Investigation of Pressurized Entrained-Flow Kraft Black Liquor Gasification in an Industrially Relevant Environment

DOE Cooperative Agreement DE-FC26-04NT42261

Quarterly Technical Progress Report, Year 1 Quarter 1

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Reporting Period End Date: 12/31/2004

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(DE-FC26-04NT42261)

Quarterly Report for Project Budget Period 1, Quarter 1

Principal Author:
Kevin Whitty
University of Utah

OBJECTIVES

The overall objective of this project is to acquire critical data necessary for successful commercialization of entrained-flow black liquor gasification through a combination of laboratory-scale experiments and operation of a small-scale gasifier operating under conditions representative of those in a commercial system. The project focuses on the gasifier reactor itself, and takes into consideration the entire range of conversion, from the initial black liquor droplet to the final smelt and gas products. Specifically, the project has the following four technical objectives: (1) to characterize black liquor droplet and particle formation in a pressurized, high temperature environment, (2) to generate data on the chemical and physical aspects of black liquor conversion in a high temperature gasifier, (3) to characterize major and minor components in the synthesis gas produced during high temperature kraft black liquor gasification, and (4) to use the information acquired to develop tools useful for design, optimization and troubleshooting of entrained-flow back liquor gasifiers.

BACKGROUND

Black liquor gasification has long been recognized as a promising technology for the pulp and paper industry. Not only does it have the potential to increase energy efficiency and environmental performance of the black liquor recovery system, but gasification opens up opportunities for advanced pulping technologies that can increase pulp yield. Recently, it has been recognized that the syngas from a black liquor gasification system could be used as feedstock for production of chemicals or automotive fuels, making a pulp mill a natural site for a forest biorefinery system. This additional product stream would give the pulp and paper industry more flexibility in challenging market conditions, and could displace petroleum otherwise imported with a domestically-produced, renewable fuel.

Despite the advantages of black liquor gasification and many efforts over the past few decades to develop an effective gasification technology, black liquor gasification has not yet achieved commercial success. Several technical hurdles have yet to be overcome, and there is a notable lack of information about the processes that take place inside an entrained-flow gasifier. Having detailed information on the conversion behavior of black liquor in high temperature gasification systems, from droplet formation through to properties of the smelt and syngas products, would greatly improve the understanding of the process and aid successful commercialization of the technology. This project aims to provide this needed information.
STATEMENT OF WORK

This project is broken down into five technical tasks, described in the sections that follow.

Task 1: Design and construction of an entrained-flow gasifier

A new entrained-flow gasifier will be designed, built and installed in the existing Black Liquor Gasification Research System at the University of Utah. This reactor will be capable of operating either at atmospheric pressure or under pressurized conditions (up to 10 atm) and wall temperatures as high as 1200°C. The design of the gasifier will be unique. It will not simply be a scaled-down version of an industrial-scale gasifier. Rather, it will be designed to meet the specific objectives of this project, namely to obtain data on chemical and physical properties of the liquor and products throughout the entire range of conversion. Compared to an industrial unit, the gasifier will have a higher length-to-diameter (L/D) ratio and several ports for sampling along the length of the unit. However, the gasifier should be able to produce a syngas quite representative of syngas from an industrial system.

Deliverables from this task include a report detailing the design of the gasifier and at least one follow-up report on the performance of the system.

Task 2: Evaluation of droplet formation and burner performance

The purpose of this task is to characterize and model the process of droplet formation under pressurized, high temperature conditions, and to correlate observed droplet characteristics with the performance of the burner and gasifier. There are three components to the task, described below.

Subtask 2a: Spray and droplet formation characterization. Imaging will be performed in two complementary systems. The proposed gasifier is designed to allow optical access of the liquor injector tip and the region just downstream of the burner. The University of Utah will use its high-speed camera to video the spray where optical access is possible within the high pressure gasification chamber. More controlled, complementary tests will be performed in an existing atmospheric pressure optical access drop tube furnace at University of Utah. Small black liquor droplets from an injector will be videoed as they undergo drying and pyrolysis to identify swelling behavior under high heating rate conditions.

