Fundamental Study of Black Liquor Gasification Kinetics

Quarterly Progress Report for the Period October 1999 to December 1999

Date of Report: 31 January 2000

Performing Organization: Air Products and Chemicals, Inc.
Address: 7201 Hamilton Boulevard
Allentown, PA 18195-1501

Prepared for the United States
Department of Energy
Under Cooperative Agreement
No. **DE-FC36-98GO10369**

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Project Manager(s): Dr. John J. Lewnard
Project Manager
610-481-6932 (Telephone)
610-481-5136 (Fax)
email: lewnarjj@apci.com

Date Initiated 1 October 1998 **Duration** 24 months
Total DOE-OIT Funding Requested: \$280,832
Total Industry Funding Committed: \$97,822

Current Performance Year 10/99 - 09/00 **Quarterly Report Period** 10/99 - 12/99

DOE Program Manager: Douglas Hooker

Project Objectives:

The overall objective of this research is to evaluate the kinetics of gasification of kraft black liquor under laboratory conditions simulating pressurized, oxygen-blown gasification. The significant independent variables are gasifier temperature, black liquor composition, particle size, and particle residence time. We will quantify their impact on the concentration of major and trace gas phase species, as well as the composition of condensed phase inorganic products, including specification of the Na- and S-containing compounds and overall carbon conversion. The specific objectives by task are:

Task 1.1: Preparation for Combined PEFR/TMBMS Operation

Objective: to quantify the effect of gasifier temperature, black liquor composition, particle size, and particle residence time on:

- gas composition and fuel value
- carbon conversion
- distribution of sulfur between the condensed phase (Na₂S) and gas phase (H₂S and TRS compounds)
- NaOH formation in the condensed phase
formation of trace species, including NH₃, HCl, and

IPST and Air Products will conduct background experimental, design, and economic evaluation work required to establish the experimental conditions for the program. Total duration is 10 months.

IPST, lead by Dr. Jim Frederick, will finalize the check-out of the PEFR, including installation/calibration of instruments and analyzers required for operation with black liquor; check-out of the control system; completion of all feed and product gas piping; and initial operation tests with carbon. IPST may use contract labor when specific crafts, such as electrical, instrumentation, pipe-fitting, etc. are required to complete a task. Upon completion of these tasks, IPST will commission the PEFR on black liquor, and run an extensive set of process variable scans to delineate the commercially practical operating window for pressurized, oxygen-blown gasification. The project team anticipates at least one hardwood and one softwood kraft black liquor will be collected by Air Products. IPST will prepare the samples for the PEFR by drying in vacuum to prevent oxidation, followed by grinding and sieving to produce dry black liquor particles in the size range 90-125 μm . The particles will be gasified in a controlled gas atmosphere (O₂/water vapor/N₂ mixtures) at temperatures between 900-1200°C and pressures between 20-50 bar. Coarse particles (residue of feed particles) will be collected in a 3- μm cutoff cyclone downstream of the product collector and quench. The fine particles (fume) produced will be collected quantitatively on a fine particle filter

after removal of the larger droplet residues. Each of these product particles will be weighed to determine the amount of each produced, and analyzed to determine their elemental and inorganic species composition. During these preliminary tests, IPST will rely on in-house analytical equipment to quantify the effect of operating variables on the composition of major components in the gas and smelt phases. Gas composition will be analyzed by a combination of Fourier Transform Infrared Spectrometry (FT-IR) and chemiluminescence. FT-IR has been used extensively in conjunction with the IPST LEFR for analysis of carbon- and sulfur-containing gas species generated during pyrolysis of kraft black liquors. Chemiluminescence has been used simultaneously in many of these studies to measure the concentrations of NO-NO_x in the product gases. Smelt phases will be analyzed with standard gravimetric techniques, such as the ABC titration method.

Air Products, under Dr. Jack Lewnard, will use the results of the IPST PERF process variable scans to identify the most promising commercial operating conditions. The economic assessment will focus on estimated cold gas efficiency for an integrated combined-cycle black liquor gasification facility, as well as consideration of capital and operating costs associated with fuel gas cleaning. IPST will provide input during the sensitivity analysis, particularly in regard to data quality.

