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FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

Report No. 2—Phase I for the Period October 1984—November 1986

By
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January 1987

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For
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Office of Industrial Programs
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By
The Institute of Paper Chemistry
Appleton, Wisconsin

and

The National Bureau of Standards
Gaithersburg, Maryland

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FUNDAMENTAL STUDIES OF BLACK LIQUOR COMBUSTION

REPORT NO. 2 - PHASE 1

(October 1984 - November 1986)

By

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ABSTRACT

The fundamentals of kraft black liquor combustion are being studied in a five year project. This report covers the second and third years of work by The Institute of Paper Chemistry (IPC) and the National Bureau of Standards (NBS) for the U.S. Department of Energy. The burning processes are being studied in two continuous flow reactor systems designed to both study overall process and single particle phenomena. Black liquor burning is divided into four distinct phases: drying, volatiles burning, char burning, and smelt coalescence. Phase 1, In-flight Processes, is the main focus of this report. In-flight processes include mainly the stages of drying and volatiles burning. Test results in both flow reactors and in two specially designed single particle reactors are presented. Dynamic droplet velocity and swelling have been measured for the first time. A direct link between initial liquor viscosity and burning behavior in the early stages has also been identified. During the fourth year Phase 1 will be completed and Phases 2 (Char Burning) and 3 (Fume Processes) will begin.

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EXECUTIVE SUMMARY

The efficient recovery of chemicals and high level energy from black liquor contributes heavily toward the dominance of the kraft pulping process. Kraft chemical recovery boilers have been used to burn black liquor for over 50 years. The potential still exists, however, for significant improvements in energy recovery and black liquor throughput. This contract addresses both areas.

The identified industry-wide potential energy benefits amount to over 3×10^{13} Btu/year (0.03 Quad/year), an approximate value of \$100,000,000/year at \$3.25/ 10^6 Btu. Energy benefits are achieved through process modifications; these same changes can increase black liquor solids throughput. Pulp production and overall mill productivity should increase as solids throughput increases for recovery boiler bottlenecked mills. This is especially significant, since the high capital intensity of recovery boilers often results in mill production being limited by recovery boiler solids throughput. Recent practice indicates that production increases of 5% are reasonable with increases above this level being quite likely. An industry wide production increase of 5% corresponds to an approximate value of \$500,000,000/year. The combustion research conducted as a part of this DOE contract seeks to provide process understanding that will assist in achieving both energy and productivity benefits.

The contract's three objectives focus on advancing kraft recovery boiler technology. First, develop test systems to study both state-of-art and advanced recovery processes. Second, apply advanced optical and spectroscopic techniques to study the burning processes. Third, develop a data base of process fundamentals which will bridge and enhance prior research findings and their commercial application.

The recovery processes of interest include all those that occur within the recovery boiler. The four burning stages of drying, volatiles burning, char burning, and smelt coalescence are being studied under flowing conditions. Where necessary, this work is supplemented with single particle studies. There are two distinctive conditions for the flow reactor work. First, reacting particles in flight from liquor injection to the char bed. Second, reacting particles on or within a char bed. These two conditions form the basis for the first two

phases of the contract. The last two phases focus specifically on fume processes (both formation and deposition) and simultaneous study of all process steps.

The four phases are specifically:

- Phase 1. In-flight chemical and thermal processes
- Phase 2. Char bed processes
- Phase 3. Inorganic fume formation processes
- Phase 4. Recovery furnace simulation

Progress Report 1 (Clay, et al., 1985) reported on the first year of work, the initial part of Phase 1. This report covers the second and third years of the contract. During this time most of Phase 1 was completed and Phase 2 was begun. The remaining Phases of the five year contract are scheduled for completion in September 1988.

Two continuous laboratory-scale flow reactor systems, one at The Institute of Paper Chemistry (IPC) and one at the National Bureau of Standards (NBS), have been operational for most of the last two years. They successfully simulate the in-flight process conditions of interest for Phase 1 tests. A char bed burning furnace has been designed and will be added to the IPC system for Phase 2 studies next year. Instrumentation will be developed by NBS, and subsequently added to the IPC system, for work in Phases 2 and 3.

