. Condensable hydrocarbons ("tars") are produced as the liquor pyrolyzes. These comprise primarily un-, mono- and di-substituted, mostly methyl phenols.

As liquor is fed to the fluidized bed, it coats the particles and the organic material reacts away. As a particle is repeatedly coated and reacted, thin layers, or "shells," build up on the particle and it becomes larger. Other mechanisms responsible for particle growth are agglomeration, sintering and "clustering," whereby several small particles are captured within a droplet of liquor, which binds them together. Agglomeration tends to occur in regions of the reactor that have low gas flow, or that are particularly hot. The heater bundles are therefore usually where agglomeration initiates. As agglomerated material builds up on the heater tubes, heat transfer decreases and the spacing between tubes becomes less. This restricts the flow of gas, creating more stagnation and heat, thereby causing further agglomeration. The mechanism of agglomeration seems to start with bridging between edges of particles. Potassium chloride may also play a role.

The heterogeneous reaction between steam and bed solids controls the overall rate of carbon conversion. This reaction is inhibited by hydrogen and carbon monoxide. In a commercial system, hydrogen formed during pyrolysis and steam reforming is estimated to average roughly 0.5 atmospheres. With this much hydrogen, the rate of conversion by heterogeneous reaction with steam is 5-10 times slower than in a steam-only environment. As such, a full-scale system can be expected to have lower carbon conversion than a small-scale, atmospheric-pressure reformer having a lower fuel/steam ratio.

The computational models indicate that bubbles do travel upwards through the tubes of the heater bundles, particularly in the center. Downflow of solids near the walls hinders bubble flow in those regions. As particle size increases, bubble density within the tube bundles decreases, suggesting that the bubbles instead prefer to flow around the heaters. This has been shown to be the case for the Utah gasifier. A commercial gasifier likely experiences similar behavior.

During the third year of the project, the focus will be on details of conversion, including both the pyrolysis and heterogeneous gasification stages. Minor species in the product gas will be identified and quantified, and a rate expression for carbon conversion as a function of temperature and H_2O , CO and H_2 partial pressures will be developed and optimized. Models describing conversion behavior, suitable for inclusion in the computational models, will be developed and the models will be updated accordingly.

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INVESTIGATION OF FUEL CHEMISTRY AND BED PERFORMANCE IN A FLUIDIZED BED BLACK LIQUOR STEAM REFORMER

1. INTRODUCTION

University of Utah's project entitled "Investigation of Fuel Chemistry and Bed Performance in a Fluidized Bed Black Liquor Steam Reformer" (DOE Cooperative Agreement DE-FC26-02NT41490) was developed in response to a solicitation released by the U.S. Department of Energy in December 2001, requesting proposals for projects targeted towards black liquor/biomass gasification technology support research and development. Specifically, the solicitation was seeking projects that would provide technical support for Department of Energy supported black liquor and biomass gasification demonstration projects under development at the time.

The primary objective of the project reported here is to provide technical support for the demonstration of MTCI's black liquor steam reforming process at Georgia-Pacific's paper mill in Big Island, Virginia. A more overarching goal is to increase the understanding of and acquire relevant data on conversion of black liquor in low temperature gasification systems. The project achieves these goals through the following technical tasks:

1. Construction of a fluidized bed black liquor gasification test system
2. Investigation of bed performance
 - 2.1 Mapping of bed properties and chemistry
 - 2.2 Evaluation of bed agglomeration propensity
 - 2.3 Evaluation of titanate addition
3. Evaluation of product gas quality
 - 3.1 Speciation of gaseous products
 - 3.2 Characterization and destruction of tars
4. Black liquor conversion analysis and modeling
5. Modeling of the Big Island gasifier
 - 5.1 1½-D model of entire reactor
 - 5.2 3-D modeling of specific parts of the reactor

The project includes four subcontracts to groups that possess expertise in technical areas relevant to the project. These subcontractors and their corresponding roles within the project are:

1. Brigham Young University (Prof. Larry Baxter): bed agglomeration studies
2. University of Maine (Prof. Adriaan van Heiningen): conversion analysis and Ti addition
3. Georgia Institute of Technology (Prof. Pradeep Agrawal): catalytic destruction of tars
4. Reaction Engineering International (Dr. Adel Sarofim): gasifier modeling

In addition to these official project members, the University of Utah is working closely with Georgia-Pacific Corporation, MTCI and ThermoChem Recovery International.

This report describes the technical achievements of the second year of the project, describes the experimental equipment and computational modeling associated with the project and presents results and conclusions of the work.

2. EXPERIMENTAL

Several experimental systems of varying size and complexity have been built under this project. The largest of these, the black fluidized bed black liquor gasification test system, is the heart of the research in the project. Other systems include a bed agglomeration test reactor, a 2-inch fluidized bed for particulate studies, a single particle reactor, a tar sampling system and a cold flow fluidized bed model. These systems are described in the sections that follow.

2.1 Fluidized Bed Black Liquor Gasification Test System

The University of Utah's pressurized fluidized bed black liquor gasification test system has been designed to simulate conditions in Georgia-Pacific's Big Island demonstration system. Design specifications for the system are listed in Table 1.

A schematic diagram of the gasifier system is presented in Figure 1. A 3-D model showing the major components and their configuration is shown in Figure 2. A photograph of the system is presented in Figure 3. The gasifier system includes five primary subsystems: (1) steam feed system, (2) black liquor feed system, (3) fluidized bed reactor, (4) solids removal system and (5) product gas (syngas) handling system. All these subsystems are necessary for the gasifier to operate. The whole system is driven by an integrated control system that monitors and controls critical process variables. The subsystems are described in detail in the sections that follow.

Figure 1. Schematic diagram of black liquor gasifier system.

Figure 2. 3-D model of the University of Utah black liquor gasification test system showing major components.

Figure 3. Photograph of the black liquor gasification test system.

TABLE 1. BLACK LIQUOR GASIFIER SPECIFICATIONS

Specification	Standard Operating		Maximum	
Reactor operating pressure (bottom of bed)	300 kPa	44.0 psia	689 kPa	100.0 psia
Reactor operating temperature	604 °C	1120 °F	718 °C	1325 °F
Black liquor feed rate (as solids)	68 kg/d	150 lb/d	218 kg/d	480 lb/d
Steam feed rate	42.2 kg/h	93.0 lb/h	90.7 kg/h	200.0 lb/h
Superficial gas velocity (bottom of bed)	0.396 m/s	1.30 ft/s	1.52 m/s	5.00 ft/s
Bed diameter	0.254 m	10.0 inch	0.254 m	10.0 inch
Bed height	1.27 m	50.0 inch	1.52 m	60.0 inch
Solids residence time	90 h	90 h	200 h	200 h

2.1.1 Steam Feed System

There are three main process units in the steam feed system: feedwater conditioner, steam generator (boiler) and steam superheater.

Feedwater conditioning. City water is brought into a water conditioning system comprising a twin-tank water softener, reverse osmosis filtration system and activated carbon filter. The conditioning system removes particulates and dissolved minerals in the water, which ensures high quality steam, minimizes blowdown requirements and extends the life of the superheater. Chemicals to maintain boiler life are added to the water exiting the RO unit, which is pumped to a 150 gallon bladder tank for storage. The feedwater conditioning system and boiler are shown in Figure 4.

Figure 4. Steam generation system.

Boiler. The clean water passes to the boiler system, a Parker Boiler model 103-9.5 natural gas-fired drum boiler. The boiler is rated at 1034 kPa (150 psi), and at Salt Lake City's elevation can deliver up to 120 kg/hr (265 lb/hr) steam. The boiler package includes a feedwater storage tank, pump and chemicals addition system. The boiler has a blowdown valve for purging dissolved solids from the system.

Immediately after generation, the steam passes through a condensate knockout drum to an adjustable pressure regulator then lowers the steam pressure to a pressure closer to the reactor pressure. This improves controllability of the steam flow rate and raises the level of superheat in the steam. The steam runs through a control valve and v-cone flowmeter, which are coupled to the control system and used to control the steam flow rate. All steam lines to between the boiler and superheater are electrically heat traced to minimize heat losses and associated condensation.

Superheater. Before entering the reactor, the steam passes through the superheater to increase the temperature to as much as 620°C (1150°F). The superheater is a 35 kW circulation heater built by AccuTherm, housing 24 Incoloy 840 sheathed elements in a stainless steel pressure vessel (Figure 5). The pressure vessel is rated for 2070 kPa (300 psi) at 621°C (1150°F), which matches the design pressure of the reactor itself. The superheater's power is enough to heat up to 90 kg/hr (200 lb/hr) steam at 1034 kPa (150 psi) to 620°C (1150°F).

Figure 5. 35-kW steam superheater. Steam flows downwards into the heater on the left side and exits from the port in the foreground.

The system was designed to be able to accommodate a product gas recycle line. Steam exiting the superheater would be the motive gas to entrain product gas taken from the exit of the reformer. The recycle line has not yet been installed.

2.1.2 Black Liquor Feed System

The black liquor feed system comprises a liquor storage tank, recirculation pump, metering pump and cooled injector.

Black liquor is loaded from drums into a heated storage tank. The tank holds approximately 570 liters (150 gallons) of liquor, or enough for roughly 3 days of continuous testing at standard conditions. The exterior of the tank is electrically heated and insulated. A centrifugal pump circulates black liquor from the tank outlet on the bottom back to the top of tank, and provides a means of mixing the liquor. Both the pump and recirculation line are electrically heat traced. The tank, pump and recirculation line are mounted on a platform secured to four load cells, thus allowing the weight of liquor in the tank to be determined.

A high-pressure metering pump (FMI QV-Q1CSC) feeds the liquor from the recirculation line to the injector at pressures up to 690 kPa (100 psi). The metering pump is calibrated using a graduated cylinder. The flow rate can be confirmed by following the weight loss of the tank over several hours. The liquor is fed to an injector near the bottom of the reactor. The injector has a nitrogen-purged annulus around the barrel through which the liquor is fed. A second nitrogen flow, also metered through a mass flow controller, is mixed and fed with the black liquor through the barrel to help keep the injector from plugging.

Figure 6. Black liquor feed system.

2.1.3 Fluidized Bed Reactor

The fluidized bed reactor is built in five sections, and consists of a gas distributor, bed section and freeboard. The reactor shell is 0.75 meter (30 inches) diameter, and the total height of the reactor is approximately 5.2 meters (17 feet). The bed section is 0.25 meters (10 in.) diameter, 1.4 meters (55 in.)

tall. The reactor is an ASME-certified pressure vessel rated at 800°F and 300 psi, with 300-class flanges. In order to minimize heat losses and avoid condensation against the inside of the shell, the entire vessel is insulated.

Distributor section. The distributor section is the lowest section of the reactor, and is made up of a plenum and distributor for gas introduction and distribution. The distributor has twenty evenly-spaced bubble caps, which have an orifice in the bottom to create high enough pressure drop to ensure even gas distribution. A pipe for solids removal runs from the center of the distributor plate through the plenum and out to the solids removal lock hopper system. A parallel pipe for steam enters the bottom of the system and runs to the plenum below the distributor plate. The space between the plenum and reactor shell is filled with castable insulating refractory.

Figure 7. Distributor section and split view of same. Steam enters from the left. Solids exit through the central pipe.

Bed section. The bed section (Figure 8) is the heart of the system. It is 1.5 meters (60 inches) tall, with the bed itself occupying the lower 1.4 meters (55 inches). Two layers of refractory are cast such that a 0.25 meter (10 inch) diameter bed cavity results.

Five 8-inch nozzles are welded to the shell, above one another and offset 90 degrees for insertion of the four in-bed heater bundles. (The top nozzle allows addition of a fifth heater bundle if desired. Alternately, the bottom bundle can be moved to the top position if, for example, it is observed that black liquor is contacting the bottom heater bundle before the liquor is fully dry.) Each bundle contains 20 half-inch ID thermowells in a 4x5 staggered configuration, welded to a an 8-inch blind flange. A refractory plug cast around the thermowells fits into the nozzle and a corresponding hole in the refractory of the bed section. A 0.5-inch diameter cartridge heater is inserted into each thermowell. The cartridge heater is as long as the thermowell, but only 165 mm (6.5 inches) at the end, where the thermowell is in the bed, is heated. In total, 32 kW of energy can be input to the bed through the heater bundles.

The eighty heaters each have an internal thermocouple that measures temperature in the core of the heated section. These are connected to the system's digital control system and used as feedback for the bed heating system. The tube bundle sections each have an additional, smaller thermowell extending into the

bed for measurement of bed temperature. A fifth thermocouple above the heater bundles also monitors bed temperature. Comparison of the five thermocouples in the bed provides an indication of how well the bed is fluidized. When the bed is fluidized well, the thermocouples all read within five degrees of one another. The bed temperature control system calculates an average temperature from these five thermocouples and periodically adjusts the setpoint average temperature of the heaters in the bundles up or down by the same number of degrees as the bed setpoint and measured average temperature differ.

Figure 8. Photograph of the bed section of reactor and rendering showing a split view. The four bundles of heaters can be clearly seen, as can the two angled liquor injection ports at the bottom, sample ports and thermocouple ports.

Two 3-inch nozzles are welded at a 15-degree downwards angle near the bottom of the bed section. One of these is dedicated for liquor injection. The other can either be used for liquor injection, sampling or measurement of temperature and pressure. The liquor is injected approximately 3 inches above the distributor. Two 3-inch ports just above and just below the heater bundles allow for sampling or insertion of coupons for material testing. An additional 1-inch port near the top of the bed section allows temperature or pressure measurement, and will house the pressure tap used to control bed height.

The height of the bed is continuously monitored by measuring the differential pressure across the bed, and plugging this in to formula calibrated to give the amount of bed material as a function of differential pressure. The high side of the dP transmitter is connected to the nitrogen purge line entering the tube connecting the reactor to the lock hopper. The low side is in the freeboard. The bed height is used to determine when the lock hopper needs to be cycled.

Freeboard section. The freeboard section (Figure 9) occupies the top three shell sections, and is approximately 3 meters (10 feet) tall. The bottom half has the same diameter as the bed, 0.25 meters (10 inches). This expands to 0.36 meters (14 inches) about halfway up the freeboard to reduce the gas velocity and limit particle entrainment. An internal cyclone is installed in the top of the reactor, and a dipleg from the cyclone into the bed returns captured particulate matter to the system.

Pairs of diametrically opposed 3-inch sample ports are located approximately every half meter (20 inches) along the length of the freeboard section. Diametrically opposed 1-inch ports for temperature and pressure measurement are located approximately every meter (40 inches). A 2-inch nozzle for product gas outlet is located in the top of the unit. This nozzle connects to a flange on the inside of the vessel, to which the internal cyclone is mounted. A downwards-angled 4-inch port located halfway up the freeboard section allows loading of bed solids into the reactor.

Figure 9. Freeboard section of reactor, and split view of same. The port for loading bed solids is on the left.

2.1.4 Solids Removal System

The solids removal system is located below the reactor and is made up of a lock hopper and nitrogen purge system. The lock hopper comprises a section of pipe between two valves, plus a purge valve for pressure relief. During operation, the upper valve, an Everlasting Process Valve for solids handling, opens momentarily to allow solids to fall from the reactor via a 1½-inch pipe running through the distributor into the hopper. The top valve is then closed and the hopper purge valve is opened to depressurize the lock hopper. Once depressurized, the bottom valve, a metal-seated double-actuated ball valve, opens to release the solids into a receiving receptacle. Each cycle of the lock hopper releases about 2.5 pounds of bed material.

The section of pipe above the lock hopper is continuously purged with nitrogen so the solids and surrounding gas are cool and non-reactive when they are removed from the system. The purge also removes any steam from the solids removal pipe, so that there is no risk of condensation and associated pluggage in the lock hopper.

Figure 10. Lock hopper system for solids removal.

2.1.5 Product Gas Handling System

The product gas handling system safely disposes of the synthesis gas produced in the gasifier. After passing through the internal cyclone in the reactor, the gas runs through a control valve, coupled to a pressure transmitter in the reactor freeboard, that sets the pressure of the system. Downstream of this valve the gas is essentially at atmospheric pressure. A sample line from this atmospheric, pre-combustion section of the system feeds the product gas to the on-line analyzers. Sampling and return ports are also installed to allow installation of slipstream reactors around the pressure control valve. The pressure difference upstream and downstream of the pressure control valve can be used to flow gas through slipstream reactors.

Afterburner. The product gas must be combusted before being exhausted, so it is fed to a downwards-flowing natural gas-fired afterburner (Figure 11). The afterburner is a 4.6 meter (15 foot) tall vessel lined with two layers of refractory to make a 14-inch diameter reaction chamber. Gas enters the top of the vessel and is combusted by two opposing natural gas burners in the top two ports. The gas is burned at a minimum temperature of 1093°C (2000°F) for at least two seconds to ensure efficient destruction of any tars remaining in the gas at this point. Additional ports downstream are provided for sampling or viewing. The afterburner is operated under slightly negative pressure, provided by the facility's indirect-draft fan.