Subtask 2b: Computational modeling of black liquor droplet formation. Under this subtask, the data from the imaging tests described above will be used to improve and validate an existing computational model describing black liquor droplet formation. Data from Subtask 2a will be used to validate that the fundamental mechanics of the computational model are correct. This results in a higher level of confidence in the model when it is applied to an industrial burner.

Subtask 2c: Computational model validation. The third component of this task involves comparison of model predictions versus unique droplet formation scenarios not already characterized in Task 2a. Since the model is optimized/calibrated with the data collected in Task 2a, reproducing these findings is not a true validation of model accuracy. Rather, a unique scenario of inputs shall be tested following the same criteria specified in Task 2a for model validation. The imaging results will then be compared to the model’s predictions for both scenarios with and without atomizing gas and model validation will be determined. If this comparison proves to be unacceptable, the model may be refined and Subtask 2c will be repeated with another unique droplet formation scenario.

Deliverables from this task include data and photographs from the imaging studies, a description of the computational model, results of simulations performed with the model, model predictions for a commercial burner, and a model validation analysis.
Task 3: Detailed analysis of black liquor conversion

This task takes over where Task 2 ends – when droplets have been formed but have not yet begun to convert. The objective of this task is to characterize the progression of physical (subtask 2a) and chemical (subtask 2b) properties of black liquor as it is converted from droplet to char to fully converted smelt bead. This will be achieved through a combination of sampling in the Utah gasifier operating under pressurized, industrially relevant conditions and more fundamental laboratory experiments. Particular attention will be paid to the near-burner region, where the liquor undergoes its most dynamic changes.

Subtask 3a: Physical characterization of black liquor during conversion. This subtask will provide new information on physical properties of the liquor such as density, porosity, structure, internal surface area and sticking propensity. Properties throughout the entire range of conversion will be measured.

Subtask 3b: Chemistry of black liquor conversion. This task aims to characterize chemical transformations that occur as black liquor progresses through the various stages of conversion in the gasifier. Both gas and condensed-phase material will be analyzed. By comparing gas and condensed-phase samples throughout the reactor, it will be possible to generate a map of the environment, and to identify rates and mechanisms of conversion of the liquor to gas.

Deliverables from this task include reports on the progression of chemical and physical characteristics of black liquor as it undergoes conversion under a variety of conditions. Submodels describing liquor conversion, suitable for incorporation into CFD models, will be made available.

Task 4: Transport and radiative properties of black liquor smelt

The aim of this task is to provide quantitative data on transport properties (viscosity, thermal conductivity) and emissivity of molten kraft black liquor smelt. These properties impact gasifier performance, and are essential for understanding and modeling the behavior of the gasifier. Smelt viscosity will be measured using a slag viscometer, essentially a viscometer immersed into a bath of molten smelt at a given temperature. Approximate thermal conductivity measurements will be made by heating smelt in a 1-D heat pipe and measuring heat flux and temperature difference. Radiative properties and smelt emissivity will be analyzed by optical methods including visible and IR emission measurements. Total emissivity will be obtained by measuring total emissive power with a radiometer and smelt surface temperature. Efforts will also be made to measure spectral emissivity. The smelt will be doped with different concentrations of carbon, since carbon has a broad-band and relatively high emissivity.

Deliverables will include data on viscosity, thermal conductivity, and radiative properties of smelt and carbon-smelt mixtures.

Task 5: Characterization of synthesis gas from an entrained-flow gasifier

This task involves detailed analysis of the product gas produced in the Utah entrained-flow gasifier. The product gas will be analyzed by several techniques. Major species will be monitored using existing on-line continuous emission monitors. Minor species will be measured through a combination of existing on-line gas chromatography and GC/MS of extracted samples. Particular attention will be paid to reduced sulfur species and tars, and efforts will be made to characterize particulate matter in the quenched gas. In addition to sampling at the exit to the quench, sampling at the gasifier reactor exit will also be attempted. The impact of system disturbances on the quality of the syngas will be identified by intentionally upsetting operation of the gasifier.

Deliverables from this task include detailed reports of measured concentration ranges during stable and upset conditions.
SUMMARY OF TECHNICAL PROGRESS THIS QUARTER

Accomplishments for the various technical tasks during this quarter are presented in the sections that follow.