The NBS system, short-height Dilute Phase Flow Reactor (DPFR), is used to study dynamic behavior of falling single droplets of black liquor in varying thermal environments. These have been the first studies to measure velocity and swelling of free falling black liquor droplets in hot environments. Similar tests with the full height of the DPFR will be made in the coming year. Successful development of a droplet injector for black liquor at high temperatures during this report by NBS was essential for both the NBS and the IPC systems. NBS also used a previously developed two-color optical pyrometer to dynamically measure the temperature of a burning single droplet of kraft black liquor. The IPC flow reactor system is used to study overall process performance with streams of black liquor droplets. Three main test groups have been completed to date. Their overall objective was to evaluate the impact of process variable changes on the chemical and physical characteristics of forming char particles.

In addition, droplet drying studies have been completed. These studies are the first to obtain data on intermediate free-falling black liquor droplets as they dry and begin to burn in a hot environment. To date, both the IPC and NBS systems have been tested in only the gas upflow mode. The remaining Phase 1 tests in the IPC system will be in the gas downflow mode. Single particle pyrolysis and burning tests were also done at IPC to characterize liquor performance via IPC developed tests.

The detailed test results from both the IPC and NBS systems are contained in the report text. The project testing to date coupled with supportive research at IPC has begun to expand our knowledge of early in-flight burning of kraft black liquor. A summary of this understanding, at present limited to the drop size range (2-4 mm) and liquor tested, is given below.

The early stages of black liquor burning, for conditions similar to recovery furnaces, are dominated by the influence of black liquor droplet characteristics. Heat transfer to and through the droplet is the controlling phenomenon. The three dominant effects are initial size, initial solids content, and initial viscosity and injection temperature. During drying the droplet swells and collapses in rapid succession, expanding its surface area and mixing the droplet contents. The extent of swelling and the mixing determine the ability of the droplet to absorb heat.

When the droplet viscosity is increased, a reduction in swelling and mixing occurs, reducing heat flux to the droplet core. Since external heat flux to the droplet by the environment is initially unchanged, the surface temperature will rise. Increasing surface temperature then reduces the external heat flux to the droplet. This situation effectively stops rapid drying of the liquor droplet above average solids levels of 95%. The surface progresses into the volatiles burning stage while the inner core is still drying.

A reduction in initial liquor viscosity improves inner droplet heat transfer, reduces inner droplet temperature gradient, and droplets reach higher solids levels before surface burning. The influence of size is analogous to viscosity with larger droplets developing larger temperature gradients. The influence of solids is first through viscosity, since they are exponentially related. Solids

are, however, directly related to the extent of drying. Higher initial solids give chars with lower moisture contents.

When the surface temperature of the droplets exceeds approximately 400°F (210°C) thermal degradation (pyrolysis) of the solids will become significant. The gaseous decomposition products will mainly be CO, CO₂, H₂O, hydrocarbons, and reduced sulfur compounds. The solid product will be highly aromatic char carbon, Na₂CO₃, and sodium salts of sulfur in various oxidation states. During pyrolysis the particle undergoes permanent swelling as the generated gases expand the pliable pyrolyzing solids. The outer surface can then rapidly increase in temperature, reaching and exceeding the melting point of the inorganics.

The droplet initial size and viscosity will affect the burning pattern in the early part of the volatiles burning stage. With increasing size or viscosity the outer surface can be fully molten while the inner core is still undergoing pyrolysis. If the particle remains intact while in flight, then pyrolysis gases will contact the molten outer surface. Such a condition is viewed favorably, since a major portion of the reduced sulfur gases would react and be retained in the droplet.

The direct link between drying/burning characteristics and initial liquor droplet size and viscosity is extremely important. Droplet size and viscosity can be controlled as a part of the recovery operations directly at the nozzle. The opportunity therefore exists for on-line control of the initial burning processes. Our work to date further shows that unless these two black liquor characteristics are controlled, optimum furnace control cannot be achieved.

Near-term efforts at IPC will focus on installation of the bed burning furnace and operation of the in-flight section in the downflow gas mode. Testing for Phase 2 will begin. NBS will complete start-up of the full-height DPFR and collect velocity and diameter data at longer residence times. The third progress report will cover this work plus initial Phase 3 work.