In parallel, under a separate Field Work Proposal (FWP), NREL personnel led by Dr. David Dayton will begin design and safety review for a high-pressure sample probe to interface between their TMBMS and the PEFR. The TMBMS is a three-stage, differentially pumped vacuum system that can be used for directly extracting and continuously analyzing hot, particulate-laden, reactive gas streams. In their FWP, NREL will address the specific safety issues of coupling the equipment for the first time to a pressurized gasifier. We anticipate that the design effort will require retrofits to both the PEFR and the TMBMS.

Due to the high pressures, temperatures, and potentially hazardous and flammable gas compositions involved in these tests, safety is a paramount concern. Consequently, all parties will participate in a safety review prior to modification of any equipment.

At the conclusion of Task 1.1, there will be a go/no-go decision based on the ability of the team to identify a critical operating window meriting detailed investigation, and the assessment of the operability of the combined PEFR and TMBMS.

Task 1.2: Combined PEFR/TMBMS Operation

Objective: to develop kinetic models for pressurized, oxygen-blown gasification

Activity during this task involves the combined operation of the PEFR and TMBMS over the optimal operating window identified in Task 1.1. Total duration is 7 months. Note that the first 2 months overlap with Task 1.1, and the last 5 months start at the end of Task 1.1.

IPST is responsible for the construction of the sample probe that interfaces between the high-pressure, high-temperature PEFR and the TMBMS, per the NREL design. Once the probe is completed IPST will operate the PEFR in an intensive series of process variable scans. NREL personnel, under their FWP, will join the IPST team and be responsible for installation and start-up of the TMBMS, and provide training to IPST personnel in its operation, ultimately for which IPST may assume responsibility for routine operations. During combined PEFR/TMBMS operation, black liquor gasification kinetics for the critical major and trace gas and smelt phase components will be measured in real time.

At the end of Task 1.2, the team will make a go/no-go decision based on the quality of the data and the breadth of the operating window.

Task 1.3: Kinetic Model Development

Objective: to investigate the feasibility of smelt/gas separation in the reactor, thereby preserving the NaOH formed during gasification.

Development of the detailed kinetic model for major, trace, and smelt species during black liquor gasification will be conducted during Task 1.3. Total duration is 9 months. During the first six months, all team members will be responsible for their respective data work-ups. Air Products will coordinate the consolidation of the results and be responsible for the final report.

Program Baseline:

Black liquor gasification has been under development for a decade and the first commercial implementation of atmospheric pressure, air blown gasification technology is in place in mills in Sweden and the U.S. Initial developments have focused on both low temperature ($< 700^{\circ}\text{C}$) gasification (air-blown and steam/indirect heated) and on air-blown gasification at $900\text{--}1000^{\circ}\text{C}$. Pressurized, oxygen-blown gasification using entrained-flow reactor technology has significant advantages for reducing capital cost, simplifying gas clean-up and facilitating its use in gas turbines to produce greater electrical output compared to the current commercial black liquor gasification processes. The overall objective of this research is to evaluate the kinetics of gasification of kraft black liquor under laboratory conditions simulating pressurized, oxygen-blown gasification. The significant independent variables are gasifier temperature, black liquor composition, particle size, and particle residence time. We will quantify their impact on the major gas phase species, as well as trace species and on the condensed phase inorganic products, including speciation of the Na- and S-containing phases and overall carbon conversion. *The work proposed here marks the first time that black liquor gasification kinetics will be studied in a laboratory/pilot scale high-pressure, high-temperature gasification reactor with on-line molecular beam mass spectrometry analysis of the synthesis gas, including trace components.* Air Products will use the results obtained from this work to answer questions necessary for the commercialization of pressurized, oxygen-blown gasification. Upon commercialization of this technology energy savings of 100 trillion BTU/year can be realized together with potential reduction of CO_2 emissions of 20 million tons/year.

Technical Progress and Impact:

31 December 99

Task 1.1: Preparation for Combined PEFR/TMBMS Operation

The first series of gasification runs with the IPST PEFR was begun in August, 1999. During this quarter, 19 runs were completed at a pressurized conditions. Most of these were made with CO_2 as the gasifying agent, and two with oxygen or O_2 and water vapor as the gasifying agent. Prior runs included pyrolysis runs made in nitrogen. The objective of these runs were to evaluate the performance and reproducibility of gasification runs with black liquor, and to assess the impact of pressure and temperature at elevated pressures on gasification rate, sulfur species evolution, and the fate of sodium, potassium, and chloride. Table 1 summarizes runs and conditions during the quarter.

