ADMINISTRATIVE INFORMATION

1. **Project Name:** Materials for High Temperature Black Liquor Gasification (CPS# 16540)

2. **Lead Organization:** Oak Ridge National Laboratory
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3. **Principal Investigator:** Dr. Jim Keiser: phone (865) 574-4453, fax (865) 241-0215
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4. **Project Partners:**

Weyerhaeuser Company	Dr. Peter Gorog
University of Missouri – Rolla	Dr. Bill Headrick
Process Simulations Limited	Dr. Jerry Yuan
Simulent, Inc.	Dr. Nasser Ashgriz
Monofrax Refractories	Dr. Amul Gupta
Harbison-Walker Refractory Co.	Mr. Mike Wallen

5. **Date Project Initiated:** 11/19/2003

6. **Expected Completion Date:** 9/30/2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** This project focuses on the development of degradation-resistant refractory materials for high-temperature, near atmospheric-pressure black liquor gasification units to give a service life of at least one year. The project includes CFD modeling to better characterize the fluid flow in the gasifier, and a study of the liquor injection nozzle. The nozzle studies involve modeling work as well as experimental measurements with more erosion-resistant materials. High-temperature, high-pressure black liquor gasification would result in a: 14% energy savings, 18% reduction in CO_2 emissions, and reduction in NO_X, SO_X and particulates from pulping mills.

8. **Technical Barrier(s) Being Addressed:** Previously, refractory materials had limited life (< 12 months) making them unacceptable both in terms of plant maintenance scheduling and cost. Refractory degradation products also adversely affect the quality of green liquor, the operation of downstream equipment, and the structural integrity of the gasifier unit.

   High alkali concentrations (Na_2SO_4, Na_2CO_3, *etc.*) and high temperature (~950°C) result in unacceptable materials interactions. These types of reactions with refractories cause expansion of the surface, spalling and the development of other mechanical /structural refractory faults. The physical loss of as much as 40% of some refractory material has been observed. Refractory expansion (chemical and thermal) and the resultant material degradation creates structural and safety issues, thermal efficiency losses, unacceptable maintenance

cost and downtime. In addition, the flow characteristics within the gasifier impact the performance of refractory materials.

The major technical barriers relate to the development of a refractory material that:

- Is essentially inert or whose reaction products do not cause the lining to expand creating unacceptably high stresses in the containment vessel
- Has sufficient service lifetime and costs to perform in the industry
- Does not adversely affect the quality of green liquor or the performance of downstream equipment.

And the major barriers with fuel injectors and black liquor nozzles include:

- Prevent localized heating with oil firing
- Reduce high levels of oxygen required to burn the black liquor which degrade the heating value of the syngas and increase the temperatures on the inner surface of the refractory lining

9. **Project Pathway:** The project partners recognized that new refractory materials and surface treatments and improved fuel injection would be required to provide the performance required under industrial conditions. The partners undertook a program to:
   - Identify the failure mechanisms of current refractories and liquor injection nozzles
   - Develop a test system for new refractory materials and nozzle materials that would accurately simulate the industrial environment
   - Test new materials under simulated gasifier conditions in the laboratory
   - Develop commercial fabrication protocols and manufacture new refractories and nozzle materials
   - Perform in-situ (in service) commercial gasifier testing
   - Characterize in-situ tested refractories, and
   - Model the flow characteristics in the gasifier.

10. **Critical Technical Metrics:**

Baseline Metrics (at start of project):

- Current refractory lifetime is six to nine months
- Refractory life-cycle costs are currently over $1,000,000 per year for a 500,000 lb/day gasifier
- Nozzle lifetime is four weeks
- Operating temperature > 1,000°C

Project Metrics:

- Minimum lifetime of one year – Black liquor recovery is a critical operation in a pulp plant. Equipment is maintained typically during a yearly shutdown. Refractories and other structural materials including nozzles ideally would have lifetimes measured in 12 month increments (i.e., 12 months, 24 months, 36 months, etc…)
- Refractory Life-cycle costs less than $300,000 per year for a 500,000 lb/day gasifier
- Operating temperature below 1,000°C

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:** This project is the continuation of a project that was initially begun under the ITP Forest Products IOF, transferred to the Biomass program and then transferred back to the ITP IMF program. Under the previous programs project partners have successfully:

    1. Developed a characterization of the gasifier environment to determine the physical operating conditions required for gasifier simulation in laboratory testing of refractory materials.