1.0 INTRODUCTION

1.1 Objectives

The research work initiated with this project is a systematic long range effort. It is primarily directed at current kraft recovery boiler technology. However, the data base and the measurement techniques developed will also be applicable to advanced recovery technologies involving partial or complete combustion of kraft black liquor. Basic and applied research will be carried out to understand and advance our knowledge of the internal chemical and thermal burning processes. The three main objectives of the work are

- a) to develop laboratory-scale flow reactor systems which will enable the study of both state-of-the-art and advanced recovery systems,
- b) to study gas phase and char bed mechanistic processes under realistic and controlled environments with advanced optical and spectroscopic techniques, and
- c) to develop a data base which will bridge the gap between ongoing fundamental research and commercial application of the resultant findings, culminating in increased thermal efficiency, productivity, and capital effectiveness.

These objectives will be accomplished in four project phases:

- Phase 1. In-flight chemical and thermal processes
- Phase 2. Char bed process
- Phase 3. Inorganic fume formation processes
- Phase 4. Recovery furnace simulation

The importance of the kraft chemical recovery cycle and the Tomlinson recovery boiler in particular is discussed in detail in Progress Report One of this project (Clay et al., 1985). This project is one of several sponsored by the Department of Energy which focuses on ways to improve the kraft chemical recovery cycle. Background on the recovery cycle, the recovery boiler and the other DOE related projects are discussed in Progress Report One.

1.2 Deliverables

This research project is expected to result in the following specific outputs:

- a) Modular laboratory-scale reactor systems which can simulate in-flight, char bed, and gaseous processes found in present recovery boilers, as well as advanced recovery processes.
- b) Quantitative process and mechanistic description of liquor/solids burning phenomenon. This will result from detailed studies of the drying, pyrolysis, gasification, and reduction processes.
- c) Laboratory-scale continuous flow demonstration of suggested process improvements and/or advancements emerging from this or other basic research.
- d) Diagnostic procedures and/or instrumentation which will advance recovery boiler technology and assist in successful transfer of these advancements from the laboratory to commercial practice.

A significant portion of Deliverable (a) is complete. Two modular laboratory-scale reactors which simulate in-flight processes present in recovery boilers are operational. This report presents performance results.

Deliverable (b) is partially covered in this report. Quantitative data on various burning stages of black liquor are now available.

Only limited work has been done which relates directly to Deliverables (c) and (d). Work in these areas will be concentrated more toward the end of the project.

1.3 Benefits

Although this research is long range and fundamental, it has significant benefits to the pulp and paper industry. The results of this research are vital links toward reaching improved thermal efficiency and process productivity goals. The increased thermal efficiency value for the industry is approximately 100 million dollars per year. The minimum process productivity value for the industry is estimated at \$500 million/year. Table 1-1 provides supporting detail of these estimates. These values reflect savings increments above the best state-of-the-art

recovery boiler technology currently available. Increments from industry average conditions to improved levels could approach 1.5 to 2.5 times the above values.

Table 1-1. Benefits from fundamental studies of black liquor combustion.

Goals:

1. Increased thermal efficiency
2. Increased process productivity
3. Improved equipment design potential
4. Improved process control potential

Targets:

1. Increased thermal efficiency	Improvement	Value (a,b)	
		10 ⁵ Btu/adtp	\$/adtp
Increased fired percent solids	70 to 80%	4.3	1.5
Reduced flue gas temperature	350 to 325°F	1.2	0.74
Reduced carbon in smelt	1.5 to 1.0%	0.86	0.54
Reduced sootblowing steam	3.0 to 2.5%	0.71	0.45
	(Total)	7.1	3.2

2. Increased Process productivity

Incremental production 5% increase at 225 \$/adtp

INDUSTRY VALUE:

1. Increased thermal efficiency
 $7.1 \times 10^5 \text{ Btu/adtp} \times 44 \times 10^6 \text{ adtp/yr} = 3.1 \times 10^{13} \text{ Btu/yr}$
 $3.1 \times 10^{13} \text{ Btu/yr} \times \$3.25 \times 10^{-6}/\text{Btu} = \$100,000,000/\text{yr}$
2. Increased process productivity through operation improvements and minimizing downtime (5%)
 $0.05 \times \$225/\text{adtp} \times 44 \times 10^6 \text{ adtp/yr} = \$500,000,000/\text{yr}$

- NOTES:
- a. adtp = air dried ton of pulp
 - b. details of calculation are in Progress Report One (Clay et al., 1985)
 - c. Fuel value updated to 1987 costs
 - d. Production increases on average of 5% appear reasonable. Reduction in boiler plugging a significant benefit

1.4 Organization

The Fundamental Studies of Black Liquor Combustion project is sponsored by the Office of Industrial Programs, United States Department of Energy. Stanley F. Sobczynski is the program manager. Substantial in-house contributions have also

been made by both The Institute of Paper Chemistry and the National Bureau of Standards.