The syngas is not cooled before being fired in the afterburner, but kept hot to avoid tar condensation and to avoid risks associated with hydrogen sulfide in a concentrated syngas that would result if the gas were first cooled and condensed. Because the gasifier product gas is primarily steam, this results in a relatively large afterburner and natural gas requirement. This was determined to be preferable to potential operating problems and safety risks associated with cooling the gas first.

Figure 11. Photograph of afterburner and cooler, plus rendering and split view of afterburner. The bottom sections of the afterburner and cooler aren't seen in the photo.

Cooler/condenser. The hot product gas from the afterburner is fed to a water-cooled heat exchanger (Figure 12) to cool the gas and condense out water. The cooler is approximately 3.3 meters (11 feet) tall and an 0.3 meters (12 inches) diameter. It contains forty $\frac{3}{4}$ " heat exchange tubes, and is designed to condense the whole load of superheater product gas, condensing out the steam, when the gasifier is running under pressure with 90 kg/hr (200 lb/hr) steam feed. Gas from the afterburner travels upwards through the cooler. Condensed water flows down the outside of the heat exchange tubes and drops out the bottom of the vessel into a sump drain in the floor. The cooling water is on a closed loop, and runs through a cooling tower outside the building.

The cooled gas from the heat exchanger runs to the facility's flue gas handling system. An ID fan draws the exhaust to the stack. Various dampers in the exhaust system are used to control the pressure. These are adjusted such that the afterburner runs slightly negative.

2.1.6 Process Control System

The entire gasification test system is controlled by an OPTO-22 based computerized process control system. The control system logs critical process variables and has control loops to control temperatures, pressures and flow rates. The control system includes several safety subsystems that will safely shut down the system in case of a system trip or unexpected event such as a power outage. The operator interfaces with the control system through a PC having a multi-screen customized graphical interface. A common control interface is used for operation of the gasification system and all auxiliary systems (e.g. cooling tower, exhaust gas handling system). The interface for control of the gasification system is shown in Figure 13. The operator can adjust values by clicking on the appropriate reading.

Figure 12. Rendering of the cooler/condenser and split view of same. Gas enters through the side port in the bottom and exits through the top. Condensate drains out the bottom.

Figure 13. Graphical operator interface for gasification system.

2.2 Bed Agglomeration Test Reactor

As part of their experimental study on agglomeration of bed material in a low temperature black liquor gasifier, Brigham Young University has developed a small-scale experimental fluidized bed reactor capable of determining fluidization characteristics. The reactor (Figure 14) is square, six inches on a side, and 45 inches tall. It is constructed of 316L stainless steel L-channel frame with 316L stainless steel panels on two sides and three panes of high temperature glass on each of the remaining two sides. The glass, Neosurround made by Jones Paint and Glass, can withstand temperatures up to 800°C (1470°F). The panels and glass are sealed with 0.125-inch high-temperature Grafoil graphite gasket.

The distributor for the reactor has an air straightener to minimize any non-congruencies in the reactor's air inlet. The distributor plate itself comprises a stainless steel plate with many small (~1/16 inch) holes separated by about 0.5 inches, covered by a fine screen to keep particles from falling through.

The bed is fluidized with nitrogen. The gas is metered with a flowmeter, after which it passes through a 1.65 kW electric preheater, which can heat the gas to 250°C (480°F). The rest of the heat for the bed is provided by sixteen 0.5-inch cartridge heaters oriented in four perpendicular levels of four heaters each. Some heaters have internal thermocouples to measure their core temperature. In addition, several of the heaters have an external thermocouple glued to the surface with a high-temperature, thermally conductive adhesive. Four more thermocouples within the bed section monitor the temperature of the bed solids.

Figure 14. Photographs of the fluidized bed reactor for bed agglomeration studies, with close-ups of the sixteen cartridge heaters and the air straightener/plenum section.

Bed agglomeration reactor cold-flow model. Prior to building the actual test unit, Brigham Young University built a cold flow model of the test reactor to assist in design of the real system. The cold flow fluidized bed is four feet tall, constructed of ABS with a Plexiglas window secured by mechanical straps and sealed using flexible tubing, thus allowing for a greater pressure at the distributor. Photographs of the cold flow model are presented in Figure 15.

Compressed air is fed to the cold flow model through a rotameter to adjust the flow rate. A series of six pressure transducers, attached to the back of the reactor, show pressure at varying locations vertically along the bed. An analog pressure gauge is attached to the upstream air supply to determine the total pressure necessary for fluidization.

Preliminary experiments with 300 micron sand indicated that modifications were needed for the stainless steel high-temperature reactor. It was determined that the original design of a hemi-cylindrical reactor generated an unevenly distributed flow profile and create zones of low fluidization. The design for the full-scale reactor was therefore modified to the square design described above.

Figure 15. Brigham Young University's cold flow model: side view (left) and operating (right).

2.3 Single Droplet Reactor

The University of Utah has constructed a laboratory reactor for studying pyrolysis and gasification behavior of single droplets or particles of black liquor. The design is based on a similar reactor that has been successfully used for black liquor studies at Åbo Akademi University in Finland. The Utah reactor is constructed from two concentric quartz tubes positioned in a vertical tube furnace. The inner tube is approximately 1 meter (40 inches) long, 38 millimeters (1.5 inches) diameter. The outer tube is approximately 0.7 meter (28 inches) long and 63 millimeters (2.5 inches) in diameter. The outer tube is centered around the inner tube and sealed on the top and bottom. Gas is fed through a flowmeter, enters the bottom of the outer tube and flows upwards between the outer and inner tubes, where it is heated. The heated gas then enters the inner tube through a series of small holes, flows downwards through the hot part of the reactor and is exhausted through a port in the bottom of the reactor. A photograph of the top part of the reactor is presented in Figure 16.

A purge chamber at the top of the reactor provides a cool, inert environment for sample preparation and cooling after an experiment. A small flow of nitrogen (approximately 20% of the total flow) is fed into this chamber and flows downwards through the inner tube. It meets and mixes with the preheated primary gas just inside the heated section of the furnace. This design produces a sharp temperature transition, thereby maximizing heating rate. The top section of the reactor containing the purge chamber can be removed from the main body by removing a ground glass fitting, thereby facilitating sample loading and unloading.

In a typical pyrolysis experiment, approximately 10 mg of concentrated black liquor is attached to a coil of fine wire. The wire is attached to a glass ring on the bottom of the glass rod, and is pulled into position in the purge chamber. The top section of the reactor is put into place and purge and reactor gas are set to the desired setpoints. The rod is then quickly lowered into the hot zone of the furnace and kept there for the desired amount of time, after which the sample is pulled back up into the purge zone. The sample is allowed to cool and stabilize in this zone, after which it is removed and carefully weighed to determine pyrolysis yield. The resulting char is saved for possible further analysis.

Figure 16. Single-droplet reactor.

2.4 2-inch Fluidized Bed Reactor

The University of Utah has constructed a 2-inch fluidized bed reactor to study growth particles and variations in particle size distribution when liquor is injected into a hot fluidized bed. The reactor is essentially a 2-inch piece of either quartz tubing or stainless steel pipe secured to a specially machined base. The base comprises the distributor, nitrogen feed inlet port, a thermocouple port for measuring the plenum temperature and a port to allow injection of black liquor. The distributor is simply a plate of porous stainless steel attached to the reactor base. A second thermocouple for measuring the bed temperature extends from the top of the reactor into the bed.

Nitrogen is used as a fluidizing medium. The nitrogen flow is controlled by a variable area flowmeter, and the gas is preheated prior to feeding to the reactor. Preheating is achieved through a combination 1.1 kW rod heater and 1.9 kW tube furnace housing a stainless steel heating chamber. This is the sole source of heat to the system, i.e., there are no in-bed heaters or shell heaters. The fluidized bed is therefore installed right on the outlet from the tube furnace and nitrogen preheater. The system is well insulated and able to operate at temperatures representative of those in a full-scale system, up to 605°C (1120°F).

Two methods of introducing black liquor into the bed have been developed. The first involves injecting liquor into the bed near the distributor. The injector is made of two concentric tubes, with liquor flowing through the center tube and cooling nitrogen flowing through the outer tube to shield the liquor from the heat of the bed. The other method simply involves feeding liquor into the top of the reactor and allowing droplets to fall on the bed. For both types of injection preheated, relatively dilute liquor is fed through a peristaltic pump and then through tubing to the reactor.

Samples of bed material can be taken during operation by essentially vacuuming out a bit of the bed through the top plate of the reactor and capturing the particles on a stainless steel filter.

Figure 17. 2-inch fluidized bed. Thermocouples in the plenum and extending from the top into the bed can be seen. The liquor injector is located just above the lower yellow thermocouple.

2.5 Fluidized Bed Gasifier Cold-Flow Model

A cold flow model of the University of Utah fluidized bed gasifier has been built as an aid in system design, visualization of reactor flows and interpretation of data. The cold flow model is also useful as a validation tool for the program's modeling efforts.

In order to ensure that the cold flow model accurately simulates the behavior of the bed in the true gasifier system, it is important that four dimensionless scaling parameters are kept the same between the two systems [1]:

$\frac{d_p u \rho_g}{\mu}$	$\frac{\rho_s}{\rho_g}$	$\frac{u}{(g d_p)^{0.5}}$	$\frac{L}{d_p}$
Reynolds number	Density ratio	Froude number	Geometric similarity of distributor, bed, particle

The cold flow model was designed to keep these scaling parameters equal between the systems when the gasifier is operating at standard conditions. The final cold flow model design calls for a bed diameter of 6.5 inches, fluidizing 200 micron soda lime glass beads with a 50/50 mixture of helium and air at room temperature. A comparison of specifications for the true gasifier and the cold flow model is presented in Table 2. No visually discernable difference can be detected when fluidizing with pure air as opposed to the 50/50 helium/air mix, so most of the tests are run with pure air.

TABLE 2. COLD FLOW MODEL DESIGN SPECIFICATIONS

Characteristic	Gasifier		Model	
Average pressure in bed	290 kPa	42 psia	103 kPa	15 psia
Operating temperature	604 °C	1120 °F	20 °C	68 °F
Bed diameter	0.254 m	10.0 in	0.164 m	6.5 in.
Expanded bed height	1.27 m	50.0 in	0.864 m	34.0 in.
Heating tube diameter	0.0173 m	0.680 in	0.0109 m	0.433 in.
Particle diameter	300 µm	0.0118 in	200 µm	0.00787 in
Particle density	2,275 kg/m ³	142 lb/ft ³	2,500 kg/m ³	156 lb/ft ³
Superficial gas velocity	0.396 m/s	1.30 ft/s	0.326 m/s	1.07 ft/s
Gas density	0.633 kg/m ³	0.0395 lb/ft ³	0.700 kg/m ³	0.0437 lb/ft ³
Gas viscosity (x 10 ⁵)	3.08 kg/m-s	2.07 lb/ft-s	1.89 kg/m-s	1.27 lb/ft-s
Reynolds number	2.44		2.36	
Froude number	7.30		7.36	
Density ratio	3,595		3,641	
Geometric similarity (bed/particle)	10,160		9,906	

As seen by the nearly identical values for the critical dimensionless scaling parameters, one can be confident that the behavior of the cold flow model is representative of the real system. It is of interest to note that the time scale factor for the cold flow model is 0.82, meaning that processes that occur in 1

second in the real system require only 0.82 seconds in the cold flow model. Hence, videos of the cold flow model must be played back at 82% of their recorded speed to give an accurate representation of the speed at which the real system is fluidizing.

Pictures of the cold flow model are shown in Figure 18. The body is fabricated in sections from cast acrylic (Plexiglas) tube (0.164 m, 6.5 in ID) with grooves machined into the ends to allow the individual pieces to be stacked on top of one another. The "heating tubes" in the tube bundle sections are glass tubes (11 mm OD). Two sets of four tube bank sections were constructed, one with staggered tubes and one with parallel tubes. Several pieces of different lengths were constructed for the bottom section below the tube bundles. The modular design allows different arrangements to be constructed, and permits individual sections to be independently rotated. The tube bank sections can be oriented parallel or perpendicular to one another, and the height below the tube banks can be changed by using different length pieces.

The distributor (Figure 19) is made of two plates with forty-two 9/16" holes evenly distributed over the area. Two layers of tight-weave fabric are sandwiched between these plates to create high pressure drop across the distributor to ensure even distribution of the fluidizing gas. As in the real system, a solids removal port runs through the center of the distributor. This connects to a pipe running through the plenum, and to a ball valve below the reactor to allow easy drainage of bed solids.

Figure 18. Rendering and photographs of the cold flow model of the University of Utah fluidized bed gasifier. The photo on the right shows the system during operation.

Figure 19. Cold flow model distributor.

During operation, compressed air and helium are fed through variable area flowmeters to the plenum of the fluidized bed, below the distributor, and flow evenly through the distributor. At standard operating conditions (14.8 scfm total flow, 26" slumped bed height), pressure drop across the distributor accounts for approximately 40% of the total pressure drop across the system.

The cold flow model has a number of uses. Generally speaking, it provides visual insight into the behavior of the fluidized bed gasifier. The bed can be videotaped during operation and played back at slower speed to identify flow patterns of solids and gas. The cold flow model is a useful tool for developing and validating computerized models of the fluidized bed gasification system, particularly with regard to flow of gas and solids around and through the horizontal heat exchange tubes. One such application is shown in Figure 20. Two probes are inserted into adjacent glass tubes. One probe has a light source, either visible or infrared. The other probe has a photodetector. As bubbles pass between the tubes, light from the source is seen by the detector. By coupling the detector to a computerized data acquisition system, variations in light intensity, corresponding to bubble size and frequency, can be tracked. By setting zero and full scale intensities for a packed bed and empty bed, respectively, the average bed density between tubes can be determined and mapped for the entire tube bundle region.

Figure 20. Tube section of cold flow model showing light source and detector probes inserted into "heater" tubes.

2.6 Tar Sampling System

The University of Utah has constructed a system for sampling tars from a fluidized bed steam reformer. This system comprises a few different components: an impinger column, a sample pump and a dry gas meter. The impinger column is a special design, a so-called "Petersen column" that was suggested in the IEA Bioenergy Tar Protocol [2] as an alternative to the classic series of impingers commonly used in this type of sampling. This type of sampler is much more fieldable than a normal impinger train. A photograph of the University of Utah's Petersen column is presented in Figure 21.

Figure 21. Schematic [2] and photograph of the "Petersen column" used for tar sampling.

The sampling column has two stages. In the first, gas flows through an impinger containing an organic solvent. The gas flows upwards from this first stage to the second, where it flows through a glass frit at the bottom of another level of solvent. The fine bubbles create a large surface area that enhances transfer of condensable organics to the solvent. Both stages are surrounded by cooling jackets to minimize vaporization of solvent. Once sampling is complete, the solvent can easily be drawing into a bottle in the bottom of the column by applying a vacuum to the bottle. This system allows the user to quickly prepare for another round of sampling.

3. COMPUTATIONAL MODELS

Several computational models of fluidized bed steam reformers have developed under this project. The first, developed at the University of Utah, is a general, idealized model for any fluidized bed black liquor steam reformer that maps the gas compositions and flow rates throughout the reactor. The second model, developed by Reaction Engineering International, is a "1½-D" model of the entire Big Island reactor that predicts bubble development and rise, liquor conversion, temperature distributions and gas compositions. A third model developed specifically for heat transfer predictions is described in Section 3.3.

3.1 Generic Steam Reformer Model (UU Model)

3.1.1 General Description

This model was developed primarily as an aid for designing the University of Utah black liquor gasification test system, and is essentially a glorified mass balance for the steam reformer. Given the reactor geometry, inputs to the system (black liquor properties and flow, steam flow, fraction of product gas recycled) and conditions in the reactor (freeboard pressure, bed temperature), the model predicts the pressure, gas composition, superficial and actual gas velocities, and residence times throughout the bed. The entire model is contained on one Microsoft Excel worksheet, has a user-friendly interface, is portable and can easily be modified. A screen shot of the model interface is shown in Figure 22.

In designing the University of Utah test gasifier, the model was first set up to simulate the Big Island steam reformer. A copy of that model was made and the reactor geometry, conditions and flows were manipulated to create a system that would simulate conditions in the bottom section of the Big Island steam reformer to the extent possible, and that would be reasonably sized with regard to space available, construction and operating costs, and operator demand.