Task 1: Design and construction of an entrained-flow gasifier

The focus during these months was on the gasifier vessel itself, since that is not an off-the-shelf item and the process for getting it constructed (code documentation, design reviews, etc.) is relatively time consuming. A model to aid in designing and dimensioning the gasifier has been developed. It turns out that the capacity of the system will be larger than originally envisioned without having to make the vessel or burner any larger. The basic design for the entrained-flow gasifier and how it will be incorporated into the existing gasification research facility has been worked out. Computer aided design (CAD) drawings for the gasifier have been developed, but have yet to be finalized or turned into fabrication drawings.

Task 2: Evaluation of droplet formation and burner performance

Development of a feed system for the optical access drop tube furnace has begun. The ambition is to create a feed system employing a vibrating orifice droplet generator. Such systems are able to create a very uniform stream of monodisperse droplets for low viscosity fluids such as water. One group has succeeded in using a vibrating orifice feeder to create droplets of fuel oil #6, which is similar to black liquor in terms of viscosity and flow behavior. In theory it should be possible to use the same approach for hot black liquor. A small, heated reservoir for concentrated black liquor has been constructed and the feed head of a TSI Instruments vibrating orifice droplet generator is being modified to be heated and so that it will fit into the optical furnace that will be used for the imaging studies.

Brigham Young University will make a detailed investigation of the mechanism of droplet formation when liquor is fed through an atomized injector. A key question to be answered is whether droplets form via the same mechanism as in recovery boilers, where the liquor is distributed by splash plate nozzles and forms sheets that break up into non-spherical ligaments. Initial preparations for setting up this system have begun.

Task 3: Detailed analysis of black liquor conversion

A review of literature that may be relevant to entrained-flow black liquor gasification has begun. The design of lab-scale experimental systems to study conversion under well-controlled conditions has also begun. It turns out that the feed system and optical furnace described above will also be useful for studying high temperature pyrolysis and conversion of droplets of black liquor.

Task 4: Transport and radiative properties of black liquor smelt

There was little activity on this task this quarter. The University of Utah is looking into purchasing and existing used slag viscometer from a commercial laboratory that is closing down. There exist very few such instruments, and if the University can pick up a working unit for a reasonable price it will allow us to leapfrog over system development and move right into the experimental phase.

Task 5: Characterization of synthesis gas from an entrained-flow gasifier

No activity for this task will take place until after Task 1 is complete.
**PLANS FOR NEXT QUARTER**

For the period January-March 2005, efforts will focus on the issues outlined below:

**Entrained-flow gasifier construction.** The CAD model of the basic design will be finalized and fabrication drawings will be created. Based on these, bids for the vessel will be requested and the fabricator will be identified. The fabricator will have to review and possibly modify the design to ensure that the vessel meets ASME Section VIII pressure vessel codes before procurement of material can begin. Work will continue to identify a suitable refractory material to line the gasifier reactor, and the auxiliary equipment for the system will be sized and specified.

**Droplet imaging and modeling studies.** A first version of the vibrating orifice droplet generator will be constructed and tested. A parallel feeding system comprising a pressure- or gas-atomized nozzle will also be put together. This other feed system, though not as well controlled, is more likely to work and will allow us to work out the imaging techniques. Also, the nozzle feeder will allow much higher flows of liquor, which will be useful for the studies on liquor conversion.

BYU will continue work on their system to identify to what extent droplet formation from a gasifier-type nozzle follows the same mechanism as for splash plates in recovery boilers. The nozzle that will be initially used in the Utah gasifier will be identified. A spray chamber using this nozzle will be set up, and efforts will be made to gather preliminary data on droplet properties using surrogate liquids (and possibly black liquor).

**Black liquor conversion studies.** The literature review of studies relevant to entrained-flow black liquor gasification will continue, and work will begin on a report summarizing the relevant studies. Preliminary lab-scale experiments of black liquor conversion using the atomized nozzle in a lab scale reactor will be conducted to see if this is a reasonable approach to gathering fundamental data.