This project is a joint effort between the National Bureau of Standards (NBS) and The Institute of Paper Chemistry (IPC). IPC is the prime DOE contractor, NBS has a subcontract with IPC. At IPC, the project is being conducted in the Chemical Sciences Division, Dr. E. W. Malcolm, Director. The principal investigator and project manager at IPC is Dr. D. T. Clay, Associate Professor. Major technical contributions and guidance are also given by Dr. T. M. Grace, Professor, Chemical Recovery. Other professional staff members who contribute to the project are Dr. J. H. Cameron and Mr. S. J. Lien. At NBS, the project is conducted in the Center for Chemical Engineering, Mr. Jesse Hord, Director. The principal investigator at NBS is Dr. H. G. Semerjian, Group Leader, Combustion Metrology. Other professional staff members who contribute to the project are Dr. A. Macek and Dr. S. R. Charagundla.

1.5 Schedule

The planned time for this project is 5 years, beginning September 26, 1983. The project's third year has just ended. The 5-year project schedule is shown in Figure 1-1. Both the IPC and NBS efforts are indicated. Progress Report One (Clay et al., 1985) covers the first year of the project. This report covers the second and third years. This figure is an updated version of the schedule consistent with the latest set of DOE milestones shown in Table 1-2.

Work still remains in Phase 1, specifically the study of fine particles burning in downward flowing gas. Since it has been two years since the last report, this report is being issued prior to Phase 1 completion. Although it contains mainly Phase 1 work, design work for the Phase 2 bed burning furnace is also included. Progress Report 3, which will be issued in approximately one year, will contain the remaining Phase 1 work as well as Phase 2 studies to date.

1.6 Technology Transfer

Progress reports are issued throughout the project's life. This is the second report. Two additional progress reports and one final report are planned.

Figure 1-1. Fundamental studies of black liquor combustion, project schedule.

These reports are reviewed by industry representatives and other DOE contractors working in the black liquor research area. In addition, the Recovery Boiler Research Subcommittee of the American Paper Institute (API) also reviews them. The principal investigators acknowledge their assistance with thanks.

Table 1-2. Fundamental studies of black liquor combustion.

Project Milestones (10/15/86 revision)

Phase	Milestone	Target	Complete
1	In-Flight Chemical Processes		
	1. Reactor preengineering	Mar '84	X
	2. Preliminary combustion experiments	Sep '84	X
	3. Phase 1 reactor detailed engineering	Dec '84	X
	4. IPC reactor central units and NBS reactor first modules installed	Jun '85	X
	5. Reactor temperature/flow/droplet characterization	Sep '85	On-going
	6. IPC Phase 1 reactor completely installed	Dec '85	X
	7. NBS Phase 1 reactor completely installed	Aug '86	X
	8. IPC Phase 1 reactor fully operational	Mar '86	X
	9. NBS Phase 1 reactor fully operational	Dec '86	On-going
	10. Process and diagnostic tests, liquid feed	Sep '86	On-going
	11. Process and diagnostic tests, solid feed		On hold
	12. Phase 1 Report (draft to DOE)	Dec '86	X
2	Char Bed Processes		
	1. Design of char chamber	Aug '86	X
	2. Installation of char chamber	Jan '87	On-going
	3. Char oxidation and reduction tests (IPC)	Sep '87	
	4. Above-bed diagnostics (NBS)	Sep '87	Started
	5. Phase 2 Report (draft to DOE)	Dec '87	
3	Inorganic Fume Formation Processes		
	1. Design of fume equipment	Mar '87	
	2. Installation of fume equipment	Jun '87	
	3. Gas phase reaction tests (NBS)	Dec '87	
	4. Fume formation tests (IPC)	Dec '87	
	5. Phase 3 Report (draft to DOE)	Mar '88	
4	Recovery Furnace Simulation		
	1. Process variable interaction tests	Mar '88	
	2. Control strategy tests	Jun '88	
	3. Next generation tests	Sep '88	
	4. Final report (draft to DOE)	Sep '88	

Program reviews are periodically held, during which new findings on this project are reported. The participants are from industry, government, and academic

groups involved in either the use of, the manufacture of, or research relating to the kraft chemical recovery boiler. Such program reviews have been held December 1984, Washington, D.C.; July 1985, Orono, ME; February 1986, Gainesville, FL; October 1986, Appleton, WI. Nominally 35-50 people attend.