The model makes the following simplifying assumptions:

- The entire reactor (bed and freeboard) is at one given temperature
- Gas flows uniformly (plug flow, with no channeling) through the reactor
- Solids are perfectly mixed throughout the bed
- Black liquor is injected at the very bottom of the bed
- Black liquor dries and pyrolyzes immediately upon entering the reactor
- The gas consists only of H₂O, CO₂, H₂, CO and H₂S
- The gas is always at equilibrium with regard to the water-gas shift reaction

The model does not take into consideration energy entering or exiting the system, nor does it consider rates or kinetics of the conversion reactions. Overall carbon conversion is given as input to the model.

Figure 22. Screen shot of UU model interface.

All gas phase equilibrium calculations are performed by the following procedure:

1. The C, H, O and S atoms entering the system or level are totaled.
2. All S atoms and 2xS hydrogen atoms are removed from the system.
3. The equilibrium composition of H₂O, CO₂, H₂ and CO for the remaining atoms is calculated.
4. The H₂S removed in step 2 is returned to the mixture.

In step 3, the composition is calculated by determining the equilibrium constant for the water-gas shift reaction at the specified temperature, manipulating gas species concentrations into a quadratic equation with one real root and identifying this root. The solution can thus be found directly, eliminating the need for iteration or a solver. Through this approach, the model solution updates immediately when a change is made to the inputs.

The model considers gas flow through the bed from the bottom up. The bed is divided into ten sections of equal volume, and the compositions and flows into and out of each section (labeled Levels 0 through 10) are determined. In addition, there is a "bottom" level below Level 0 that considers only the incoming steam and recycled syngas, if any. Descriptions of the different sections and processes that take place in these sections are described in the sections that follow.

3.1.2 Treatment of Chemistry and Liquor Conversion

3.1.2.1 Bottom Level: Steam and Recycled Syngas Feed

The user can input the steam feed rate as well as the recycle ratio, defined as mass of recycled syngas to mass of steam introduced into the reactor. The model first performs an initial mass balance for the total system to determine the final product gas composition. The appropriate flow of this product gas (based on recycle ratio) is combined with the incoming steam flow and the equilibrium composition of this mixture is determined. This mixture is passed on to Section 0.

3.1.2.2 Section 0: Black Liquor Feeding, Drying, Pyrolysis

In the model, black liquor is fed in Section 0. It is assumed that drying and pyrolysis are instantaneous, and that all gas generated by pyrolysis and gasification impacts gas flow in this section. H₂O from drying of the liquor is added to the gas phase of the system. Carbon, hydrogen, oxygen and sulfur released from the liquor during pyrolysis are added to the gas phase as described below.

Carbon: Frederick and Hupa [3] investigated black liquor pyrolysis, and offer a relation to determine the percentage of carbon retained in the char as a function of temperature:

$$\text{Percentage of carbon retained in char} = 645 \exp(-0.00332T) \quad (\text{Eq. 1})$$

where T is in °C.

Hydrogen: There has not been much interest in studying hydrogen release during pyrolysis, and no published results on this issue are available. Elemental compositions of liquor and chars are available, however. Hydrogen contents in black liquor solids are on the order of 3.5%. Reported hydrogen contents of chars are in the range 2 wt%. Char yield during formation of such chars is roughly 65%. An estimate of hydrogen released can thus be calculated: $(3.5 - (2.0 \times 0.65)) / 3.5 = 63\%$. The release is undoubtedly affected by temperature, but until data to model this are available, a constant 63% H loss is assumed.

Oxygen: Like hydrogen, there is essentially no data on oxygen release during pyrolysis. Data on component release versus temperature are available for carbon, sodium and sulfur, and the total volatiles yield versus temperature are also available. Using this information, a relation for oxygen release as a function of temperature was back-calculated such that the total volatiles yield agrees with that estimated from Frederick and Hupa [3]:

$$\text{Volatiles yield (\%)} = -39.7 + 0.1T \quad (\text{Eq. 2})$$

Data between 700 and 900°C were fit, and the relation can comfortably be extrapolated to 600°C. The resulting relation for the percent oxygen volatilized is:

$$\text{Percent oxygen release} = 3.77 \exp(0.00292T) \quad (\text{Eq. 3})$$

where T is in °C.

Sulfur: Frederick et al. [4] offer a correlation for sulfur release during black liquor devolatilization. The correlation depends only on temperature. For temperatures between 250 and 1018°C,

$$\text{Percent sulfur released} = -163.27 + 0.9717T - 1.15e^{-3}T^2 + 4.283e^{-7}T^3 \quad (\text{Eq. 4})$$

Other elements: Volatilization of all other elements (Na, K, Cl, N, Ca, Si, etc.) is ignored.

3.1.2.3 Sections 1–10: Black Liquor Char Gasification

Once the liquor has devolatilized, a char remains. This char is slowly gasified until an inorganic residue (ash) remains. It is assumed that, since the bed is well mixed, this gasification occurs uniformly throughout the bed. Each of the ten bed sections thus contributes equally to C, H, O and S release through gasification. For example, if 20% of the incoming carbon is released during pyrolysis in Section 1 and 10% of the incoming carbon exits the reactor in the solids (as carbonate or unreacted carbon), the remaining 70% is released equally over the 10 sections, with 7% of the incoming carbon being released in each section.

It is assumed that the final solid product is pure sodium carbonate, Na_2CO_3 , plus residual unreacted organic carbon. (The percent conversion of total carbon is an input variable.) Consequently, all sulfur and hydrogen are assumed to exit in the gas phase. The production rate of sodium carbonate is calculated based on the amount of incoming sodium (and potassium, which was treated as sodium). The associated carbon and oxygen in the carbonate are then calculated. The amounts of carbon and oxygen released during gasification are determined by subtracting the amounts released during pyrolysis and exiting with the solid from the amount input with the black liquor solids.

3.1.3 Level-by-Level Calculations

Conditions at each level are calculated as follows:

Level 0 (below Section 1): The model starts with the bottom of Section 1 (Level 0) and adds all gas-phase C, H, O and S contributed by (1) steam and recycle gas fed to the distributor, (2) drying of the black liquor, and (3) devolatilization of the black liquor solids. The equilibrium composition is calculated, as is the pressure at this point based on the given freeboard pressure, bed height and bed density. Since the temperature, pressure, volumetric gas flow rate, reactor geometry and bed void fraction are known, the superficial and actual gas velocities (after drying/devolatilization) are calculated.

Level 1 (above Section 1): At Level 1, the gas has gone through 10% of the volume of the bed. During its passage through this section, C, H, O and S corresponding to 10% of the total char gasification (since this is one of 10 sections) are added to the gas phase. The equilibrium gas composition, pressure, superficial and actual velocities are all recomputed. The residence time in Section 1 is calculated by dividing the height of the section by the average gas velocity through the section (taken as the average of the incoming and outgoing gas velocities).

Levels (and Sections) 2-10: Conditions in the rest of the bed are determined essentially the same as for Level 1. The gas composition is updated and brought to equilibrium, then pressure, gas velocity and residence time are calculated. The final gas exiting the top of the bed (Section 10) is taken to be the product gas from the reactor.

Freeboard: The geometry of the freeboard, including the expansion section at the top of the reactor, is input and the freeboard volume is calculated. The gas velocity and residence time in this section is subsequently calculated. It is assumed that no chemical reactions occur in the freeboard.

The UofU model thus offers a simple, portable tool useful for quick checks on approximate conditions in fluidized bed black liquor reformers. Comparison of predicted gas compositions to measured compositions from commercial units show good agreement.

3.2 Advanced Model of Entire Reactor (REI Model)

Reaction Engineering International (REI) has developed a "1½-D" three-phase countercurrent backmixing model based on an existing fluidized bed model that REI developed under a DOE-sponsored Vision 21 program. The model takes into account vertical temperature and concentration gradients and downflow near the wall. The model for the entire Big Island reactor describes the fluid dynamics, chemistry and heat transfer in the reactor. Details of the system, such as interaction between bubbles and the pulsed heater tube bundles, are estimated from the correlations for heat exchange tubes in fluidized bed combustors.

The model uses literature data for system chemistry and fluid dynamics. This model is periodically improved over time by incorporating data on conversion from specific laboratory experiments and the gasification test system. As development progresses, the model will be validated through comparison with results from the Utah gasifier. Once the Big Island facility is operating, the ambition is to validate the model with data from this system.

The model assumes that the fluidized bed consists of three distinct phases:

- A particle-free bubble phase where the gas moves upward in plug flow
- A wake phase where the gas and the solids move upward with the bubbles
- A dense phase in which the solids move downward. The voidage in the dense phase is assumed to be the same as that in the wake phase and is assumed to be the voidage at minimum fluidization.

The bubble sizes are calculated allowing for bubble growth by coalescence with increasing height in the bed and decrease in bubble size as a result of bubble intersection with tubes. Different bubble sizes are calculated for the bubbles in the heater tube banks, the voids between the tube banks and the confining cylindrical walls, and the bubbles that flow through the open wedges between the overlap of tube banks. In the model the bubble sizes are averaged across a cylindrical cross section. Details of the model are given in the following sections.

3.2.1 Bubble hydrodynamics

3.2.1.1 Bubble size.

Bubble hydrodynamics in the tube banks differ from that outside the tube banks. With the presence of tube bundles, bubbles interact with the tubes, leading to bubble splitting thereby counteracting the tendency of bubble growth by coalescence. Thus, it is necessary to estimate bubble sizes using different approaches for the regions with and without tube bundles.

Regions below and above the tube bundles of the pulse combustors. For three-dimensional fluidized beds, the Darton correlation [5] has been widely used to predict bubble growth

$$d_b = 0.54(u_0 - u_{mf})^{2/5} (h + 4\sqrt{A_0})^{4/5} / g^{1/5} \quad (\text{Eq. 5})$$

where A_0 is the catchment area at the distributor plate. For the Big Island process, this is calculated to be 0.0355 m^2 .

Tube bundle regions of the pulse combustors. When bubbles strike tubes, the interaction between the tubes and bubbles may cause bubbles to break up. The size of the daughter bubbles can be predicted using a probabilistic approach developed by Hull et al. [6]. This approach may be summarized briefly as follows.

Assume that the parent bubble has a size, d_b , less than the horizontal spacing between the tubes, L . The probability of the parent bubble striking the tube and splitting to form daughter bubbles is $p = (d_t + d_b)/(d_t + L)$. The probability of the parent bubble slipping through the horizontal spacing between the tubes without splitting is then $(1 - p)$. Assume also that on encounter with the tube, the parent bubble of size $d_b < L$ breaks up at most into two daughter bubbles of equal size. Therefore, for a three-dimensional bubble, $d_b^3 = 2d_{b,d}^3$, where $d_{b,d}$ is the size of the daughter bubbles. The average size of the bubbles leaving the tube banks, $d_{b,e}$, can now be estimated as $d_{b,e} = pd_{b,d} + (1 - p)d_b$:

$$\frac{d_{b,e}}{d_b} = 1 - \left(1 - \frac{1}{\sqrt[3]{2}}\right) \left(\frac{d_t + d_b}{d_t + L}\right) \quad \text{for } d_b < L \quad (\text{Eq. 6})$$

If $L \leq d_b < d_t + 2L$, the probability of a bubble encountering two tubes simultaneously is $p = (d_b - L)/(d_t + L)$. It is assumed that such an encounter leads to the parent bubble breaking up into three daughter bubbles, one with diameter L , and the other two daughter bubbles being of equal size. Then, $d_b^3 = L^3 + 2d_{b,d}^3$ for three-dimensional bubbles. The probability of the parent bubble striking only one tube is $(1 - p)$. In this case, the parent bubble splits into two bubbles with equal diameters, thus, $d_b^3 = 2d_{b,d}^3$. Using these relationships, the average daughter bubble size is given by

$$d_{b,e} = \frac{d_b}{\sqrt[3]{2}} \left(\frac{d_t + 2L - d_b}{d_t + L}\right) + \frac{L + 2\sqrt[3]{\frac{d_b^3 - L^3}{2}}}{3} \left(\frac{d_b - L}{d_t + L}\right) \quad (\text{Eq. 7})$$

For $d_t + 2L \leq d_b < 2d_t + 3L$, this approach yields

$$d_{b,e} = \frac{L + 2\sqrt[3]{\frac{d_b^3 - L^3}{2}}}{3} \left(\frac{2d_t + 3L - d_b}{d_t + L}\right) + \frac{L + \sqrt[3]{\frac{d_b^3 - 2L^3}{2}}}{2} \left(\frac{d_b - d_t - 2L}{d_t + L}\right) \quad (\text{Eq. 8})$$

Similarly, for $d_t + 2L \leq d_b < 2d_t + 3L$, the daughter bubble size is

$$d_{b,e} = \frac{L + \sqrt[3]{\frac{d_b^3 - 2L^3}{2}}}{2} \left(\frac{3d_t + 4L - d_b}{d_t + L}\right) + \frac{3L + 2\sqrt[3]{\frac{d_b^3 - 3L^3}{2}}}{5} \left(\frac{d_b - 2d_t - 3L}{d_t + L}\right) \quad (\text{Eq. 9})$$

For $d_{b,e} \geq 2d_t + 3L$, equations similar to Equation 9 can be derived. This model has been validated through comparison of model predictions with measurements taken from a thin fluidized bed using a CCD video camera. The applicability of the model to three-dimensional bubbles was also examined. Yates and co-workers [7,8] reported measurements that relate the parent bubble size with the average size of daughter bubbles resulting from encounter with horizontal rows of tubes. Calculations using the above model compared favorably with their experimental data [6].

3.2.1.2 Bubble Rise Velocity

The most frequently adopted two-phase theory shows that bubble rise velocity is the sum of the excess gas velocity and the isolated bubble rise velocity [9]:

$$u_b = u_0 - u_{mf} + 0.71\sqrt{gd_b} \quad (\text{Eq. 10})$$

The excess gas velocity represents the visible bubble flow according to the two-phase theory. Several experimental investigations, however, indicate that the visible bubble flow is somewhat smaller than that predicted by the two-phase theory [10,11]. For simplicity, Equation 10 is used in this work.

3.2.1.3 Bubble Wake Fraction

Bubble wake fraction varies in a wide range as the operating conditions change. Measurements suggest that wake fraction depends on both particle and bubble sizes [12]. The scatter in the existing experimental data, however, makes it difficult to use an unequivocal correlation for bubble wake fraction. In the modeling of fluidized beds, it is generally assumed that wake fraction is constant [13]; in this work, we assume that wake fraction is 0.30.

3.2.1.4 Bubble Fraction

Based on the assumption that the fluidized bed consists of the bubble phase, wake and dense phases, the overall gas balance can be written as

$$u_0 = f_b u_b + f_b f_w \varepsilon_{mf} u_b + [1 - f_b(1 + f_w)] \varepsilon_{mf} u_{g,d} \quad (\text{Eq. 11})$$

where u_0 is the local superficial gas velocity and $u_{g,d}$ is the gas velocity in the dense phase. Since there is not net particle flow in the vertical direction, particles moving upward in the wake phase must be balanced by the downward motion of particles in the dense phase, hence,

$$-f_b u_b f_w = [1 - f_b(1 + f_w)] u_{p,d} \quad (\text{Eq. 12})$$

where $u_{p,d}$ is the particle velocity in the dense phase. The slip velocity between the gas and the particles in the dense phase is assumed to be the ratio of the minimum fluidization velocity to the bed voidage at minimum fluidization. Hence, the absolute gas velocity in the dense phase is given by

$$u_{g,d} = u_{p,d} + u_{mf} / \varepsilon_{mf} \quad (\text{Eq. 13})$$

Equations 11 to 13 can then be employed to determine bubble fraction as a function of bed height. Note that when the superficial gas velocity is sufficiently high, $u_{g,d}$ may become negative indicating gas in the dense phase moving downward.

3.2.2 Overall Gas Balances

Since the total gas mass flow rate may change along the bed height as drying, devolatilization and gasification of black liquor proceed, the superficial gas velocity also changes; it can be written as

$$u_0 = \frac{m_g}{A\rho_g}; \quad m_{g,j} = m_{g,j-1} + \sum_{i=1}^n fR_i M_i Ah \quad (\text{Eq. 14})$$

where j is the computational cell index starting from the bottom of the bed; f is the phase fraction and R_i , M_i , and h are gas species formation rate ($\text{kmol/m}^3\text{s}$), species molecular weight and the cell height, respectively.