2. Developed refractory screening equipment and test procedures. Two immersion test systems (see figure) have been constructed and are being used for evaluating materials. A rotary refractory test furnace was also constructed, and is available when longer term testing is warranted
3. Evaluated degradation mechanism of refractory materials from the only gasifier operating in the USA and refractory materials after exposure in the immersion test system to determine the reactions based on individual refractory components with the gasifier environment. Examination of the refractories included optical microscopy, scanning electron microscope, electron microprobe, and X-ray diffraction.
4. Evaluated a series of mullite ($3Al_2O_3$ - $2SiO_2$), alumina ($3Al_2O_3$), alumina –magnesium, alumina-zirconia, and alumina-silica based refractories exposed in the immersion test system.
5. Incorporated refractory performance into a new design for the refractory lining. Key elements included
   - Identified best fusion-cast alumina material
   - Identified crushable material to control chemical growth of the refractory lining
   - Conducted finite element modeling to address stress issues in the gasifier shell design

Under the current ITP-IMF program the project partners have:
1. Evaluated performance of test samples of refractories and selected a new refractory material and surface treatment for in-situ evaluation.
2. Selected fusion-cast magnesia-alumina spinel for installation as the next generation lining for installation later this year.

12. **Future Plans:**

The major milestones to be accomplished are to:
1. Develop industrial scale refractory fabrication protocols based on new materials and surface treatments (continuing)
2. Manufacture and install a test panel of alternate lower-cost refractories (lithium- treated mullite, bonded magnesia-alumina spinels), October 2004)
3. Perform evaluations of in-service refractory materials from the test panels at New Bern (continuing; March, 2004; October, 2004)
4. Go/ No Go Decision – Decision to replace a major portion of the New Bern gasifier lining with new type of refractory (completed March, 2004 (for spinel); installation planned for September, 2004)

13. **Project Changes:**

Under the current program there have been no changes in the project direction or timetable.

14. **Commercialization Potential, Plans, and Activities:**

There are 278 black liquor recovery boilers in the United States. The majority of these were built in the 1960s and 1970s. About 35% of these units have been rebuilt. Boiler lifetimes are 30 to 40 years. Many of the current units are approaching the point where they will need to be replaced or rebuilt. This presents an opportunity for the introduction of new technology (i.e., black liquor gasification).

This project is developing the refractories and nozzle materials; and will demonstrate their performance in a commercially operating gasifier. Once demonstrated, the industry will view gasification as a practical and economic alternative to the traditional recovery boiler. Refractory manufacturers (including two project partners) have the business incentive to promote this technology.

Pulp mills also have the business incentive (both financial and "green" image') to pursue this technology. Gasification of black liquor with combined cycle cogeneration of steam and electricity results in greater

energy output per unit input for the pulping industry. This will change the pulp industry from importing 20-40% of their electrical energy requirement to a 15+% net exporter of electric energy. The additional revenue from exporting electricity plus any environmental credits for using renewable resources gives gasification a higher internal rate of return (IRR) (16 to 24% IRRs*) than the traditional Tomlinson black liquor recovery boiler system (14% IRR*). This higher return offsets the higher capital requirement (60 %*) for gasification.

Both the timing of the technology (soon to be proven) and the enhanced IRR will make this technology attractive to industry.

Fusion cast spinel – steel ; lithium treated mullite -

* Princeton University, Navigant Consulting, Politecnico di Milano report on *Gasification Power Generation in the Pulp & Paper Industry*, 8 Oct 2003, pages S16 and S20.

15. **Patents, publications, presentations:** (Please list number and reference, if applicable. If more than 10, please list only 10 most recent.)

2 Patents -

Patent submitted "Alkali Resistant Refractories"
Second patent being prepared on other refractory work

4 Publications -

"Materials Issues in High Temperature Black Liquor Gasification", Proceedings of TAPPI 2003 Fall Technical Conference
"Performance of Materials in Black Liquor Gasification Environments", CORROSION 2004, Paper 04251 NACE International
"Selection and Development of Refractory Structural Materials for Black Liquor Gasification", Proceedings of TAPPI Paper Summit 2004.
"Selection of Materials for Low-Temperature Black Liquor Gasification" Proceedings of TAPPI Paper Summit 2004.

4 Presentations -

"Materials Issues in High Temperature Black Liquor Gasification", TAPPI 2003 Fall Technical Conference, Chicago, October 26-30, 2003.
"Performance of Materials in Black Liquor Gasification Environments", CORROSION 2004, Paper 04251, New Orleans, March 28-April 1, 2004.
"Selection and Development of Refractory Structural Materials for Black Liquor Gasification", TAPPI Paper Summit 2004, Atlanta, May 2-5, 2004.
"Selection of Materials for Low-Temperature Black Liquor Gasification" TAPPI Paper Summit 2004, Atlanta, May 2-5, 2004.