Project status reports are presented every six months to the Project Advisory Committee on Pulping Processes at The Institute of Paper Chemistry (IPC). An annual written report is prepared. These meetings and reports are open to all IPC member companies and the DOE.

Laboratory demonstrations are given annually at the IPC Executives Conference. The IPC flow reactor system is operating. The conference usually draws approximately 150 top level executives from IPC member companies. The Conference is open to the DOE.

Project summary reports are given on an as needed basis to various groups and individuals that visit the IPC and NBS facilities. Visitors to the IPC facility have included at least five large manufacturing company groups, two recovery boiler manufacturing companies, and several foreign visitors.

Direct involvement by a pulp manufacturing company in this research project will begin in the fall of 1987. Weyerhaeuser Paper Company has committed to support one of their chemical recovery research scientists at the IPC for a period of approximately one year. Mr. Craig Brown will be directly involved with various research aspects of char burning and with char bed burning behavior in particular. Craig's participation as a team member with extensive experience in recovery boiler operations and testing is a vital first link for successful implementation of technology improvements.

1.7 Project Review - Prior Work

The project effort prior to this report focused on the design and preliminary tests required before construction of the two reactor systems. The details are listed in Clay et al. (1985). A brief summary is listed below.

The conceptual design for the reactor system was developed by IPC and NBS with support from a subcontractor, Xytel Inc., Mt. Prospect, IL. The preliminary

design included the entire system necessary for all four project phases. Its focus was mainly to obtain a reliable cost estimate. The detailed design and construction of the two systems were done in stages closely paralleling the project's four phases. The first stage of the IPC system was the Central Units, consisting of the in-flight section and accessory equipment. The first stage of the NBS system was the short-height DPFR [referred to in Progress Report One (PR1) as the initial reactor modules]. At the writing of PR1 the Central Units were under construction and the short-height DPFR was being hot tested.

The two major design issues discussed in PR1 were the required residence time and the technique for droplet formation and injection. Preliminary tests were conducted at IPC using an existing convective single particle reactor. The nominal burning time for a 65% solids, 5 mg (1.9-mm dia.) black liquor droplet in flowing air at 1600°F (870°C) was 2.8 seconds. Significant particle expansion was observed. Based on reasonable estimates for mass loss and drag, an in-flight height of nominally 12 ft (4 m) was chosen. This meant that for 1-mm particles, pyrolysis would essentially be complete, but 3 mm particles may only be partially dried. Since higher temperatures were expected possible in both continuous systems than existed in the single particle reactor, this constraint was acceptable.

A major experimental focus of the early NBS work was the development of the droplet injector. The developed injector provided consistently sized droplets on demand without plugging. Positive displacement of the black liquor, humidified coaxial assist gas flow near the droplet forming tip, and a cooled injector housing were the major concepts embodied in the injector. Although preliminary tests were conducted with 50% solids black liquor to verify the injector's operation, no quantitative tests on injector performance were given in PR1. The further development and subsequent testing of the droplet injector in the short-height DPFR became the next immediate task of NBS.

1.8 Black Liquor Burning Stages

The stages of black liquor burning were first identified by Hupa (1985) and Grace (1986). The three main burning stages are drying, volatiles burning, and char burning.

The drying stage is evaporation of water from black liquor as a result of heat transferred to the droplet. The volatiles burning stage consists of three major processes: volatiles evolution, volatiles combustion, and the formation of char in an inorganic matrix. A great deal of dynamic swelling and bursting occurs during the drying stage. Sustained swelling occurs only during the volatiles burning stage. When the carbon content is sufficiently low (approximately 2%) the char structure collapses, and the inorganics coalesce, in the form of molten smelt. Smelt coalescence is sometimes listed as the fourth burning stage. The stages overlap slightly, especially in the larger droplets.