3.2.3 Species Mass Balances

For steady state conditions, species mass balance equations in different phases can be written as follows:

3.2.3.1 Bubble phase

$$\frac{d(u_b f_b A C_{i,b})}{dz} - (\lambda_1 C_{i,b} + \lambda_2 C_{i,w}) \frac{d(u_b f_b A)}{dz} + f_b A K_{bw} (C_{i,b} - C_{i,w}) + A f_b R_{i,b} = 0 \quad (\text{Eq. 15})$$

where $C_{i,b}$ denotes the concentration of species i . Subscripts b , w represent the bubble and wake phases, respectively. A is the cross-sectional area of the bed; it changes along the bed height in the regions of the tube bundles and the freeboard. The first term in the above equation is the convection due to the finite velocity of the bubble phase. The second term represents the cross-flow that accounts for the variation of bubble properties along the bed height above the gas distributor. λ_1 and λ_2 are constant; if $d(u_b f_b A)/dz \geq 0$, $\lambda_1 = 0$ and $\lambda_2 = 1$; if $d(u_b f_b A)/dz < 0$, $\lambda_1 = 1$ and $\lambda_2 = 0$. The third term is the exchange of gas between the bubble phase and the wake phase. The last term represents the consumption rate of species i in the bubble phase.

3.2.3.2 Wake phase

Similarly, for the wake phase, the gas species mass balance can be written as

$$\begin{aligned} & \frac{d(u_b f_b f_w A \varepsilon_{mf} C_{i,w})}{dz} + (\lambda_1 C_{i,b} + \lambda_2 C_{i,w}) \frac{d(u_b f_b A)}{dz} \\ & + (\lambda_3 C_{i,d} + \lambda_4 C_{i,w}) \frac{d\{[1-f_b(1+f_w)]A \varepsilon_{mf} u_{g,d}\}}{dz} + f_b K_{bw} A (C_{i,w} - C_{i,b}) \\ & + f_b K_{wd} A (C_{i,w} - C_{i,d}) + f_b f_w \varepsilon_{mf} A R_{i,w,g} + f_b f_w (1 - \varepsilon_{mf}) A R_{i,w,p} = 0 \end{aligned} \quad (\text{Eq. 16})$$

The first term in the above equation is the convection term. The second and third terms are the cross-flow. The two parameters λ_3 and λ_4 are constant; if $d\{[1-f_b(1+f_w)]A \varepsilon_{mf} u_{g,d}\}/dz \geq 0$, $\lambda_3 = 0$ and $\lambda_4 = 1$; if $d\{[1-f_b(1+f_w)]A \varepsilon_{mf} u_{g,d}\}/dz < 0$, $\lambda_3 = 1$ and $\lambda_4 = 0$. The fourth and fifth terms are the exchange of gas between the bubble and wake phases and between the wake and dense phases, respectively. The last two terms represent species consumption rates due to homogeneous and heterogeneous reactions, respectively.

3.2.3.3 Dense phase

For the dense phase, the mass balance equation can be derived as

$$\begin{aligned} & \frac{d\{[1-f_b(1+f_w)]A \varepsilon_{mf} u_{g,d} C_{i,d}\}}{dz} - (\lambda_3 C_{i,d} + \lambda_4 C_{i,w}) \frac{d\{[1-f_b(1+f_w)]A \varepsilon_{mf} u_{g,d}\}}{dz} \\ & + f_b K_{wd} A (C_{i,d} - C_{i,w}) + [1-f_b(1+f_w)]A \varepsilon_{mf} R_{i,d,g} + \{1-f_b(1+f_w)\}A(1 - \varepsilon_{mf}) R_{i,d,p} = 0 \end{aligned} \quad (\text{Eq. 17})$$

The terms in the above equation represent convection, cross-flow, exchange of gas between the dense and wake phases, species consumption rates due to homogeneous and heterogeneous reactions, respectively.

3.2.3.4 Freeboard region

In the freeboard, homogeneous reactions, especially the water-gas shift reaction and the methane-steam reforming reaction, continue. The mass balance equation must account for these reactions. The species mass balance equation is

$$u_0 \frac{dC_{i,f}}{dz} + R_{i,f} = 0 \quad (\text{Eq. 18})$$

3.2.4 Exchange Coefficients

The mass exchange coefficients have been adopted from Kunii and Levenspiel [1]. The mass transfer coefficient between the bubble phase and the wake phase is

$$K_{bw} = 5.85(D_g^{0.5} g^{0.25} / d_b^{1.25}) + 4.5u_{mf} / d_b \quad (\text{Eq. 19})$$

where D_g is the gas diffusivity and d_b is the bubble diameter. The mass exchange coefficient between the wake and emulsion phases is taken as

$$K_{wd} = 6.77(0.71\sqrt{gd_b} D_g \varepsilon_{mf} / d_b^3)^{1/2} \quad (\text{Eq. 20})$$

3.2.5 Energy Balance

Assume the gas in the bubble phase, the wake phase and the dense phase has the same temperature. An energy balance for the gas phase can be written as

$$\begin{aligned} C_{pg} \rho_g u_0 \frac{dT_g}{dz} + \frac{6h_w}{d_p} f_b f_w (1 - \varepsilon_{mf})(T_g - T_{p,w}) + \frac{6h_d}{d_p} [1 - f_b(1 + f_w)](1 - \varepsilon_{mf})(T_g - T_{p,d}) \\ + f_b \sum_{i=1}^n (-\Delta H_{i,b}) R_{i,b} + f_b f_w \varepsilon_{mf} \sum_{i=1}^n (-\Delta H_{i,w,g}) R_{i,w,g} \\ + [1 - f_b(1 + f_w)] \varepsilon_{mf} \sum_{i=1}^n (-\Delta H_{i,d,g}) R_{i,d,g} + Q_t = 0 \end{aligned} \quad (\text{Eq. 21})$$

where d_p is the particle diameter; h_w and h_d are the heat transfer coefficients between the gas and the particles in the wake phase, and between the gas and the particles in the dense phase, respectively, and can be readily estimated using correlations given in Kunii and Levenspiel [1]. The first term in the above equation arises due to particle motion. The second term represents the convective heat transfer between the gas in the wake phase and the solids in the wake phase. Similarly, the third term accounts for the convective transfer between the gas in the dense phase and the solids in the dense phase. The fourth, fifth and sixth terms represent the gas phase reactions in the bubble phase, the wake phase and the dense phase, respectively. The last term is the heat transferred to the bed from the pulse combustors. Similarly, for the particles in the wake phase, the energy balance equation can be derived as

$$\begin{aligned}
& C_{pp}\rho_p(1-\varepsilon_{mf})\frac{d(u_b f_b f_w A T_{p,w})}{dz} + C_{pp}\rho_p f_b f_w (1-\varepsilon_{mf})AK_{wd,p}(T_{p,w} - T_{p,d}) \\
& - C_{pp}\rho_p(1-\varepsilon_{mf})(\lambda_5 T_{p,w} + \lambda_6 T_{p,d})\frac{d(u_b f_b f_w A)}{dz} \\
& + f_b f_w A(1-\varepsilon_{mf})\left\{\frac{6h_w}{d_p}(T_{p,w} - T_g) + \sum_{i=1}^n (-\Delta H_{i,w,s})R_{i,w,p}\right\} + AQ_{vap} = 0
\end{aligned} \tag{Eq. 22}$$

where Q_{vap} is the energy required to vaporize the water in the black liquor. The second term accounts for the heat transfer due to the solids exchange between the wake phase and the dense phase. The fourth term represents heat exchange between the solids and the gas in the wake phase and the energy consumption due to the heterogeneous reactions in the wake phase. Other terms are similar to those in the previous equations. A similar energy balance equation can be written for the particles in the dense phase,

$$\begin{aligned}
& C_{pp}\rho_p \frac{d\{u_{p,d}[1-f_b(1+f_w)]AT_{p,d}\}}{dz} + C_{pp}\rho_p f_b f_w AK_{wd,p}(T_{p,d} - T_{p,w}) \\
& + C_{pp}\rho_p(\lambda_5 T_{p,w} + \lambda_6 T_{p,d})\frac{d(u_b f_b f_w A)}{dz} \\
& + [1-f_b(1+f_w)]A\left\{\frac{6h_d}{d_p}(T_{p,d} - T_g) + \sum_{i=1}^n (-\Delta H_{i,d,p})R_{i,d,p}\right\} = 0
\end{aligned} \tag{Eq. 23}$$

Assume that there is not heat exchange between the gas phase and the reactor wall in the freeboard, the energy balance for the freeboard is then given by

$$u_0 C_{pg}\rho_g \frac{dT_g}{dz} + \sum_{i=1}^n (-\Delta H_{i,f})R_{i,f} = 0 \tag{Eq. 24}$$

The second term represents heat of reactions due to the homogeneous reactions.

3.2.6 Boundary Conditions

The boundary conditions for the energy balance equations are: at the bottom of the bed,

$$T_g = T_{g,inlet}; \quad T_{p,w} = \frac{m_p T_{p0} - [1-f_b(1+f_w)](1-\varepsilon_{mf})u_{p,d}A\rho_p T_{p,d}}{f_b f_w u_b (1-\varepsilon_{mf})A\rho_p} \quad \text{at } z = 0 \tag{Eq. 25}$$

at the top surface of the fluidized bed,

$$T_{p,d} = T_{p,w} \quad \text{at } z = H_t \tag{Eq. 26}$$

The boundary conditions for the mass balance equations depend on the direction of the gas flow in the dense phase. If $u_{g,e} > 0$ at $z = 0$, then, at the gas distributor,

$$C_{i,b} = C_{i,w} = C_{i,d} = C_{i,inlet} \quad \text{at } z = 0 \tag{Eq. 27}$$

However, if $u_{g,d} < 0$ at $z = 0$, then, at the bottom of the bed,

$$C_{i,b} = C_{i,inlet}; C_{i,w} = \frac{(u_0 - f_b u_b) C_{i,inlet} - [1 - f_b(1 + f_w)] \varepsilon_{mf} u_{g,e} C_{i,e}}{f_b f_w \varepsilon_{mf} u_b} \quad \text{at } z = 0 \quad (\text{Eq. 28})$$

and at the top of the bed,

$$C_{i,d} = C_{i,w} \quad \text{at } z = H_t \quad (\text{Eq. 29})$$

3.2.7 Drying and Devolatilization of Black Liquor

Experimental data show that drying and devolatilization of black liquor are heat transfer controlled processes under recovery furnace conditions [14]. Experiments and model simulations also indicate that, under these conditions, drying and devolatilization take place simultaneously as black liquor droplets are heated [15,16]. However, under the conditions considered here, it is expected that drying and devolatilization occur consecutively. It is assumed that devolatilization takes place only after the droplets are completely dry. The energy balance for a single black liquor droplet can be written as

$$C_{pp} \rho_p \frac{dT_p}{dt} = \frac{6h_w}{d_p} (T_g - T_p) - m_{vap} \lambda_{vap} \quad (\text{Eq. 30})$$

where m_{vap} is the volumetric evaporation rate ($\text{kg}/\text{m}^3\text{s}$) of black liquor water and λ_{vap} is the latent heat of evaporation. If drying is a heat transfer controlled process, black liquor droplets can then be assumed to be at pseudo-steady state, thus,

$$m_{vap} = \frac{6h_w}{d_p \lambda_{vap}} (T_g - T_p) \quad (\text{Eq. 31})$$

where T_g is the local gas temperature. Droplet temperature, T_p , can be assumed to be the temperature of the boiling point of water at the local pressure. Drying begins once black liquor enters the fluidized bed and is complete when all the water in black liquor vaporizes.

For simplicity, it is assumed that devolatilization time is the same as that of drying. The fraction of each component in black liquor released into the gas phase depends on the environmental temperature to which the black liquor subjects. Reported correlations [3,4] are used to determine C, H, O and S release rates. Volatiles are assumed to consist of CH_4 , CO , H_2O and H_2S . The amount of each gas species released can be determined from an elemental mass balance.

3.2.8 Gasification Kinetics

Global reaction mechanisms are used to describe black liquor gasification. The reactions considered in the model include:

Steam gasification (Li and van Heiningen, 1991 [17])

$$\text{Rate} = 2.56 \times 10^9 \exp\left(-\frac{25300}{T_p}\right) \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2\text{O}} + 1.42 p_{\text{H}_2}} C_c \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 32})$$

CO₂ gasification (Li and van Heiningen, 1990 [18])

$$\text{Rate} = 6.30 \times 10^{10} \exp\left(-\frac{30070}{T_p}\right) \frac{p_{\text{CO}_2}}{p_{\text{CO}_2} + 3.4 p_{\text{CO}}} C_c \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 33})$$

Methane-steam reforming reaction (Jones and Lindstedt, 1988 [19])

$$\text{Rate} = 3.00 \times 10^8 \exp\left(-\frac{15105}{T_g}\right) C_{\text{CH}_4} C_{\text{H}_2\text{O}} \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 34})$$

Kinetics for other reactions have been adopted from MFIX (Guenther et al. [20]), which is a modified version of the reaction scheme used in Syamlal and Bissett [21], and is based on gasification kinetics proposed by Wen et al. [22].

Methanation (Wen et al. [22], Syamlal and Bissett [21])

$$\text{Rate} = 9.87 \times 10^{-6} \exp\left(-7.087 - \frac{8078}{T_p}\right) (p_{\text{H}_2} - p_{\text{H}_2}^*) C_c \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 35})$$

where

$$p_{\text{H}_2}^* = \sqrt{\frac{1.01325 \times 10^5 p_{\text{CH}_4}}{\exp(-13.43 + 10999/T_p)}} \quad (\text{Eq. 36})$$

Carbon combustion (Wen et al. [22], Syamlal and Bissett [21])

$$\text{Rate} = \frac{5.9215 \times 10^{-4} p_{\text{O}_2}}{d_p \left(\frac{1}{k_f} + \frac{1}{k_r} \right)} \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 37})$$

where the film resistance is given by

$$k_f = \frac{100 D_{O_2} Sh}{d_p R_{O_2} T_f} \quad (\text{Eq. 38})$$

where R_{O_2} is the gas constant for oxygen, $R_{O_2} = 0.25982 \text{ m}^3 \cdot \text{Pa} / \text{g} \cdot \text{K}$; T_f is the film temperature and can be calculated as

$$T_f = (T_g + T_p) / 2 \quad (\text{Eq. 39})$$

The Sherwood number is given by (Gunn [23])

$$Sh = (7 - 10 \epsilon_g + 5 \epsilon_g^2) (1 + 0.7 Re^{0.2} Sc^{1/3}) + (1.33 - 2.4 \epsilon_g + 1.2 \epsilon_g^2) Re^{0.7} Sc^{1/3} \quad (\text{Eq. 40})$$

The surface reaction rate is given by (Desai and Wen [24])

$$k_r = 860 \exp\left(-\frac{13587}{T_p}\right) \text{ g} / \text{Pa} \cdot \text{m}^2 \cdot \text{s} \quad (\text{Eq. 41})$$

CO combustion (Westbrook and Dryer [25])

$$\text{Rate} = 2.238 \times 10^{12} \exp\left(\frac{-20130}{T_g}\right) C_{O_2}^{0.25} C_{CO} C_{H_2O}^{0.5} \text{ kmol} / \text{m}^3 \text{s} \quad (\text{Eq. 42})$$

CH₄ combustion (Westbrook and Dryer [25])

$$\text{Rate} = 2.12 \times 10^{11} \exp\left(\frac{-24356}{T_g}\right) C_{O_2}^{1.3} C_{CH_4}^{0.2} \text{ kmol} / \text{m}^3 \text{s} \quad (\text{Eq. 43})$$

H₂ combustion (Peters [26])

$$\text{Rate} = 1.08 \times 10^3 \exp\left(\frac{-15100}{T_g}\right) C_{O_2} C_{H_2} \text{ kmol} / \text{m}^3 \text{s} \quad (\text{Eq. 44})$$

Water-gas shift reaction (Wen et al. [22])

$$\text{Rate} = 1.956 \times 10^6 f_3 \left(\frac{P}{1.01325 \times 10^5} \right)^{\left(0.5 - \frac{P}{250 \times 1.01325 \times 10^5}\right)} \exp\left(\frac{-13969}{T_g}\right) (C_{\text{CO}} C_{\text{H}_2\text{O}} - C_{\text{CO}_2} C_{\text{H}_2} / K_3) \quad \text{kmol/m}^3\text{s} \quad (\text{Eq. 45})$$

where

$$f_3 = 10^{-3} \exp(-8.91 + 5553/T_g) C_{\text{ash}} \quad (\text{Eq. 46})$$

and the equilibrium constant is given by

$$K_3 = \exp(-3.63061 + 3955.71/T_g) \quad (\text{Eq. 47})$$

The reactions involving oxygen are insignificant since for the system considered here, there is not oxygen in the inlet streams or oxygen formed in the bed. However, these reactions are included so that the computer code developed may also be used for combustion of black liquor. The above mechanisms only account for gasification and combustion of carbon in black liquor. Since black liquor contains significant amount of oxygen and considerable amount of hydrogen, it is important to also consider the release of elemental oxygen and hydrogen from black liquor during gasification. It is assumed that ash consists of sodium carbonate and potassium carbonate. The release rates of elemental oxygen and hydrogen are assumed to be proportional to the carbon gasification/combustion rate and the ratio of the amount of elemental oxygen or hydrogen available for release to the amount of carbon available for gasification. Elemental oxygen and elemental hydrogen are assumed to release as water vapor and hydrogen or carbon monoxide depending on the relative release rates of elemental oxygen and hydrogen.

