



## INDUSTRIAL TECHNOLOGIES PROGRAM

# Fundamental Study of Black Liquor Gasification Kinetics

## Gasification Offers Industry the Potential to Become Energy Self-Sufficient Using Biomass Fuels

The aging recovery boilers of the pulp and paper industry will need replacing in the near future, and the industry has the opportunity to consider black liquor gasification technology in their place. Black liquor gasification offers pulp and paper mills the most efficient method for converting biomass energy to electric power, with thermal efficiencies of 74 percent compared to 64 percent in modern recovery boilers. Black liquor gasification also has environmental benefits, such as fewer CO<sub>2</sub> emissions and wastewater discharges, the potential for self-generation of power, and the potential for improved pulping operations.

Air-blown gasification technology, which operates at atmospheric pressure, is in place in mills in Sweden and the United States. This project explored the feasibility of commercializing pressurized, oxygen-blown gasification using entrained-flow reactor technology. The design offers a number of advantages to the technology in use including lower capital costs, simpler gas cleanup, and greater electrical output when used in gas turbines. Moreover, the technology's greater thermal efficiency could potentially save more than 100 trillion Btus annually, and if mills replace their coal-fired power systems with gasifiers that self-generate power, CO<sub>2</sub> emissions could fall by 20 million tons/yr.



*A milestone for IPST was the acquisition of a pressurized entrained flow reactor (PEFR) for black liquor and biomass gasification. Operating limits of 1500°C, 1200 psi, and 10 sec residence time make it a unique addition to black liquor research capabilities.*



### Benefits for Our Industry and Our Nation

- Improvements in thermal efficiencies
- Reduction in energy consumption of >100 trillion Btus annually
- Twice the electricity output of atmospheric, gas-blown gasification
- Potential reduction in CO<sub>2</sub> emissions of 20 million tons/yr
- Lower capital costs than recovery boilers
- Improvements in pulping and other processes

### Applications in Our Nation's Industry

Recovery boilers in use in the pulp and paper industry are nearing the end of their useful lives. Adoption of oxygen-blown gasification technology in their place will generate significant energy and environmental benefits to mills.

## Project Description

Goal: To evaluate the kinetics of gasification of kraft black liquor under laboratory conditions simulating pressurized, oxygen-blown gasification.

Kraft black liquor from both hardwoods and softwoods was used in this study. Initial analysis of gases exiting the black liquor gasification reactor were performed using Fourier Transform Infrared Spectrometry, and chemiluminescence. The next step was a coupling of a pressurized, laminar-entrained-flow reactor (PEFR) and the National Renewable Energy Laboratory's Transportable Molecular-Beam Mass Spectrometer (TMBMS). This will be the first time that black liquor gasification kinetics was studied in a laboratory/pilot scale high-temperature, high-pressure reactor using a spectrometer to analyze the synthetic gas. The last task was to develop a kinetic model of the product gases. The fate of trace components is of particular interest to researchers, especially of whether the nitrogen from the black liquor produces significant amounts of NO and NH<sub>3</sub> during gasification at high temperatures and high pressures.

## Results

- Evaluated the performance and reproducibility of gasification runs with black liquor.
- Assessed the impact of pressure and temperature at elevated pressures on gasification rate, sulfur species evolution, and the fate of sodium, potassium, and chloride.
- Deemed PEFR ready for combined operation with the TMBMS or as a stand-alone gasifier. It has the highest pressure and temperature operating range for any experimental black liquor gasifier in the U.S.
- Main tar products during pyrolysis tests: benzene, toluene, naphthalene
- Found that overall char yield decreases with increasing pressure.
- TMBMS quantified secondary tar species in the PEFR: Char and tar concentrations decrease with pressure; CO and CO<sub>2</sub> concentrations increase with pressure; less H<sub>2</sub>S is formed as pressure increases; residence time at the peak H<sub>2</sub>S level is close to that observed in the atmospheric pressure reactor.
- A comparison between the experimentally measured distributions of carbon and sulfur with those predicted by chemical equilibrium calculations shows that all of the reaction products are far from chemical equilibrium.
- Including electrolyte chemistry in the process model is critical to determine the performance of commercial black liquor gasification processes.
- Found that commercial units should minimize green liquor/raw gas contacting.

## Project Partners

Air Products and Chemicals, Inc.  
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## A Strong Energy Portfolio for a Strong America

Energy efficiency and clean, renewable energy will mean a stronger economy, a cleaner environment, and greater energy independence for America. Working with a wide array of state, community, industry, and university partners, the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy invests in a diverse portfolio of energy technologies.



U.S. Department of Energy  
**Energy Efficiency  
and Renewable Energy**  
Bringing you a prosperous future where energy  
is clean, abundant, reliable, and affordable

October 2006  
Project completed by Sept 2000  
Full award #DE-FC36-98GO10369