Figure 1-2 shows photographs of a single droplet of kraft black liquor progressing through the four burning stages. As practiced in a recovery furnace the first two burning stages occur to varying degrees in flight from the nozzle to the char bed. These are the subject of the Phase 1 effort. Phase 2 char burning studies will cover both char burning and smelt coalescence. These studies will be in a char bed configuration. During the char burning stage and possibly during the volatiles burning stage inorganic fume is volatilized. Phase 3 will cover both fume formation for in-flight burning and for char bed burning.

The present report focuses on the first two burning stages, drying and volatiles burning.

Drying

Volatiles Burning

Char Burning

Smelt Coalescence

Figure 1-2. Burning stages of a kraft black liquor droplet. Black liquor droplet suspended on a wire in the IPC Single Particle Reactor.

2.0 DROPLET GENERATION

2.1 Requirements

The study of in-flight histories of black liquor droplets in gas environments which simulate conditions in recovery boilers requires a technique for reliable, on-demand generation of black liquor droplets having diameters of about 1 to 3 mm, or even larger. Furthermore, any technique developed for generation of droplets must be usable in flowing streams of high-temperature gases.

Most previous techniques for controlled droplet generation produce smaller diameters than required for the purpose of the present study and were therefore not immediately applicable. Also, it was found early in this project that black liquor containing 60% solids or higher presents exceptionally difficult droplet generation problems. Black liquor has both high viscosity and a strong tendency to dry via surface skin formation. Two approaches to overcome these difficulties were pursued at NBS.

The first approach, positive-displacement extrusion of droplets from a syringe, was developed to the point where it could be used routinely both in the NBS dilute-phase flow reactor (DPFR) and in the IPC process flow reactor. Although the basic concept is similar, there are significant differences between the two systems. The development and operation of the equipment for these applications are described in Sections 2.2, 2.3, and 4.2.3.3. In addition, efforts were made by NBS to develop a piezoelectric droplet injector apparatus. Other techniques appeared more promising, so this work was curtailed after limited efforts.

2.2 Equipment

A positive displacement technique was developed at NBS and used for generation of black liquor droplets. Before the injector was designed and built, experiments using a modified hypodermic syringe were done with glycerol to study droplet formation of viscous fluids. Good droplets in the desired size range could be generated on demand. The diameter of the injector needle and the velocity of an assisting gas (usually nitrogen), flowing coaxially to the needle, were the principal factors in determining the diameter of droplets.

Similar tests were then attempted using 60% black liquor. No droplets would form at room temperature, because of increasing surface viscosity. The assisting gas dried the liquor as soon as it was extruded from the injector. These factors were considered when the injector was designed.

The basic principle of the droplet-injector technique is simple. The stepper motor causes the displacement of the syringe piston, thereby extruding a small amount of liquid. However, application to black liquor imposes four special requirements. The first requirement is the heating of black liquor to reduce its viscosity and simulate the injector temperatures in recovery boilers. The second requirement is the assisting gas-flow capability. The third requirement is saturation of the assisting gas with water to prevent drying of the liquor. The fourth requirement is cooling the entire injector for use in hot reactor gases.

Before the final design, construction, and integration of the injector with the DPFR, preliminary tests were made outside the reactor with heated and humidified assisting-gas flows. As in the case of glycerol, the size of black liquor droplets was a function of two parameters, the diameter of the syringe needle and the flow velocity of nitrogen, coaxial to the needle. For fixed needle diameters, the coaxial flow is, by far, the most dominating factor. Thus, when there is no coaxial flow, the droplet size, to the first approximation, is determined only by the needle diameter. The stepper motor displacement determines mainly the frequency of droplet detachments from the needle tip.

A schematic of the droplet injector and its accessories is shown in Figure 2-1. The experimental apparatus consists of a stepper motor, a syringe with piston, the injector, and a nitrogen humidifier.

The stepper motor apparatus consists of four parts: a computer, a controller, the stepper motor itself, and a translating stage. The minimum displacement is 0.0005 inch (12.7 μm). The motor and the translating stage are installed for vertical translation above the piston. An aluminum angle, 4-inch X 4-inch, is attached to the translating stage to provide the displacement of the syringe piston.

Figure 2-1. Droplet injection system.