3.3 Heat Transfer Model for Heater Bundles

A computational model to predict heater bundle tube surface temperatures and particle temperatures in the tube bundle region has been developed. The hydrodynamics for the model are MFI simulation results, provided by NETL through a collaborative effort. REI uses these models to calculate the heat transfer and temperatures in the heater bundles. The heat transfer model consists of three components.

Heat transfer from the combustion gases to the heater tubes. The energy balance for a single tube at a certain axial location (cell i) of the tube can be written as

$$q_{g2t,i} = A_i h_{g2t} (T_g - T_{in}) \quad (\text{Eq. 48})$$

where A_i is the inner surface area of the tube for cell i and T_{in} is the local inner surface temperature of the tube; $q_{g2t,i}$ is the heat transfer for the particular tube cell. The heat transfer coefficient from the pulse combustor gases to the heater tube has been found to be significantly enhanced with the use of resonance tubes. The enhancement can be explained using the quasi-steady-state theory [27]. Measurements of the heat transfer in the MTCI PulseEnhanced combustor indicate that the quasi-steady-state theory correlates

well with the measured data [28], but attempts to duplicate the results in the report raise some questions. Further work by Arpaci et al. [29] takes into account the effect of frequency of the velocity oscillations and shows that the heat transfer coefficient can be estimated using

$$Nu = 0.028 \overline{Re}^{3/4} \left[1 + 0.21 \frac{U_0}{\overline{U}} \left(1 + 7.36 \frac{(\omega - 46)D}{\overline{U}} \right) \right]^{3/4} \quad (\text{Eq. 49})$$

where Nu denotes the Nusselt number based on the hydraulic diameter D of the heater tube, $\overline{Re}$ is the Reynolds number based on the mean velocity $\overline{U}$ and U_0 is the amplitude of velocity oscillations with a frequency of ω . Equation 49 has been found to be in very good agreement with experimental data (Arpaci et al., 1993). For the present simulation conditions, calculation using Equation 49 indicates a heat transfer coefficient of 63 W/m²·K, much lower than 170 W/m²·K reported in the design qualification test of the pulse combustor [28]; the latter is used in the simulation reported here.

Gas temperature inside the tube changes along the tube length. Assuming that the gas inside the tube is in plug flow, the energy balance for the gas can be derived as

$$\overline{U} \rho_g C_{pg} \frac{dT_g}{dL} + \frac{4h_{g2t}}{d_t} (T_g - T_{in}) = 0 \quad (\text{Eq. 50})$$

where d_t is the tube inner diameter and L is the coordinate along the length of the tube. Boundary condition for the preceding equation is $T_g = T_{g,in}$ at $L = 0$. $T_{g,in}$ can be assumed to be the adiabatic flame temperature of the pulse combustor.

Total heat transfer from the combustion gases to a single tube is given by

$$Q_{g2t} = \sum_{i=1}^n q_{g2t,i} \quad (\text{Eq. 51})$$

where n is the number of cells along the tube.

Heat transfer from the electrical heater to the glass tubes in the University of Utah cold flow model can be calculated using a similar energy balance on elements of the tubes.

Heat transfer distribution along the tubes. Conduction heat transfer from the inner surface to the outer surface of the tube metal or glass tube can be calculated for the pulsed combustion conditions used in the GP unit or for the applicable heater configuration of the University of Utah unit. The temperature profile on the outer surface of the heater tubes may then be calculated. The energy balance can be written as

$$\frac{1}{r} \frac{d}{dr} \left(-r \frac{dT}{dr} \right) = 0 \quad (\text{Eq. 52})$$

with a boundary condition of $T = T_{in}$ at $r = r_{in}$ and $T = T_{out}$ at $r = r_{out}$. Integration of the above equation leads to

$$T = \frac{T_{out} - T_{in}}{\ln\left(\frac{r_{out}}{r_{in}}\right)} \ln\left(\frac{r}{r_{in}}\right) + T_{in} \quad (\text{Eq. 53})$$

Heat transfer from the inner surface to the outer surface for cell i of length ΔL is given by

$$q_{i2o,i} = \frac{2\pi k_t \Delta L (T_{in} - T_{out})}{\ln\left(\frac{r_{out}}{r_{in}}\right)} \quad (\text{Eq. 54})$$

In the above equation, k_t is thermal conductivity of the tube metal. Total conduction heat transfer for a single tube is

$$Q_{i2o} = \sum_{i=1}^n q_{i2o,i} \quad (\text{Eq. 55})$$

Heat transfer from the tubes to the dense phase. Heat transfer between the bed solids and submerged horizontal tubes has been studied by many investigators. Many empirical correlations in the form of power relationships in terms of Re , Nu and Pr numbers have been developed. Glicksman et al. [30] compared the predictions of the heat transfer coefficients from six correlations with a large common experimental data base and found that the resulting RMS ranged from 38.5% to 94.0%. The possible reason for the poor agreement is that the original correlations were developed from a limited data base, with narrow ranges of pertinent variables. It was found that the modified Vreedenberg correlation, developed by Andeen and Glicksman [31], was relatively more successful on an overall basis. The modified Vreedenberg correlation can be written as

$$\frac{h_{t2p} D_t}{k_g} = 900(1 - \varepsilon) \left(\frac{u D_t \rho_p}{\mu} \frac{\mu^2}{d_p^3 \rho_p^2 g} \right)^{0.326} \left(\frac{C_{pg} \mu}{k_g} \right)^{0.3} \quad (\text{Eq. 56})$$

where

- h_{t2p} = heat transfer coefficient, $W/(m^2 \cdot K)$
- C_{pg} = specific heat of gas, $J/(kg \cdot K)$
- d_p = particle size, m
- D_t = tube outer diameter, m
- g = acceleration of gravity, m/s^2
- k_g = thermal conductivity of gas, $W/(m \cdot K)$
- u = superficial gas velocity, m/s
- ε = bed voidage
- μ = gas viscosity, $Pa \cdot s$
- ρ_p = particle density, kg/m^3
- ρ_g = gas density, kg/m^3

The above correlation is applicable for particles with mean diameters less than 1 mm. Since the modified Vreedenberg correlation excludes terms which account for fluid inertia effects, an upper limit on its applicability is that fluid inertia terms are of the same order of magnitude as viscous terms. This limit can be approximated as

$$\frac{u d_p \rho_p}{\mu} < 10 \quad (\text{Eq. 57})$$

Bed void fraction inside the tube bundles is provided through MFIX simulations conducted at NETL. The temperature of the bed solids is calculated by coupling the heat transfer through the tube walls with a balance on the solids flowing through the tube bundle. The particle energy balance can be written as

$$\begin{aligned} & \frac{\partial}{\partial x} (m_x C_{pp} T_p) + \frac{\partial}{\partial y} (m_y C_{pp} T_p) + \frac{\partial}{\partial z} (m_z C_{pp} T_p) \\ & = h_{t2p} A_t''' (T_{out} - T_p) - (1 - \varepsilon) \sum (-\Delta H_{i,p}) R_{i,p} \end{aligned} \quad (\text{Eq. 58})$$

where

A_t'''	= tube outer surface area per unit bed volume, m^2/m^3
C_{pp}	= specific heat of solids, $\text{J}/(\text{kg} \cdot \text{K})$
m	= particle mass flux, $\text{kg}/(\text{m}^2 \cdot \text{s})$
T_p	= particle temperature, K
$-\Delta H_{i,p}$	= heat of heterogeneous reaction, J/kmol
$R_{i,p}$	= heterogeneous reaction rate, $\text{kmol}/\text{m}^3 \cdot \text{s}$

Assume C_{pp} is constant. Then, under steady state conditions, the above equation can be simplified as

$$\begin{aligned} & m_x C_{pp} \frac{\partial T_p}{\partial x} + m_y C_{pp} \frac{\partial T_p}{\partial y} + m_z C_{pp} \frac{\partial T_p}{\partial z} \\ & = h_{t2p} A_t''' (T_{out} - T_p) - (1 - \varepsilon) \sum (-\Delta H_{i,p}) R_{i,p} \end{aligned} \quad (\text{Eq. 59})$$

Particle mass flux is obtained from MFIX simulation results. Boundary conditions for the above equation can be determined from the REI 1½-D model developed earlier [32]; heat transfer to the gasifier wall is assumed to be negligible. Equations 50, 51, 55 and 59 have to be solved simultaneously. Iteration is necessary and is performed until all energy balances are satisfied. Note that the following equation also holds

$$NQ_{g2t} = NQ_{i2o} = h_{t2p} A_t''' V (T_{out,avg} - T_{p,avg}) \quad (\text{Eq. 60})$$

where N is the total number of the heat tubes and V is the bed volume in each pulse combustor section. $T_{out,avg}$ and $T_{p,avg}$ are the average temperature of the outer surface of the heater tubes and average particle temperature, respectively, in the pulse combustor sections.

4. RESULTS AND DISCUSSION

The project's second year was quite productive in terms of acquiring useful data, from both experimental and modeling activities. Results from the project are presented in the sections below, ordered according to the four experimental and modeling tasks (Tasks 2-5) described in the Introduction.

4.1 Investigation of Bed Performance

Task 2, "Investigation of Bed Performance" includes two subtasks that involve characterization of the bed solids and changes in the solid properties during conversion, and (2) identification of factors contributing to bed agglomeration.

4.1.1 Bed Characterization

4.1.1.1 Particle Size Distributions

The distribution of particle sizes (diameters) was determined for material from a steam reforming process development unit and a full-scale steam reformer by sieving samples from these units. For both types of samples, the particle size distributions were quite broad. For the commercial system, 90% of the particles were in the range 75-850 microns, with roughly half the particles in the range 150-300 microns. The harmonic mean diameter was roughly 250 microns.

Solids from a commercial unit having an initial organic carbon concentration of roughly 17 wt% was used as starting material for a "steam-out" test in the University of Utah steam reformer, during which no liquor was injected but carbon was gasified from the material. The progression of particle size distribution was followed as a function of conversion, and is shown in Figure 23. Clearly, there is very little change in particle size as the carbon is gasified away, suggesting that the inorganic matrix of the solids, which dictates the particles' size, remains relatively intact as the carbon is removed.

Figure 23. Progression of particle size distribution during a "steam out" run. Samples 1, 7 and 10 correspond to roughly 0%, 10% and 100% conversion, respectively.

In addition to studying how particle size changes as carbon is reacted away, tests were performed in University of Utah's 2-inch fluidized bed to study how particle size develops when liquor is fed to the system but no heterogeneous reaction takes place. For these tests, reagent-grade sodium carbonate was used as initial bed material. Black liquor was injected into the freeboard of the reactor and allowed to fall onto the bed. The resulting mean particle diameter was tracked as a function of time, and the results of two such tests having different initial particle sizes and liquor injection rates can be seen in Figure 24.

Figure 24. Development of mean particle diameter during an experiment in the 2-inch fluidized bed.

As seen in the figure, the mean particle diameter grew significantly over a relatively short period of time. Much of this can be attributed to the manner in which liquor was injected into the bed. As droplets fell onto the bed, they often captured several particles already in the bed and formed clusters of particles according to the clustering mechanism described below in Section 4.1.1.4. This was confirmed through microscopy, where large particles could be seen to be made up of several small particles held together by pyrolyzed liquor.

4.1.1.2 Optical Imaging of Particles

Samples of solids from commercial units as well as solids from the Utah steam reformer and the 2-inch fluidized bed were photographed through an optical microscope to gain a qualitative understanding of particle structure. In order to study the internal structure of the particles, and to get a sense of development of liquor coating on particles, some of the samples were captured in epoxy, then cross-sectioned and polished.

Evidence of particle growth through clustering is seen in Figure 25, which shows initial and final samples from experiments in the 2-inch fluidized bed with liquor injection. Particularly notable are the samples from Experiment 2 on the left. That starting material was glass beads, and the beads can clearly be seen to have been captured within the material. A theory about the specific mechanism of clustering could be that the wet liquor actually partly dissolves the edges of particles, and that the sticky edges fuse together. Unlike normal bed solids or sodium carbonate, however, the glass beads in Experiment 2 would not partly dissolve upon contact with the wet liquor. This indicates that the clustering mechanism is in fact a direct result of the wet liquor capturing many smaller particles to make a large particle.

Figure 25. High magnification photographs of bed material from the 2-inch fluidized bed after operation under inert conditions with liquor injection. Initial bed materials for experiments 2, 3 and 4 were glass beads, unsieved sodium carbonate and pre-sieved sodium carbonate.

4.1.1.3 Scanning Electron Microscopy (SEM) Analysis

In addition to the optical microscopy studies described above, samples of bed material from commercial systems, the Utah steam reformer and the 2-inch fluidized bed were analyzed by scanning electron microscopy to identify structural and compositional properties of the material. Samples of bed solids cast in epoxy, sectioned and polished were also analyzed to study internal structure and development of layers formed by liquor coating.

In one series of experiments, limestone particles were fluidized in the 2-inch reactor while liquor was injected. Samples of the original limestone and particles removed after various exposure times were examined with the electron microscope. Results of these analyses as well as photos taken through an optical microscope are presented in Figure 26. As one would expect, the particles became darker over time due to deposition of liquor on the surface. This can be seen in the photos in the top row of the figure. At low magnification under the SEM, the surface of the particles appears to have become more textured over time, but higher magnification indicates that the microstructure became much more smooth, possibly resulting in less surface area. Surface area analyses were not performed on the limestone particles, but BET surface area measurements for glass bead starting material indicate that the surface area decreased as exposure time increased.

Evidence of liquor coating the particles is also clear from the SEM images. Figure 27 shows a cross-section of the edge of a limestone particle exposed to liquor injection in the 2-inch fluidized bed reactor for 8 hours. Layers of material on the edge of the particle are clearly visible. The combined thickness of these layers for this sample is about 15 microns. The images in (b) and (c) of Figure 27 show the same edge at lower magnification, and EDAX maps for calcium and sodium. Clearly, the liquor coats the particles and forms layers.

In some of the experiments, particles were observed to have bound together to form larger particles. A sample of this type of binding together is shown in Figure 28. Though the particles are held together by the coating, this type of structure is somewhat different than was observed for the clustered particles. The exact nature of this type of particle binding is still under investigation.

Figure 26. Optical and SEM images of particles sampled at various times after liquor injection began.

Figure 27. Photo (a) shows a close-up of the 8-hour sample, in which layers of material can clearly be seen. Photos (b) and (c) show the same particle at lower magnification with corresponding calcium and sodium maps. The strong presence of sodium in the coated layers is evident.

Figure 28. SEM images showing details of bridges formed between particles.

4.1.1.4 Particle Growth and Shrinkage Mechanisms

Several mechanisms for increases and decreases in mean particle size have been identified. Growth can follow one or more of the following mechanisms:

- **Agglomeration.** Particle size enlargement from the adhering of at least two initial particles by solid bridges between them. The added substance, in this case black liquor, forms these bridges.
- **Coating.** Deposition process in which one or several consecutive layers accumulate on the entire particle surface.
- **Sintering.** Binding process of at least two initial particles due to the softening of the particle surface.
- **Clustering.** Capturing process of at least two initial particles due to a droplet-particle collision.

Shrinkage can follow one or more of the following mechanisms:

- **Fragmentation.** A number of smaller particle fragments results from this shrinking mechanism. It yields a rapid disappearance of the original particles but promotes particle formation due to these new fragments.
- **Attrition.** The removal of asperities and fines from the particle surfaces creates a gradual change in the size of the attriting particles. This new group of small particles can form new material or be elutriated by the gas stream.
- **Cluster breaking.** The liquor that was responsible for clustering several smaller particles into a large particle reacts away enough to release these captured particles.

Combining observations of particle structure, particle growth and particle-particle interactions described above with experience reported in literature of similar systems, a scheme describing mechanisms and pathways for particle growth has been postulated. This is presented schematically in Figure 29. The ultimate particle size distribution will be a function of the relative contributions of these mechanisms and the shrinkage mechanisms described above.

Figure 29. Pathways and mechanisms for particle growth.

4.1.2 Bed Agglomeration Studies

Brigham Young University has performed valuable experiments to shed light on agglomeration temperatures and mechanisms of agglomeration for various bed materials.