**Smelt properties studies.** The slag viscometer, if available for a reasonable price, will be purchased and sent to the University of Utah, where work will begin on getting it installed. If this system is not purchased, design for a similar system will commence. The design of the system for measuring the thermal conductivity of smelt will be worked out, and work will begin on building that system. Finally, paper companies will be contacted to see if they are able to supply samples of black liquor smelt for the experimental work.
SCHEDULE AND PROJECT STATUS

The major milestones for the project and the planned actual dates of completion are listed in Table 1.

<table>
<thead>
<tr>
<th>ID No.</th>
<th>Task/Milestone Description</th>
<th>Planned Completion</th>
<th>Actual Completion</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Design and construction of entrained-flow gasifier</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>Basic design finalized</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Design finalized, components specified, request bids</td>
<td>3</td>
<td></td>
<td>In progress</td>
</tr>
<tr>
<td>1.3</td>
<td>All components ordered</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Construction of gasifier complete</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.5</td>
<td>Installation of system complete</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>Report on gasifier design/operation</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Evaluation of droplet formation, burner performance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Foundation for computational model complete</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2</td>
<td>Initial droplet imaging/LDA tests complete</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Follow-up imaging/LDA tests complete</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>Computational model of droplet formation complete</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>Report on droplet formation/burner performance</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Detailed analysis of black liquor conversion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Literature review complete</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Sampling procedure established</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Acquisition of data complete</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Development of models describing conversion complete</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Report of physical properties vs. conversion</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Report on conversion chemistry</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Transport and radiative properties of smelt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Construction of molten smelt exptl device complete</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Acquisition of viscosity data complete</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Acquisition of thermal conductivity data complete</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Acquisition of radiative properties complete</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Report on transport/radiative properties</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Characterization of syngas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Initial syngas characterization complete</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Measurement of trace species complete</td>
<td>22</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>Evaluation of syngas during upsets complete</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>Report on syngas characteristics</td>
<td>36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
BUDGET DATA

As of the end of the quarter, only 2% of the overall project budget had been spent, mainly because things were just getting started, students for the research had not yet been employed, etc. As the project progresses spending will pick up. Table 2 shows the estimated expenditures for the current quarter, as well projected expenditures for the next quarter. As construction of the entrained-flow gasifier progresses, spending in that category will pick up notably. Estimates for subcontracts assume that the subcontractors will spend the difference between what was budgeted and what was spent to date proportionally over the remainder of the budget period.

<table>
<thead>
<tr>
<th>Current Quarter Expenditures 09/30/04 - 12/31/04</th>
<th>Budget Category</th>
<th>Next Quarter Projection 01/01/05 - 03/31/05</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,752 Personnel</td>
<td>12,270</td>
<td></td>
</tr>
<tr>
<td>1,778 Fringe Benefits</td>
<td>3,255</td>
<td></td>
</tr>
<tr>
<td>0 Travel</td>
<td>2,091</td>
<td></td>
</tr>
<tr>
<td>0 Equipment</td>
<td>25,000</td>
<td></td>
</tr>
<tr>
<td>0 Supplies</td>
<td>6,145</td>
<td></td>
</tr>
<tr>
<td>5,672 Subcontracts</td>
<td>29,776</td>
<td></td>
</tr>
<tr>
<td>0 Other</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td><strong>13,201 TOTAL DIRECT</strong></td>
<td><strong>78,537</strong></td>
<td></td>
</tr>
<tr>
<td>5,785 Indirect</td>
<td>21,870</td>
<td></td>
</tr>
<tr>
<td><strong>18,986 TOTAL</strong></td>
<td><strong>100,407</strong></td>
<td></td>
</tr>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>DOE (80%)</th>
<th>Cost Share (20%)</th>
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<tbody>
<tr>
<td>15,189</td>
<td>80,325</td>
<td></td>
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<tr>
<td>3,797</td>
<td>20,081</td>
<td></td>
</tr>
<tr>
<td><strong>18,986 TOTAL</strong></td>
<td><strong>100,407</strong></td>
<td></td>
</tr>
</tbody>
</table>

ACKNOWLEDGEMENTS

The U.S. Department of Energy Office of Energy Efficiency and Renewable Energy is gratefully acknowledged for funding this project.