The stepper motor controller can be operated manually or with a computer using a RS-232 port. In the manual mode, the motor can only operate at one speed and nondiscrete displacements. The computer can be programmed to set motor velocity, acceleration, amplitude, and frequency of displacement steps. Also, the sequence of motor displacements can be programmed. For example, the motor can be programmed to move 0.1 inch (2.5 mm) in the positive direction and then immediately 0.05 inch (1.3 mm) in the negative direction for a net positive displacement of 0.05 inch. This pulsation technique decreases the delay time between the piston displacement and droplet extrusion.

The injector, Figure 2-2, consists of three coannular stainless steel tubes, enclosing two annular clearances. The outer clearance is for a cooling water

Figure 2-2. Black liquor droplet injector.

flow and the inner clearance for saturated nitrogen flows. Both flows are coaxial to the needle. It is important that the water and saturated nitrogen be at nearly the same temperature. If the cooling water temperature is above that of nitrogen, the relative humidity in nitrogen will decrease and result in drying of liquor droplets at the needle tip. If the water temperature is below that of the nitrogen temperature, water will condense on the inside wall of the injector and be discharged into the reactor. In the actual operation of the injector in the DPFR, both temperatures were about 212°F (100°C).

The needle is made of three segments. The upper part is made from a gage 13 hypodermic needle. It is approximately 2 inches (5 cm) long with an O.D. of 0.04 inch (1 mm), and has an adapter at one end which allows it to mate with a standard hypodermic syringe. The middle portion is 13.8 inches (35 cm) long and has an O.D. of 0.125 inch (3.2 mm). The third segment is a standard hypodermic needle. Different needle diameters were used, ranging from gage 18 (largest) to gage 24 (smallest). The different parts of the needle are silver-soldered to each other. Care was taken to assure that smooth transitions occur between the different diameter sections. When the needle is inserted into the injector, it is important that the needle tip be centered at the injector exit point, assuring a uniform velocity distribution of nitrogen. Otherwise the droplets may tend to fall at an angle.

Several syringe sizes were used. A 20 cc syringe with 0.75 inch (1.9 cm) barrel and piston diameters is convenient because it holds enough black liquor to form about 600 droplets 0.08 inch (2 mm) in diameter. This size permits a number of runs in the DPFR without refilling. Initially, problems were encountered with this relatively large size because black liquor trapped between the syringe walls and the piston caused considerable friction, thereby making droplet extrusion increasingly difficult with increased diameters. To avoid these difficulties, the syringe is placed in a high temperature water bath. The viscosity of the liquor decreases in the bath, which eases piston movement. The water temperature is maintained at 203°F (95°C).

The humidifier and the water heater share the same basic design, except for a few minor differences. Both are made from 3-inch O.D. brass tubing, 9 inch (23 cm) long and have circular plates soldered at both ends. The inlet to both

systems consists of 1/4-inch copper tubing that is attached to the top and brought to the bottom, where it is circularly bent and multiple holes drilled into it. Inlet water to the water heater and nitrogen to the humidifier are introduced at the bottom of the respective vessels. The fluid rises and passes through a packed bed of 1/8-inch diameter alumina pebbles. This increases the surface area for the water heater and allows the nitrogen bubbles to break up in the humidifier.

The mode of operation for the two systems is different. The water heater is in a continuous mode, while the humidifier is in a semibatch mode. Water in the humidifier has to be added before each run while the nitrogen flow is continuous. Ceramic band electric heaters are used for both systems. The water heater dissipates higher power. The temperature in both systems is controlled through a voltage variac and monitored by a K-type thermocouple.

2.3 Operation and Performance

Diameters of black liquor droplets generated by the injector were determined in two ways. A high-resolution video camera and a display has been used for observation of droplet formation at the tip of the injector needle with magnification factors of 10 to 15. The droplet diameter was measured directly from a video monitor. The injector tip diameter was the reference length. Close examination of droplets before detachment from the needle indicated that they were nonspherical. Droplets had slightly larger diameters at the bottom than at the top. It was the larger diameter that was recorded. Droplet diameters were also obtained from volumetric measurements. A number of droplets were collected in a liquid-filled graduated cylinder and an average diameter was calculated from volumetric displacement, assuming sphericity. These volumetric diameters were somewhat larger than those measured by the video screen (see Section 2.3.2).