4.1.2.1 Agglomeration Temperatures and Mechanisms

The test matrix included thirteen complete runs that were performed in the fluidized bed reactor; three with Na_2SO_4 bed material, eight runs using Na_2CO_3 bed material with KCl impurity, and two runs using Na_2CO_3 bed material with KCl impurity and black liquor injected into the bed. Figure 30 shows the agglomeration temperatures for each experiment. For pure Na_2CO_3 bed material, the bed began to agglomerate at a bed temperature of 520 °C. The agglomeration temperature rapidly decreased with the inclusion of KCl impurity in the bed. With 0.5% KCl impurity by weight added to the bed, agglomeration temperature decreased 40 °C. Replicate experiments with impurity concentrations of 0.0% and 2.0% KCl

establish the precision of the experiments ($\pm 5^\circ\text{C}$). The indicated agglomeration temperatures differed by 3°C and 5°C respectively. Because of the difficulty in determining an exact temperature at which agglomeration begins, a difference in temperature within 0.6% and 1.0% of the total temperature, respectively, represents an acceptable range for showing repeatability.

Results from the three runs performed with a Na_2SO_4 bed material indicate that agglomeration began at a bed temperature of approximately 490°C for pure Na_2SO_4 and 440°C for Na_2SO_4 containing KCl impurity concentration of 2.0%.

Figure 30. Agglomeration temperatures for various bed materials.

The repeated test conducted with 2.0% impurity indicated two types of agglomeration. The first type was bed particles agglomerating to heater surfaces in partially stagnant regions of the reactor at approximately 465°C . Figure 31 shows the bed material agglomerated to heater surfaces. As evident from the picture, surface agglomeration occurred to a greater degree on the top of the heater surfaces (where flows are most stagnant). These data indicate that, with an increasing KCl concentration, the mass diffusion towards high-energy surface contact points increases and accordingly, the necessary contact time between particles for sintering to occur decreases.

A particularly useful analysis for this investigation involves generating elemental maps from SEM/XDS data based on these principles. Figure 32 shows a set of data from such maps that typically include the secondary-electron image, the backscattered-electron image, and a series of images that show the spatially resolved concentrations of each element of interest.

Figure 31. Agglomeration on heater surfaces

Figure 32. SEM elemental mapping example showing KCl binding particles together in a sample of sintered bed material. The first two images are the secondary electron and backscatter images, respectively. The remaining images are, in order of appearance from left to right and then top to bottom, Na, Si, S, Cl, and K.

The upper left hand corner of each image indicates the type of map. For example, the top left hand corner is marked “SE”. This is the secondary-electron or topographical image of the sample. The elemental maps are marked first with the element and then the orbital from which the electron was detected. The map in the top right hand corner is “NaKa1”, indicating that this is the map of sodium with electrons being detected from the k-alpha orbital of the sodium valence electrons.

The detector and window used in this analysis prevented detection of Na. However, the Cl and K plots strongly suggest that KCl forms a thin coating on the particles that helps adhere them together. As demonstrated earlier, these particles are well below the melting points of either pure compound or any eutectic that normally forms from such compounds, indicating that there is no molten phase involved in this sintering. Nevertheless, the KCl forms an apparent binding surface layer.

Figure 33 shows the backscatter SEM image of a sample taken from the same 2.0% impurity test. The dark regions in the picture are voids while the gray regions are Na_2CO_3 and the white regions are KCl. The regional compositions were determined using x-ray diffraction. The Na_2CO_3 regions seem to be surrounded by a KCl boundary. This suggests a possible mass diffusion resulting from a concentration gradient between the KCl and Na_2CO_3 . Diffusion from a difference in concentration in addition to mass diffusion from surface energy reduction could be one explanation for the decrease in sintering temperature with increasing KCl concentration.

Figure 33. Backscatter image of an agglomerated particle at 6.0% impurity concentration

Repeated experiments with no impurity in the bed material confirmed that agglomeration and sintering temperatures were difficult to distinguish because, unlike tests with impurity, the results did not show a spike in bed or heater surface temperature, as mentioned previously.

Particle sizes of bed material removed from the reactor for the no-impurity test were sized using varying sieves. Figure 34 shows the change in particle size before and after these tests. Note that the x-axis is the natural log of the particle diameter. The fraction of particles smaller than 100 μm was not included in both initial and final mass fraction calculations because these particles could easily have become entrained in the exiting gases instead of sintering.

A factor of 5 increase in the weight fraction of particles larger than 500 μm , indicates that particle sintering occurred in the free bed material consistent with the increase in temperature between bed material and heater surfaces temperature. Figure 35 shows the enlargement of the particles before and after the agglomeration tests with excellent repeatability between the two post test measurements.

Figure 34. Particle size distributions for pure Na_2CO_3 bed material before and after agglomeration tests. Note that the x-axis is the natural log of the particle diameter.

Figure 36 and Figure 37 show the sintering of pure Na_2CO_3 at 520 $^{\circ}\text{C}$ occurring at the grain boundaries for particles that contact each other in the fluidized bed. The agglomerates in these figures came from the free bed and were not attached to the surface of the heaters, showing that agglomeration and sintering occurs even away from stagnant regions of the reactor. As is evident from these figures, sintering seems to have occurred at the edges of particles where the surface energy would be the highest. Thus, diffusion of material from regions of lower surface energy towards regions of higher surface energy is apparent.

Figure 35. Sodium Carbonate bed material before and after agglomeration tests

Figure 36. Bridging between particles at the onset of sintering between particles at 520 °C

Figure 37. The onset of bridging between two particles at 520 °C

Commercial gasification operation does not use pure bed materials but rather bed materials coated with residual char and inorganics from the liquor. Two types of experiments more closely simulated commercial systems. In the first, liquor was added to our laboratory reactor in small quantities, while ramping the temperature up, similar to the pure bed experiments. The feed rate and bed temperature range of liquor injection varied in these experiments. The second type of experiment involved using bed material from commercial-scale demonstration projects of this technology.

One of the runs with black liquor injection resulted in bed agglomeration in the same manner and at the same temperatures as those runs that did not involve black liquor injection. Water dilution lowered liquor viscosity to manageable levels (9.8% dry solids) in these liquor injection tests. In one of these runs, the black liquor was injected when the bed temperature reached 400 °C. The large amount of water in the black liquor caused the bed temperature to decrease rapidly; the heater set point was still at 400 °C and the heaters began heating up rapidly to compensate. Heater surface temperatures increased to over 550 °C and the bed began to agglomerate to these surfaces. For the other run, the black liquor was injected at a lower bed temperature (300 °C) and more slowly. The bed temperature did not drop as rapidly and agglomeration was avoided. After all of the black liquor was injected, the temperature was again incrementally increased. The bed began to agglomerate at a slightly higher temperature (470°C vs. 465 °C) as the run with the same amount of impurity (2.0%) but without the black liquor. However, this difference is within agglomeration temperature uncertainty of about 20 °C to 25 °C determined by a combination of bed to heater temperature difference, bed to heater set-point difference, and a visual assessment of fluidization quality in the reactor. The black liquor runs also contained agglomerated particles in the bed comprising bed particles coated with black liquor.

The effect of a black liquor coating on the agglomeration temperature cannot be determined from these tests because the injected black liquor did not evenly coat all the bed particles. Therefore, bed material

from a commercial black liquor steam reformer was used to determine the impact on agglomeration temperature and sintering characteristics of a carbon-coated bed material. For this test, the bed temperatures reached a maximum of 640°C with the heater surface temperatures at a temperature of 650°C without bed sintering or agglomerating. Higher temperatures were not obtainable because heat transfer from the reactor reached a steady state with the maximum heat input from the heaters. To achieve higher temperatures, additional insulation was needed.

The impact of the black liquor coating on sintering and agglomeration temperatures is that temperatures of at least 120°C higher than the pure Na₂CO₃ bed material are obtainable without sintering. Several explanations exist for this behavior. One explanation is that the carbon inhibits the mass diffusion from the bulk material to higher-energy surface contact points. Also, mass diffusion through the carbon due to a concentration gradient is sufficiently slow that this mechanism is also inhibited.

Upon removal of the bed material, no agglomeration was evident on heater surfaces or in stagnation points throughout the reactor. These results indicated that temperatures of at least 650°C are obtainable in a commercial facility without the agglomeration of this bed material. However, black liquor feed stocks often vary significantly in composition, especially in potassium, sodium, and chlorine content, which could significantly affect the sintering and agglomeration temperatures of the bed material.

Tests using pure Na₂CO₃ bed material show a change in the temperature difference between heater surfaces and bulk bed material beginning at approximately 9 °C and ending at around 30 °C. This could indicate that the Na₂CO₃ bed material began sintering at a much lower temperature because of the noticeable decrease in heat transfer. However, this could be attributed to an increase in heat loss as the reactor temperature increases, as explained earlier.

4.1.2.2 Sintering Model

An analytical model was developed to help understand the relationship between the measured heater surface and bed temperatures and the particle size of the bed material. For the entire reactor system at steady state, the energy inflow must equal energy flowing out of the reactor in the form of mass flow and heat transfer (convection and radiation). The energy balance for the reactor is given by Equation 61.

$$\dot{W}_{in,heaters} + \dot{m}_{out}h_{in} = \dot{m}_{out}h_{out} + \dot{Q}_{out,radiation} + \dot{Q}_{out,freeconvection} \quad (\text{Eq. 61})$$

where:

- $\dot{W}$ = energy input to heaters, watts
- $\dot{Q}$ = heat transfer from the system (by radiation or convection), watts
- $\dot{m}$ = mass flow, kg/s
- h = enthalpy, J/kg

Insulating the reactor causes the heat transfer terms to be small in comparison to the remainder of terms in Equation 61. Dropping the heat transfer terms and substitution temperatures for the enthalpy terms gives Equation 62. For the reactor, the electrical work in is equal to the heat transfer from the surface of the heaters to the bed which can be calculated from a heat transfer coefficient and temperature difference as shown in Equation 63. Finally, it should be recognized that the fluidization velocity and not the mass flow was held constant as the bed was heated. Therefore the mass flow rate can be written in terms of velocity as shown in Equation 64.

$$\dot{W}_{in,heaters} = \dot{m} C_p (T_{out} - T_{in}) \quad (\text{Eq. 62})$$

$$\dot{W}_{in,heaters} = VI = h_{heater} \cdot A_{heater} \cdot (T_{surface} - T_{bed}) \quad (\text{Eq. 63})$$

$$m_{in} = \rho_{gas} A_r V_{gas} = \frac{P_{reactor}}{R_g T_{bed}} A_r V_{gas} \quad (\text{Eq. 64})$$

where:

- C_p = gas heat capacity, J/(kg·K)
- $P_{reactor}$ = reactor absolute pressure, kPa
- R_g = gas constant, kPa·m³/(kmol·K)
- h_{heater} = heater to bed heat transfer coefficient, W/(m²·K)
- A_{heater} = total heater surface area, m²
- T_{bed} = bed temperature, K
- $T_{surface}$ = heater surface temperature, K
- ρ_{gas} = gas density, kg/m³
- A_r = Cross sectional area of the reactor, m²

Substituting Equations 63 and 64 into Equation 62 gives the final result showing the relationship between the surface and bed temperatures as shown in Equation 65. Equation 65 shows a weak dependence between the temperature in the bed and the difference between the surface and bed temperatures. As bed temperature increases, the temperature difference should approach a constant value for a given heat transfer coefficient (h_{heater}). The heat transfer coefficient is expected to be relatively constant for a given bed particle size, but will decrease as particle size increases. A continuously increasing temperature difference between the surface and bed temperatures is therefore an indication of a decreasing heat transfer coefficient or increasing particle size and sintering in the bed.

$$T_{surface} - T_{bed} = \frac{P_{reactor} A_r V_{gas} \cdot C_{p,g} \cdot (1 - \frac{T_{in}}{T_{bed}})}{R_g \cdot h_{heater} \cdot A_{heater}} = const \frac{(1 - \frac{T_{in}}{T_{bed}})}{h_{heater}} \quad (\text{Eq. 65})$$

The difference between heater surface bed temperatures were plotted versus bed temperature for two test runs with pure Na₂CO₃ and the Norampac test. Figure 38 shows a comparison of the measured data (symbols) and modeled temperature data (lines) for several fixed particle sizes.

Figure 38. Model results compared to a linear regression of data from two tests with pure Na_2CO_3 and the Norampac bed material

From the particle size distribution after each run, no change in particle size was detected for the Norampac bed material. The slope of the line for this material is flat matching the slope of modeling results for 200 micron particles. The slope of Na_2CO_3 bed material is constant and does not decrease with increasing bed temperature. This can be explained by an increasing particle size indicating that these bed materials were sintering.

4.2 Evaluation of Product Gas Quality

This task aims to provide information about the composition and properties of the gas produced in the steam reformer. The first subtask focuses on non-condensable species, particularly minor species, while the second subtask focuses on condensable hydrocarbons ("tars").

4.2.1 Speciation of Gaseous Products

The product gas from a black liquor steam reformer contains many species in various concentrations. In addition to steam, the primary gases are hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4). Minor species include other light hydrocarbons, hydrogen sulfide and possibly other reduced sulfur compounds, and condensable hydrocarbons ("tars").

The majority of tests to date have been so-called "steam-out" tests with no liquor injection. During this type of test, only the heterogeneous reaction of steam with bed solids occurs. The primary reaction is that between steam and carbon in the bed material:

From this reaction alone, one would expect the gas to consist of steam, H_2 and CO , with H_2 and CO present in equal amounts. However, there are other heterogeneous reactions, as well as gas-phase reactions occurring that affect the final composition of the gas.

The most important gas-phase reaction is the water-gas shift reaction:

Though the homogeneous gas-phase rate of this reaction is quite slow at the temperature of the steam reformer ($\sim 600^\circ\text{C}$), the reaction apparently takes place rapidly in the steam reformer. This is most likely a result of catalysis by alkali species in the bed solids. As a result, the relative concentrations of H_2 , CO and CO_2 in the dry product gas are quite close to equilibrium concentrations, rather than the 1:1 H_2 : CO ratio one would expect from the steam reforming reaction alone. The high partial pressure of water and the equilibrium ratio at steam reforming temperatures pushes reaction 2 to the right, so there is relatively little carbon monoxide in the gas, and correspondingly higher concentrations of CO_2 . Results from steam-out tests in the Utah steam reformer indicate that the CO_2 to CO ratio is on the order of 10 to 1. This ratio will be less at the exit of a commercial system since the H_2O concentration is lower and the carbon/steam feed ratio is higher. This is indicated by results from the UU model, as well (Section 4.4.2.1).

Further work on product gas speciation is planned, the objective being to identify and quantify the most significant dozen or so species, and to see how the concentrations of these vary with different operating conditions.

4.2.2 Characterization and Destruction of Tars

As part of the technical support component of the project, the University of Utah has analyzed samples of condensate from the gas conditioning system of the Big Island reformer to identify tar species present. Organics were isolated by extracting the condensate with dichloromethane and analyzing the solvent by gas chromatography-mass spectroscopy (GC-MS).

A typical chromatogram from these analyses is shown in Figure 39. Over 70 different aromatic and polyaromatic species were identified in this particular sample. Of these, 24 were present in high enough concentrations that they could be quantified by integrating the area of the peak in the chromatogram. These 24 components are listed in Table 3, ordered by abundance in the sample. The majority of the tar compounds in the condensate are un-, mono- and di-substituted, mostly methyl phenols having molecular weights ranging from 94 to 178 and boiling points generally around 225°C . Such compounds make up more than 85% of the material found in the analyses.

Many other compounds were also identified in this sample, though their concentration was too low to allow quantification. These minor species are listed in Table 4, ordered by molecular weight. These compounds are generally somewhat heavier and have higher boiling points than those that made up the majority of the sample. This is likely a consequence of the relatively low temperature of the condensate.

Figure 39. GC-MS chromatogram of tars in condensate from the Big Island steam reformer's syngas cleaning system.

TABLE 3. MAJOR TAR COMPONENTS IDENTIFIED IN CONDENSATE FROM GEORGIA-PACIFIC'S BIG ISLAND REFORMER GAS CLEANING SYSTEM.