Table 1. Run Conditions for Quarter

Run	Reactor	Reactor	Inlet gas	Particle	BLS feed	Char	Length of
No.	Temp., °C	Press., bar	Composition	Residence Time, s	Rate, g/min	Residue, g	Run, min
991012A	900	5	CO ₂ 5%	2.4	10.21	3.536	
991012B	900	5	CO ₂ 5%	2.4	10.27	4.184	12.8
991013B	900	5	CO ₂ 5%	1.2	10.23	5.296	15.4
991013C	900	5	CO ₂ 5%	1.2	10.37	5.084	17.0
991015A	900	10	CO ₂ 5%	1.2	10.52	2.369	15.8
991105A	900	5	2.3%O ₂ , 3.2%H ₂ O	0.5	12.61	4.317	
991109A							
991109B							
991116A							
991118A	900	5	20%CO ₂	9.25	16.50	4.601	
991120A	900	5	20%CO ₂	9.25	17.25	3.687	
991121A	1050	5	20%CO ₂	9.25	20.10	1.489	
991123A	1050	5	20%CO ₂	9.25	20.23	5.711	
991124A	900	5	20%CO ₂	9.25	20.25	3.033	
991203A							
991203B	900	20	20%CO ₂	9.25	19.98	0.127	
991207A	900	10	20%CO ₂	9.25	20.29	0.996	
991210A					19.93	2.661	
991211A	900	5	20%CO ₂	9.25	20.06	4.359	

The black liquor run in the PEFR is a softwood kraft liquor that had been dried in a pulse combustor dryer. Its composition and heating value are shown in Table 2. The gas flow rates for runs to-date made are included in Table 3.

Table 2. Composition and heating value of the black liquor solids used in this study.

Element	Wt-%
Total Carbon	31.94
Carbonate Carbon	1.4
Hydrogen	3.65
Oxygen	38.59
Sodium	18.6
Sulfur	5.26
Chloride	0.55
Potassium	1.76
Nitrogen	0.1
Ash	39.11
Higher heating value, Btu/lb	5554

Table 3. Gas flow rates used in the PEFR runs to-date.

Reactive gas and % of total gas input	5% CO ₂ in N ₂	20% CO ₂ in N ₂	2.3% O ₂ + 3.2% H ₂ O(v)	100% N ₂
Primary gas (N ₂) flow rate, SCMH	0.65	0.65	0.65	0.65
Secondary gas flow rate, SCMH				
CO ₂	0.30	1.20		
H ₂ O(v)			0.19	
O ₂			0.14	
N ₂	6.20	5.30	6.17	6.50
Quench (N ₂) flow rate, SCMH	1.56	1.56	1.56	1.56
Purge (N ₂) flow rate, SCMH	2.95	2.95	2.95	2.95
Total gas input, SCMH	11.66	11.66	11.66	11.66

Each run was made by

1. bringing the reactor to temperature,
2. adjusting the primary, secondary, quench, and purge gas flow rates and compositions to the desired values (see Table 2),
3. charging the solids feeder with a known weight of black liquor solids,
4. setting the solids feeder to feed at the desired feed rate,
5. analyzing on-line for C-, H-, O-, and S-containing species in the product gas by FT-IR, and
6. running until the entire batch of black liquor solids had been fed

At the end of each run, the particles collected on the filter downstream of the quench/collector were removed and weighed to determine the char residue yield. These particles were stored for further chemical analysis. Some of these samples were sent for analysis of carbon, sodium, and chloride content.

Char Residue Yields

Figure 1 shows the char residue yields from six gasification runs made 900C, five bar total pressure, to in five percent carbon dioxide in nitrogen. At these conditions, and the char yields decrease linearly with increasing particle residence time, from about 50 percent to about 23 percent of the original black liquor solids mass. The mean square difference between the pairs of replicate experiments is 10%, based on the char yields.

Figure 1. Char yield vs. particle residence time for pressurized gasification runs at 900C, 5 bar, 5% carbon dioxide in nitrogen.