Compound Name	Mol.Wt.	Boil Temp (°C)	Relative Concentration
3-Methyl-Phenol	108	202	100.0
2-Methyl-Phenol	108	191	65.2
2,5-Dimethyl-Phenol	122	211	54.8
2,4-Dimethyl-Phenol	122	211	47.7
Phenol	94	182	38.2
2,6-Dimethyl-Phenol	122	201	31.0
2,3-Dimethyl-Phenol	122	217	18.9
3,4-Dimethyl-Phenol	122	227	15.0
2-Methyl-Naphthalene	142	241	13.4
4-Methoxy-Phenol	108	202	11.5
2,6-Dimethyl-Phenol	122	201	10.9
2-Ethyl-5-Methyl-Phenol	136	224	10.2
Naphthalene	128	218	9.9
2,4,5-Trimethyl-Phenol	136	232	9.3
3-Ethyl-Phenol	122	216	9.0
2,3-Dihydro-1H-Indene-1-one	132	244	8.9
1-Methyl-Naphthalene	142	242	8.8
2,3-Dihydro-3-methyl-1H-Indene-1-one	132	244	8.4
Anthracene	178	340	7.0
2,3,5-Trimethyl-Phenol	136	234	6.7
9H-Fluorene	166	295	6.5
(1-Ethyl-2-Propenyl)-Benzene	146		6.3
1,4-Dimethyl-Naphthalene	156	265	6.1
2-Methyl-Cyclopentanone	98	140	5.9

**TABLE 4. MINOR TAR COMPONENTS IDENTIFIED
IN CONDENSATE FROM GEORGIA-PACIFIC'S
BIG ISLAND REFORMER GAS CLEANING SYSTEM.**

Compound Name	Mol.Wt.	Boil Temp (°C)
2-Methyl-Pyridine	93	128
2-Phenyl-1H-Indene	93	128
2-Methyl-Pyrene	108	191
1,2,4-Trimethyl-Benzene	120	169
1-Ethyl-4-methyl-Benzene	120	162
2-Ethyl-Phenol	122	205
[1-(2,4-cyclopentadien-1-yliden)ethyl]-Benzene	130	
2,3-Dimethyl-9H-Fluorene	132	244
4-Ethyl-3-Methyl-Phenol	136	229
3-Ethyl-5-methyl-Phenol	136	234
2,4,6-Trimethyl-Phenol	136	220
4-Ethyl-2-Methyl-Phenol	136	225
3,4,5-Trimethyl-Phenol	136	250
2,3,6-Trimethyl-Phenol	136	
Acenaphthylene	152	380
2,6-Dimethoxy-Phenol	154	261
1,1-Dimethyl-1H-Indene	154	254
Acenaphthene	154	279
1-Ethyl-Naphthalene	156	267
1,6-Dimethyl-Naphthalene	156	263
1,3-Dimethyl-Naphthalene	156	265
2,6-Dimethyl-Naphthalene	156	263
1,2-Dimethyl-Naphthalene	156	266
1H-Phenylene	166	
9H-Fluorene-9-carboxylic acid	166	295
9H-Phenylene	166	295
4-Methyl-1,1'-Biphenyl	168	268
4-Methyl-9H-Fluorene	168	268
1,4,5-Trimethyl-Naphthalene	170	
Phenanthrene	178	340
2-Methyl-9H-Fluorene	180	318
1-Methyl-9H-Fluorene	180	
1-Methyl-Phenanthrene	192	
4-Methyl-Phenanthrene	192	
1-Methyl-Anthracene	192	363
Spiro[2.4]heptan-4-one	202	404
Fluoranthene	202	384
Pyrene	202	404
2-Phenylnaphthalene	204	346
2-Ethenyl-Naphthalene	206	
2,3-Dimethyl-Phenanthrene	206	
2,7-Dimethyl-Phenanthrene	206	
7-Methyl-Benzofuran	216	410
7-Methyl-Benzofuran	216	410
11H-Benzo[a]fluorine	216	412
11H-Benzo[b]fluorine	216	401
1-Methyl-Pyrene	216	
Ethenyl-Benzaldehyde	228	448

A second chromatogram of tar components found in the condensate on a different day, when operating the gas cleaning system under different (cooler) conditions, is shown in Figure 40. The overall profile is the same as the chromatogram in Figure 39. This sample contained somewhat fewer compounds, which is likely a result of the lower temperature operation forcing many of the heavier compounds to condense to solid form. Overall, the sample was again mostly composed of un-, mono- and di-substituted, mostly methyl phenols.

Figure 40. A second GC-MS chromatogram of tars in condensate from the Big Island steam reformer's syngas cleaning system.

It should be noted that many heavier compounds were also produced, but that the condensation temperature of these components is high enough that they did not remain in condensate, but rather formed solid deposits in the system. A sample of such condensed tar material revealed a very large, complex mixture of hundreds of compounds. The complexity of the chromatogram for the sample of condensed deposit makes identification and quantification of components very challenging.

4.3 Black Liquor Conversion Analysis and Modeling

Conversion of black liquor in a low-temperature gasifier such as the fluidized bed steam reformer under investigation in this project occurs in three successive stages: (1) drying, (2) devolatilization (pyrolysis) and (3) heterogeneous gasification, or reaction of steam with the carbon in the bed material to form CO and H₂ according to reaction 1 presented above. Other components, such as sulfur, may also be gasified in this final stage, but the primary reaction is with carbon.

It is useful to consider these three processes individually when creating models that describe conversion. Drying rates have been shown to be dependent on heat transfer, so drying is not given any emphasis in this project. Devolatilization behavior, particularly the composition of pyrolysis products, accounts for a significant fraction of the conversion. Release of "tar" compounds occurs during the devolatilization stage. Component release can be investigated under well-controlled conditions through fundamental, lab-

scale experiments. Additionally, one can focus on liquor devolatilization during steam reforming in a more representative environment by operating the reformer with liquor injection, but at a temperature low enough that heterogeneous gasification rates are negligible.

The final stage of conversion, heterogeneous reaction of carbon in the bed solids and steam, can be investigated through fundamental lab-scale experiments such as TGA or pressurized TGA studies, where the weight loss of bed material can be studied when reacted with steam, with or without the presence of other gaseous components such as hydrogen and carbon monoxide. This final stage can also be focused on in a fluidized bed steam reformer by operating the steam reformer without liquor injection. That has been done in this project, and preliminary results are described below.

4.3.1 Conversion in a Steam-only Environment

Experiments were run in which bed material from a commercial steam reformer containing roughly 17% carbon was gasified by feeding pure steam at 1120°F. The progression of carbon content versus time for one such experiment is shown in Figure 41. Nearly 24 hours were required to gasify essentially all carbon (from 13.3 wt%) out of the material. (The carbon content dropped from ~17% to 13.3% as the system was brought on line and heated to 1120°F.) The rate of conversion is linear relative to the amount of carbon remaining in the sample, indicating that the steam reforming reaction is first order relative to carbon concentration.

Figure 41. Carbon content in bed material versus time for a "steam-out" run with no liquor injection and pure steam, at 1120°F (604°C).

4.3.2 Influence of Hydrogen on Carbon Conversion Rate

Earlier investigations of steam gasification of black liquor have indicated that the presence of the product gases, hydrogen and carbon monoxide, decrease the rate of gasification [17,18,33-35]. In order to investigate the extent to which the heterogeneous gasification rate is reduced, experiments were performed in which hydrogen or carbon monoxide was fed into the steam line entering the reactor. The relatively large scale of the system required that many cylinders of compressed gas (H_2 or CO) be used. Due to the expense involved, only one or two different concentrations were tested for each gas.

Results from the UU model indicate that the partial pressure of hydrogen in a commercial steam reformer averages roughly 0.5 atm. It was decided to operate the Utah steam reformer such that the partial pressure of hydrogen would be roughly half this amount. An experiment was performed in which the steam flow was decreased by 25%, and enough hydrogen was added to result in a concentration of 25 vol% in the feed, thereby maintaining the fluidizing velocity. The first couple hours of the experiment, the reformer was operated with steam only in order to compare against the steam-only run shown in Figure 41. Hydrogen was then added to the gas for 6.5 hours, after which the gas was switched back to 100% steam.

The data for these two runs are shown in Figure 42. The initial carbon content at "time zero" was similar for both. The rate of gasification for the first two hours, in a steam-only environment, is comparable for the two experiments. Once hydrogen was added to the gas, however, the rate of gasification decreased dramatically. The two lines in the figure were fit by linear regression to the data points between 2 and 8.5 hours, when the hydrogen was being fed. The rate without hydrogen present was 0.75 %-units carbon per hour. The rate when the gas contained roughly 0.25 atm hydrogen was only about one-fifth that, or 0.16 %-units carbon per hour.

Figure 42. Influence of hydrogen on carbon conversion rate. In the red run, the gas composition was changed to 75% steam, 25% hydrogen, corresponding to a H₂ partial pressure of 0.25 atm, approximately 2 hours into the run, and kept at that composition for 6.5 hours, after which it was switched back to 100% steam.

Based on the initial result above, that 0.25 atm hydrogen decreases the rate by a factor of five, one can calculate that a steam reformer that achieves 98% carbon conversion in a steam-only environment would achieve only 91% conversion with 0.25 atm hydrogen in the gas. If the effect of hydrogen on the rate were linear, such that 0.5 atm hydrogen decreased the rate by a factor of 10, the conversion in the same commercial unit with 0.5 atm hydrogen would be just 83%. It should be noted that this analysis is based on only two experiments, and that a more thorough investigation of this effect will take into consideration variations in rate with carbon content, and would include additional experiments with different hydrogen concentrations. Additional study of this effect is planned.

4.3.3 Influence of Carbon Monoxide on Carbon Conversion Rate

Earlier studies have indicated that, at equal partial pressures, carbon monoxide more strongly inhibits heterogeneous gasification of black liquor char than does hydrogen [33,34]. As noted in Section 4.2.1, however, the concentration of hydrogen is several times that of carbon monoxide. Based on the model described in Section 3.1, it is estimated that the partial pressure of carbon monoxide ranges from 0 to 0.06 atm in the full-scale steam reformers.

An experiment was therefore performed in the Utah steam reformer, similar to that described in the previous section, with no liquor injection, but with addition of carbon monoxide to the feed steam. In this experiment, two different concentrations of carbon monoxide were added. The first 1.5 hours of the run were with steam only. The steam feed was then decreased slightly and carbon monoxide was added such that its concentration was 6.4%, corresponding to roughly 0.06 atm partial pressure. The system was run under these conditions for 5.3 hours. The flow of carbon monoxide was subsequently decreased so that its concentration was 2.6% and the system was run under these conditions for an additional 8.3 hours.

The results of this test are shown in Figure 43, which displays the analyzed carbon content for the two runs versus time, with "time zero" for the steam-only run taken as that which had the same approximate carbon concentration as the first data point in the CO addition run. For the times during which 6.4% and 2.6% carbon monoxide were added, the approximate gasification rate was determined by using linear regression to fit a line to the data points over that period, and defining the slope of this line (%-units carbon/hr) as the carbon conversion rate during that period.

Figure 43. Influence of carbon monoxide on carbon conversion rate. In the green run, 6.4% carbon monoxide (~ 0.064 atm partial pressure) was added 1.5 hours into the run, and kept at that composition for 5.3 hours, after which it was lowered to 2.6% CO ($p_{\text{CO}} \sim 0.026$ atm) and kept at that composition for 8.3 more hours. It was then switched back to 100% steam.

As seen in the figure, the presence of carbon monoxide in the reacting gas has little impact on the heterogeneous gasification rate. At the higher concentration ($p_{\text{CO}} \sim 0.06$ atm), the rate was roughly two-thirds that when pure steam was the reacting gas. At the lower concentration, the difference in rates with and without carbon monoxide addition was negligible.

4.3.4 Development of Models to Describe Conversion

The data acquired to date are too limited to develop a reliable expression for the heterogeneous gasification rate. Additional experiments, including lab-scale TGA experiments, are planned. Ultimately, an expression combining partial pressures of steam, hydrogen and carbon monoxide will result. Although CO_2 is also present in the product gas as a result of the water-gas shift reaction, and is known to gasify carbon according to the reaction $\text{C(s)} + \text{CO}_2\text{(g)} \rightarrow 2 \text{CO(g)}$, it is well-established that the rate of CO_2 gasification of black liquor char (and other fuels) is 3-4 times slower than gasification by steam. The ratio of steam and CO_2 partial pressures in a commercial system is estimated by the UU model (Section 3.1) to average about 10 to 1 in a commercial system. The contribution of conversion by CO_2 is therefore estimated to be less than 5% that of steam, and can be considered negligible.

4.4 Modeling Studies

4.4.1 Cold Flow Modeling Studies

The cold flow model described in Section 2.5 was used to gain a better understanding of gas and particle flow in the Utah steam reformer. As part of a collaborative modeling effort with the National Energy Technology Laboratory (NETL), the cold-flow model was used to acquire quantitative data on bed performance. Specifically, the flow of bubbles through the heater bundles, the extent of particle segregation in the bed and heat transfer between heater tubes and the bed were studied. Results of these studies are presented in the sections that follow.

4.4.1.1 Bubble Voidage within Heater Bundles

A novel technique for identifying the presence of bubbles flowing between two adjacent tubes was developed. A two-probe system having a directional infrared light source and IR detector, shown conceptually in Figure 20 on page 19 and as a photo in Figure 44, was constructed and coupled to a data acquisition system that logged the received intensity of light 600 times per second. An example of the raw signal received is shown in Figure 45. At this sampling rate, bubble frequency (bubbles per second), approximate bubble size and average voidage between the two probes could be determined.

Figure 44. Probe for bubble detection.

Figure 45. Signal from IR bubble detection system.

The signal was logged at each of the 16 levels in 16 locations at each level, which totals to 256 data logs per particle size. Because there are five tubes on each level, there are 4 spaces between tubes that can be measured. In each of these spaces, data was measured at 4 lengths along the tube: the center, two centimeters, four centimeters and six centimeters from the center of the tubes and symmetry was assumed for the opposite end of the tubes. At each of these points, data was taken at a rate of 600 Hz for 30 to 40 seconds.

Average bubble void fraction was calculated by first calculating the void fraction at each of the data points in the log. Then this calculated data was integrated with respect to time using the trapezoidal rule, and divided by the total time to get the average void fraction. A matrix for each level with both average void fraction and average bubble frequency was then developed. From these values a three dimensional surface could be plotted at each level to further visualize the data.

Three series of experiments were performed, each using a different average particle size, 90, 200 or 625 microns. Maps of bubble voidage within each of the sixteen levels of the tube banks were prepared for each particle size. Examples of bubble voidage plots for three layers, when fluidizing 200 micron particles, are presented in Figure 46. Level 1 is the bottom row of tubes. Level 4 is the top row of the bottom bundle. Level 5 is the bottom row of the second bundle and is oriented perpendicularly to Level 4. S1 to S4 correspond to the four spaces between the five tubes in that layer, and positions 1-7 are along the axial length of the tubes, with 4 being the center. Clearly, the voidage is highest in the center, or core of the bed. This suggests that bubbles prefer to travel through the tube bundles rather than near the walls. This likely corresponds with the visually observed downflow of solids near the walls.

It is of interest to know how particle size affects the behavior of the bed, particularly the propensity of particles to flow through the heater bundles. Figure 47 shows the measured bubble voidage profiles for the fourth level from the bottom (the top row of tubes of the bottom bundle) when running 90, 200 and 625 micron particles. Clearly, as particle size increases there is less tendency for bubbles to travel through the tube bundle; for the largest particles it appears that the center of the bundle was nearly stagnant.

Figure 46. Measured bubble voidage profiles at Level 1 (bottom of the bed, left), Level 4 (middle) and Level 5 (right). S1-S4 represent the four spaces between the five tubes at that level. Positions 1-7 represent the length along the tube, with point 4 being the center of the tube.

Figure 47. Bubble voidage profiles for average particle diameters of 90 (top), 200 (middle) and 625 (bottom) microns. Superficial velocity 1.07 ft/s in all cases (corresponds to 1.3 ft/s in the Utah gasifier).

4.4.1.2 Particle Segregation Studies

Studies were conducted to identify the degree of particle segregation in the bed. Soda lime glass beads with similar properties in two different sizes, specifically 625 and 200 micron, were mixed 50/50 by bulk volume. The fluidized bed was run at a superficial velocity of 1.07 ft/sec for approximately 20 minutes to ensure that the particles had fully established their flow patterns and been given opportunity to segregate before any particle sampling was attempted.

A sampling device was designed to remove a small sample of bed particles from any location in the fluidized bed, except within the tube banks, while the bed was running. This probe was connected to a hose with vacuum on the other end. This hose was then attached to a trap that would collect the particles. A ball valve was placed in between the probe and the trap to stop the flow of particles when inserting the probe. A sample of 100-400 grams was collected at each height and sieved using a 420 micron sieve. These separated portions were then weighed to get a ratio or percentage of each size. Data was collected at 10 heights in the bed, approximately 4 inches away from each other and in between the tube banks. Three trials were performed at the center of the bed as well as against the walls of the bed. In between each trial, the particles that were removed earlier were remixed so the bed was at 26 inches and the bed was run for approximately 20 minutes again to assure proper mixing.

Results of the testing, showing the fraction of large particles in samples taken down the centerline of the bed and at the wall of the bed, are shown in Figure 48 and Figure 49, respectively. Overall, there is very little segregation of particles. The superficial velocity used in these studies, 1.07 ft/s, is higher than the minimum fluidization velocities of the particles, which were determined to be 0.13 ft/s for the 200 micron particles and 0.83 ft/s for the 625 micron particles. Generally, one can expect little segregation if the velocity is above the minimum fluidization velocities of all the particles.

As seen in the figures, there appears to be three different forms of behavior particularly at the walls of the reactor. Below the tube banks, it seems there is a good distribution of both particle sizes. Within the tube bank region, there is almost a linear relationship of particle size to height. There is a larger amount of large particles at the bottom, and fewer large particles at the top of the tubes. Above the tube region, the fraction of large particles is higher than in the tube region. The top of the bed has the highest concentration of large particles.

One interesting observation is that in the region where tube bundles are present, 12 to 30 inches in height, the fraction of large particles at the wall dropped quite significantly, becoming as low as 43%. It was observed that there was significant particle downflow near the walls, and correspondingly little gas flow in this region. The observed segregation behavior could be due to the local gas velocity near the wall being lower than the minimum fluidization velocity of the large particles. If one considers only that zone, there is a clear trend indicating that the smaller particles dominate in the top of that section. In other words, there does appear to be some local segregation near the walls in the region where the tube banks are located.

Figure 48. Fraction of large particles versus bed height when measured at the center of the bed.

Figure 49. Fraction of large particles versus bed height when measured at the wall of the bed.

4.4.1.3 Heat Transfer Studies

To determine the heat transfer coefficient between the tubes and bed, several of the horizontal glass tubes in the tube bundles were replaced with copper tubes (Figure 50). A small cartridge heater with an internal thermocouple was placed into the various copper tubes, at different depths within the tubes. Constant power was applied to the heater and the temperature of the internal thermocouple was measured. The local heat transfer coefficient at different locations could be calculated from the temperature difference and the surface area of the heated part of the tube.

Calculated heat transfer coefficients were generally 200 to 250 W/m²-K. The average heat transfer coefficients in the middle tube of the 5-tube wide rows are shown in Figure 51. It is interesting to note that measured heat transfer is slightly less in the second heater bundle from the bottom (rows 5-8). The reason for this is unclear, but may be a consequence of a difference in gas and solids flow in that bundle.

Figure 50. Photo of tube bank region with copper tubes installed.

Figure 51. Measured heat transfer coefficients for the middle tube in 12 rows of the cold flow model. 200 micron particles, 1.07 ft/s fluidizing velocity.

The influence of particle size on heat transfer was determined by performing a series of experiments with particles having average sizes of 90, 200 and 625 microns. The results of these tests are presented in Table 5. The average heat transfer coefficient in the table is for the entire bed. The measured heat transfer coefficient decreased slightly as particle size increased. This is consistent with theory for tube-bed heat transfer in such systems.

TABLE 5. HEAT TRASFER VS. PARTICLE SIZE

Particle size (micron)	Average Heat Transfer Coefficient (W/m ² ·K)
90	268
200	245
625	242

Heat transfer was also measured as a function of fluidizing velocity. A series of three experiments was performed in which 200 micron particles were fluidized with different gas velocities. The results are presented in Table 6. Theory suggests that heat transfer increases asymptotically with velocity. The results in Table 6 do not reflect this, though the variation in measured heat transfer is minor. It could be that local and solid flow patterns do not systematically change with increasing velocity.

TABLE 6. HEAT TRASFER VS. VELOCITY

Fluidizing velocity (ft/s)	Average Heat Transfer Coefficient (W/m ² ·K)
0.54	257
1.07	245
1.57	258

4.4.2 Computational Modeling Results

Several computational models have been developed under this project to address different aspects of the steam reforming system. Select results of these models are presented in the sections below.

4.4.2.1 Model Predictions of Gas Composition throughout the Reformer

The UU model, described in Section 3.1, was used to predict variations in the composition of the four major gaseous species, H₂O, CO₂, H₂ and CO, throughout the reactor. The model assumes that these four species are at equilibrium throughout the entire reactor, an assumption which appears to be appropriate based on measured gas concentrations as described in Section 4.2.1. The model also assumes that heterogeneous carbon gasification occurs at a uniform rate throughout the entire bed, an assumption that may be questionable in light of the results presented in Section 4.3. The predicted gas concentrations are presented in Figure 52.

Figure 52. Gas concentrations in the Big Island steam reformer, as predicted by the UU model (Section 3.1).

4.4.2.2 Heat Transfer Modeling

Reaction Engineering International used the heat transfer model described in Section 3.3 to estimate temperature profiles in the Big Island reformer. A first-order upwind finite-difference scheme has been used to discretize Equation 59. Along with Equations 50, 51 and 55, the discretized equation has been solved using the tri-diagonal matrix algorithm (TDMA). Solids flux and bed voidage inside the tube bundles under the gasifier normal operating conditions from the MFIX simulation have been provided by Rand Batchelder at NETL.

Figure 53 shows solids flux within the pulse combustors, predicted from the MFIX simulation. It appears that particles pass through the tube bundles and move downward near the gasifier walls. Figure 54 shows bed voidage distribution from the MFIX simulation and the predicted particle temperature profile from Equation 59. It can be seen that bed voidage is relatively low below the tube bundles. The predicted particle temperature is fairly uniform with a higher temperature in the top section. There are some locations with relatively higher particle temperature due to lower solids flux. A cross-section view of the predicted particle temperature is presented in Figure 55. Near the firing end of the pulse combustor tubes, the particle temperature is higher due to a higher flue gas temperature inside the tubes and lower solids flux.

The heat transfer model was used to predict surface temperatures of the tubes in the heater bundles in the Big Island reformer. The predictions were made using a combination of heat transfer modeling for the hot gases on the inside of the heater tubes and heat transfer from the tubes estimated using results of the MFIX simulations performed by the modeling group at DOE's National Energy Technology Laboratory.

An example of the predicted tube surface temperature is presented in Figure 56, which shows a profile of the temperature for four of the heater tubes: one on the outside plus the center tube of the row halfway up each of the bottom and top tube bundles. The bottom bundle tube temperatures are slightly less than the

top bundle temperatures. Generally, the temperatures of the outside and center tubes within a level are predicted to follow the same profile. It should be noted that these predictions did not take into consideration the shield tubes around the hot end of the heater tubes.

Figure 53. Solids flux inside the tube bundles (Side view across the centerline of the gasifier)

Figure 54. Bed voidage and predicted particle temperature (Side view across the centerline of the gasifier)

Figure 55. Predicted particle temperature (View across bottom pulse combustor)

Figure 56. Predicted tube surface temperatures across the vertical center of the bottom (B, left) and top (T, right) tube bundles.

5. CONCLUSIONS

During the second year, efforts within the University of Utah project "Investigation of Fuel Chemistry and Bed Performance in a Fluidized Bed Black Liquor Steam Reformer" focused on completing experimental equipment, acquiring data on bed material characteristics and liquor conversion behavior, and modeling of fluidized bed black liquor steam reformers.

5.1 Research Tools

Many one-of-a-kind tools for studying fluidized bed black liquor steam reforming have been constructed for this project.

Black liquor steam reformer. The University of Utah's gasification research system has a 10-inch fluidized bed that holds roughly 200 pounds of bed solids, has eighty electric heaters within the bed, and can simulate the behavior of a full-scale fluidized bed steam reformer. This system is useful for investigating syngas properties, carbon conversion rates and bed particle development under industrially-relevant conditions.

Bed agglomeration test system. A reactor specifically for investigation of bed agglomeration was constructed at Brigham Young University. The reactor is a 6 by 6-inch square nitrogen-fluidized bed containing sixteen cartridge heaters within the bed. Several thermocouples and pressure sensors allow one to follow the performance of the bed, and to identify the temperature at which the system begins to agglomerate. Agglomeration temperatures can be compared to bed material properties and compositions.

2-inch fluidized bed. A small, lab-scale fluidized bed at the University of Utah makes it possible to focus on mechanisms responsible for particle growth. Bed solids can be fluidized in nitrogen while black liquor is injected, thus coating the particles in a manner similar to that which occurs in a full-scale system. Particles grown under controlled conditions can be analyzed by electron microscopy to identify the structure of the growth, thus providing insight into the mechanisms responsible.

Single droplet reactor. A lab-scale reactor for heating small quantities of black liquor allows investigation of pyrolysis characteristics (volatiles yield and composition, swelling behavior), production of char and determination of char properties during conversion. A filter system can be appended to this reactor to allow capture of condensable hydrocarbons ("tars") formed during pyrolysis.

Cold flow model of Utah gasifier. A two-thirds scale Plexiglas cold flow model of the University of Utah steam reformer, including glass tubes representing the 80 horizontal heating tubes, allows visualization of gas and solids flow patterns. A unique system for measuring bubble frequency and average voidage within the tube banks has been developed. A system for measuring heat transfer between the "heater" tubes and the bed has also been developed.

5.2 Bed Particle Behavior

Particle size development. Several mechanisms have been identified that can contribute to growth and shrinkage of particles. Particle growth can occur by (1) liquor coating the particles and adding "shells" of material, (2) particle agglomeration, (3) particle sintering and (4) "clustering," in which several small particles are captured by a larger droplet of liquor and bound together by the liquor. Similarly, a number of mechanisms can be responsible for reductions in particles size: (1) fracturing, whereby a particle

breaks into several relatively even sized particles, (2) attrition, where asperities on the particle surface are broken off and (3) cluster breaking, where the material holding the smaller particles together reacts away to the point where they are released. The overall development of the particle size distribution depends on the relative rates of these mechanisms which, in turn, depend on reactor design and operating conditions. Based on data gathered so far, it appears that liquor coating and agglomeration are the most significant particle growth mechanisms. Work on particle breakdown is still in progress.

Bed agglomeration. Bed agglomeration is a function of particle composition, particle size distribution, bed temperature and heater temperature. For a constant power feed to the heaters, the onset of agglomeration can be detected by an increase in the temperature difference between the heaters and the bed itself, as larger particles resulting from agglomeration decrease the efficiency of heat transfer. Pure sodium carbonate was found to begin agglomerating at roughly 520°C. Addition of just 2% potassium chloride decreased the agglomeration temperature by more than 50°C. SEM analysis indicates that bridges are formed between the edges of the particles. Interestingly, particles from a commercial steam reformer could be fluidized at 650°C without agglomerating. Apparently, the presence of organic carbon in the material helps minimize particle stickiness.

5.3 Product Gas Properties

The major non-steam species in the steam reformer's product gas are H₂, CO₂, CO and CH₄. Although CO is a primary product from the reforming process, very little is present in the product gas. The water-gas shift reaction, which converts CO to CO₂, is apparently strongly catalyzed in the reformer, presumably by alkali species in the bed solids.

Black liquor steam reforming produces condensable hydrocarbons, or "tars." These tars comprise a wide array of mono- and polyaromatic compounds that may condense in or on downstream equipment. Condensate from the gas cleaning system of a commercial plant was found to contain over 100 tar species. The majority of these were un-, mono- and di-substituted, mostly methyl phenols.

5.4 Black Liquor Conversion

Conversion of black liquor in a low-temperature gasification system (operating below the melting point of the inorganic residue) occurs in three stages: (1) drying, which is nearly instantaneous, (2) pyrolysis (devolatilization), also a relatively rapid process during which volatile matter in the liquor is released (and tars are formed) and (3) heterogeneous reaction of components, primarily carbon, in the solid residue remaining after pyrolysis. The third step is by far the slowest, and determines the overall carbon conversion for a fluidized bed steam reformer. Many hours may be required to reach an acceptable degree of conversion.

In a fluidized bed steam reforming test at 604°C (1120°F), running pure steam and with no liquor injection, roughly 24 hours were required to steam reform all the carbon from commercial bed material initially containing 17 percent carbon by weight. Previous studies indicate that the product gases of the steam reforming reaction, hydrogen and carbon monoxide, slow the rate of conversion. It was found that carbon monoxide has only a slight effect on the rate of conversion when its partial pressure is 0.06 atm, approximately the same as the partial pressure in a commercial steam reformer. The presence of 0.25 atm hydrogen, however, was found to significantly slow the rate of carbon conversion, with the rate being approximately one-fifth that in a steam-only environment. The partial pressure of hydrogen in a

commercial reformer processing black liquor is estimated to average more than 0.5 atm, so it is likely that solids in a commercial reformer will have a relatively high carbon content.

5.5 System Performance Modeling

The Plexiglas cold flow model of the University of Utah's fluidized bed steam reformer has been well designed, with the four critical dimensionless scaling parameters matching nearly exactly the parameters of the actual reactor. One can be confident that behavior observed in the cold flow model is representative of behavior in the real system.

Measurement of bubble voidage within the tube banks indicates that for particles corresponding to 300 microns in the Utah gasifier, bubbles flow through the tube bundles with no problem, and generally seem to prefer the center of the bundles to the walls of the reactor. This is particularly notable as one traverses a tube; at the ends, where the tubes touch the wall, bubble voidage was much lower, presumably due to downflow of solids along the walls. The propensity for bubbles to flow within the tube bundles decreased with particle size. For small particles (corresponding to 135 microns in gasifier) there was significant variation in bubble voidage within a given row of tubes (high near the center, low near the walls). For large particles (940 microns) the bubble voidage profile was nearly flat. Within the top bundle, variations in bubble voidage were notably smaller than for the lower three bundles. This could be due to downflow of the solids above that bundle.

Segregation of particles by size is limited, at least within the range of particle sizes and conditions tested. For the most part, no segregation by particle size was observed. The range of velocities tested were all above the minimum fluidization velocity of all particles. It could be that segregation would be observed if larger particles or lower velocities were used.

Heat transfer between the heater tubes and bed material is very good, with heat transfer coefficients on the order of 200-250 W/m²·K measured in the cold flow model. Interestingly, the second tube bundle from the bottom displayed somewhat less efficient heat transfer than the other three. The reason for this is unclear. Variations in heat transfer with particle size and fluidizing velocity were negligible under the conditions studied.

Three-dimensional modeling of the Big Island steam reformer suggests that bubbles flow through the heater bundles, and that the bundles have a significant influence on solids flow. Overall, solids downflow appears to occur near the walls, but the bundles disrupt this pattern, causing the particles to shift sideways. The particles prefer to flow downwards in the open areas on the sides of the heater bundles.

As one would expect, the surface temperature of the heaters decreases as one goes from the firing end to the exhaust end. The modeling simulations suggest that the temperature drops from roughly 700°C (1300°F) to bed temperature. These simulations did not account for the shield tubes within the heater bundles, however, so the actual hot end temperature is likely less.

NOMENCLATURE

A	cross-sectional area of the bed, m^2
C	carbon concentration, kg/m^3 particles
C_p	specific heat, $\text{J}/\text{kg}\cdot\text{K}$
d	diameter, m
$d_{b,d}$	daughter bubble diameter, m
d_b	bubble diameter, m
$d_{b,e}$	average daughter diameter, m
d_p	particle diameter, m
D_g	gas diffusivity, m^2/s
D_{O_2}	oxygen diffusivity, m^2/s
f	phase fraction
g	gravitational acceleration, m/s^2
h	heat transfer coefficient, $\text{W}/\text{m}^2\cdot\text{K}$
H	computational cell height, m
H_t	expanded bed height, m
$K_{wd,p}$	solids exchange coefficient between the wake phase and the dense phase, 1/s
m_{dev}	volatiles flow rate, kg/s
m_{out}	mass outflow rate of bed material, kg/s
m_p	mass flow rate of black liquor solids, kg/s
m_{vap}	volumetric evaporation rate, $\text{kg}/\text{m}^3\cdot\text{s}$
Q_t	heat transferred from the pulse combustor, W/m^3
Q_{vap}	heat required for evaporation of water, W/m^3
R	universal gas constant, $\text{J}/\text{mol}\cdot\text{K}$
$R_{i,b}, R_{i,w,g}, R_{i,e,g}$	homogeneous reaction rate in the bubble, wake and dense phases, $\text{kmol}/\text{m}^3\cdot\text{s}$
$R_{i,w,s}, R_{i,e,s}$	heterogeneous reaction rate in the wake and dense phases, $\text{kmol}/\text{m}^3\cdot\text{s}$
T	temperature, K unless otherwise noted
u_0	superficial gas velocity, m/s
u_b	bubble rise velocity, m/s
$u_{p,d}$	particle velocity in the dense phase, m/s
X	mass fraction
ε	bed voidage
λ_{vap}	latent heat of vaporization, J/kg
ρ_g	gas density, kg/m^3
ρ_p	carbon density, kg/m^3
ΔH°	heat of reaction, J/kmol

Subscripts

b	bubble phase
C	carbon
d	dense (emulsion) phase
g	gas

i	reaction index
K	potassium
mf	minimum fluidization
Na	sodium
p	particle
tf	throughflow
w	wake phase

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