Figure 2 presents char yield the data vs. temperature and particle residence time for black liquor gasifier at 5 bar in 5% CO₂. The data points at 900C are the same ones as in Figure 7. The mean square difference between all pairs of replicate experiments in Figure 8 is 11.4%, based on the char yields.

Figure 2. Char yield vs. particle residence time for pressurized gasification runs at different gasification temperatures and residence times, at 5 bar, 5% carbon dioxide in nitrogen.

Fixed Carbon, Sodium, and Chloride Yields in Char Residue

Figure 3 shows how the carbon, sodium, and chloride recovered as char residue changes with residence time, for runs made at 900C, 5 bar, 3.9 seconds residence time, in 5% CO₂ in nitrogen. The carbon recovered as char residue decreases with residence time as expected. By 2.6 seconds, it is approaching the equilibrium carbon content predicted from Figure 1. The chloride also decreases. However, the sodium recovered as char residue remains constant with residence time. This is different than in gasification at atmospheric pressure, where sodium is volatilized continuously during gasification. The constant sodium recovery at 900C, 5 bar is probably due to suppression of sodium volatilization via stabilization of Na-O_x-C sites within the char residue. Iisa and Jing (1999) showed recently that sodium and potassium volatilization from black liquor char at atmospheric pressure are suppressed by CO₂.

Figure 3. Sodium, chloride, and carbon recovered vs. particle residence time for pressurized gasification runs at 900C, 5 bar, 5% carbon dioxide in nitrogen.

C-H-O Containing Gases

Figure 4 shows the CO yields from both gasification and pyrolysis runs at 5 bar total pressure and 3.9 seconds particle residence time. The CO yield increases rapidly with temperature in both cases. This is partly the result of more complete conversion of carbon in black liquor solids to gas. It is also a result of higher temperature favoring more CO at equilibrium. At 800C, the CO yields from pyrolysis and gasification are essentially the same since the yields are defined as CO produced/C input as BLS. The CO yields at 900C and above are higher for gasification with CO₂. This is because of the stoichiometry of the CO₂ gasification reaction – two moles of CO produced per mole of CO₂ consumed.

Figure 5 shows the methane yields from six gasification runs made at five bar total pressure, 3.9 seconds particle residence time, in five percent carbon dioxide in nitrogen. At these conditions, and the methane yields decrease

slightly with increasing particle residence time, from about 1.6% at 800C to about 1.4% at 975C. These are reported as carbon equivalent as a percent of the original black liquor solids mass. The mean square difference between the pairs of replicate experiments is 14.5%, based on the methane yields.

No other C-H-O compounds except methane, CO, and CO₂ were detected at measurable levels in these runs. Inspection of the water-cooled collector tube at the end of different runs showed that condensable organic matter and tar had collected on the cold inner surface. No attempt was made to collect or analyze the material collected there.

Figure 4 shows the CO yields from both gasification and pyrolysis runs at 5 bar total pressure and 3.9 seconds particle residence time.

Figure 5. Methane yield vs. gasification temperature for pressurized gasification runs at 3.9 s particle residence time, 5 bar, 5% carbon dioxide in nitrogen.

Sulfur-Containing Gases

Figure 6 shows the H_2S produced versus time at 900C, 5 bar, 5% CO_2 . The H_2S decreased with time, similar to COS (see Figure 8). However, the H_2S values are well below the equilibrium value.

Figure 6. H_2S versus time for gasification at 900C, 5 bar, 5% CO_2 .

Figure 7 shows the H_2S produced versus temperature, at 5 bar total pressure, in a 5% CO_2 atmosphere or in N_2 . The H_2S decreased with temperature, as predicted by equilibrium.

Figure 7. H_2S produced versus temperature, at 5 bar, in a 5% CO_2 atmosphere or in N_2 .

Figure 8. H_2S yields from runs at 5 bar and 10 bar, both at 900C, 5% CO_2 , 1.2 seconds.

Figure 8 compares H_2S yields at two different pressures (5 and 10 bar) at the same conditions otherwise. Pressure has no distinguishable effect on the fraction of sulfur input that is converted to H_2S , contrary to equilibrium.

Figure 9 shows how the COS produced changes with particle residence time at 900C, 5 bar, 5% CO_2 . The data are presented as the sulfur in the COS as a fraction of the sulfur input with black liquor solids. At these conditions and particle residence times (1-4 s), the COS produced appears to have decrease with increasing particle residence time

but leveled off at about 7.5 % of the sulfur input. This trend is consistent with the results reported by Horenziak (1999) for gasification of black liquor solids in 5% CO₂ at 900C, atmospheric pressure, and by Sricharoenchaikul et al. (1997) for pyrolysis of black liquor solids in N₂ at 1 bar total pressure. In both of the latter studies, the COS concentration increased with residence time, passed through a maximum near 1 second particle residence time, and then decreased. Horenziak's data at higher CO₂ partial pressures showed that the COS produced increased roughly in proportion to the CO₂ partial pressure.

Figure 9 also contains the predicted equilibrium concentration for COS at 900C, 5 bar, 5% CO₂. The measured COS values are above the equilibrium predictions, but are decreasing with particle residence time.

Figure 10 compares the COS/H₂S mole ratio from several experiments with equilibrium. The experimental data ratios are well above equilibrium. This is expected, since the COS values from the experimental runs were always above the equilibrium values and the H₂S concentrations were always below them.

Figure 9. Carbonyl sulfide yield vs. particle residence time for gasification and pyrolysis runs at different particle residence times. 5 bar, 5% carbon dioxide in nitrogen. The blue diamonds are data from PEFR gasification runs at 900C, 5 bar, 5% CO₂. The yellow triangles are from LEFR gasification runs at 900C, 1 bar, 5% CO₂ (Horenziak, 1999). The pink circles are from LEFR pyrolysis runs at 900C, 1 bar (Sricharoenchaikul et al. (1997).

Figure 10. Experimental and equilibrium COS/H₂S mole versus temperature from gasification runs at 5 bar, 5% CO₂.

Summary and Conclusions

Reproducibility of the char yields and product gas analyses from gasification experiments conducted in the second half of 1999 are 10-15%, calculated as a mean square value of the coefficient of variation for replicate runs. This is acceptable for gasification research. Reproducibility of measurements of minor components (K, Cl, N) will be worse.

The gaseous pyrolysis products detected during these experiments included CO, CH₄, H₂S, COS, and organosulfur species. The CO yield increased and the H₂S and COS yields decreased with increasing reaction temperature.

The product gases exiting the reactor after 4 seconds are not close to equilibrium.

The particle flow pattern in these runs was far from the ideal pattern expected in laminar, entrained-flow reactors. The problem was a poorly designed flow straightener for the secondary gas flow. That has now been replaced with a honeycomb flow straightener, very similar to the one used with the IPST LEFR.

The experimental runs were terminated when particles no longer exited the reactor. This was probably a result of deterioration of the original secondary gas flow straightener, which has since been replaced. Additional experimental runs are scheduled to begin during the second week of March.

Task 1.2: Combined PEFR/TMBMS Operation

Collection and analysis of tar and condensable organic matter after the quench/collector is not possible. After completing this set of runs in early December, the PEFR was taken out of service for modifications to the sample ports. Following recommendations by NREL, sample ports have been added along the reaction zone so that gas

samples can be removed without passing through the collector. These sample ports will be used to provide samples to NREL's MBMS in experiments to be conducted later this year.

Task 1.3: Kinetic Model Development

No activity this quarter

Current Percent Complete:

<u>Task</u>	<u>Duration</u>	<u>Percent Complete</u>
1.1	10 months	60%
1.2	7 months	10%
1.3	9 months	0%

Most Significant Technical Advance to Date:

31 December 99

PEFR is completely operational. However, we continue to modify the equipment to provide more reliable/stable operation, and enhance gas and solid sampling capabilities.

Business Issues:

Currently no Business Issues.

Summary of Project Changes:

Delay in TMBMS testing due to on-going PEFR upgrades and enhancements.

Problems and Opportunities:

Significant Program/Project Tests or Demonstrations (Next Quarter):

Complete preliminary test matrix, move TMBMS from Battelle to IPST.

Upcoming Meetings:

Currently no meetings are scheduled for the next quarter. We continue to conduct routine teleconference calls.

Upcoming Conferences at which Papers will be Presented:

Currently no conferences are scheduled.