2.3.1 Nitrogen Flow vs. Droplet Diameter

Only a certain range of nitrogen flows formed good droplets during test conditions. If the flow is zero or too low, droplets dry and distort at the needle tip even at low ambient temperatures. When surrounded by hot flowing gases, they not only dry, but also devolatilize, expand, and sometimes even ignite when still on the needle tip. If the nitrogen flow is too high, a spray of small irregularly shaped and sized black liquor droplets is created. Flows between 25 mL/second and 60 mL/second (measured at ambient) were best for droplet formation.

Table 2-1 shows the data for droplet diameter variation with the assisting nitrogen flow rate for droplet injection. The surrounding environments were stagnant air at room temperature and high temperature upward flowing gases. The droplet diameter varies inversely with the assisting nitrogen flow. As the table indicates, no appreciable difference is observed in droplet diameters whether they form in room condition and zero upward gas velocity or in upward gas velocities at high temperatures. Table 2-1 data are plotted in Figure 2-3.

Table 2-1. Black liquor (65%) droplet injection data
from video screen measurements.

Run	Reactor Temperature, ^a		Reactor Gas Velocity,		Assisting N ₂ Velocity,		Droplet D, mm
	°C	°F	cm/second	ft/second	cm/second	ft/minute	
1	Room temperature		0	0	24.0	4.7	2.2
2	Room temperature		0	0	50.0	9.8	1.7
3	Room temperature		0	0	71.5	14.1	1.3
4	1045	1913	294	9.65	24.0	4.7	2.2
5	1056	1933	297	9.74	50.0	9.8	1.6
6	1044	1911	241	7.92	71.5	14.1	1.3

Injector Needle: 0.64 mm I.D., 1.04 mm O.D.

^aAt bottom of short-height DPFR (Section 3.3). Temperature at top not measured.

2.3.2 Volumetric Diameter vs. Video Diameter

As indicated earlier, the diameter measured from a video screen is slightly smaller than the diameter measured by volumetric means. Table 2-2 compares the volumetric diameters and video diameters when the two are measured under the same conditions. The volumetric diameter is found to be about 1.1 times larger than video diameter. This discrepancy can probably be ascribed to the elongation of the droplet when it is attached to the needle.

As will be seen later (Section 3.5), the in-flight high-speed photography shows that the elongated droplet indeed becomes spherical as soon as it detaches from the needle tip. Also, high speed photography furnishes yet another measurement of droplet diameters. It is, however, less accurate than the two described in this section, and was therefore only used for confirmation.

Figure 2-3. Droplet size as a function of assisting air flow for the NBS injector. Black liquor at 65% solids.

Table 2-2. Droplet diameter measurements in millimeters, black liquor at 60% solids.

Assisting N ₂ Flow	D (Video)	D (Volumetric)
Low	2.3	2.4
Medium	1.8	2.0
High	1.3	1.45

NOTES: Injector needle O.D.: 0.041 inch (1.04 mm)

Black liquor feed system temperature: 195°F (90°C), nominal

3.0 EARLY IN-FLIGHT TESTS AT NBS

3.1 Objectives

The overall objective of Phase 1 is to characterize the physical and chemical processes which occur during in-flight travel of black liquor droplets/particles in the recovery furnace. Specifically, the NBS portion of this objective was to study single black liquor droplets/particles in high-temperature gas flows simulating those in recovery boilers.

The list of processes which are expected to take place during the in-flight stage, roughly in chronological order, but no doubt overlapping in time to a certain extent, includes: vaporization, expansion, devolatilization, pyrolysis, ignition, combustion of volatiles, and burning of char. The research reported here addresses only the early in-flight processes. The actual range studied was defined by NBS equipment limits. The experimental techniques used to date limited the observation times to a period of less than a second after droplet injection into the high-temperature gas stream.

An important aspect of the NBS task objectives, both during early in-flight stages reported herein and during the work to be undertaken subsequently, is the development of appropriate measurement procedures.

3.2 Experimental Approach and Data Analysis

The basic approach was to inject single black liquor droplets, by techniques described in Section 2, into upward flowing gases, having temperatures between 1290-1830°F (700-1000°C) and concentrations of free oxygen between 0 and 21%. The droplets exposed to the gas flows undergo some, or all, of the processes listed in Section 3.1, depending (a) on specific values of these two governing parameters and (b) on the residence time of the droplet/particle after injection.

The main diagnostic technique for the early in-flight processes was high-speed photography. It was, therefore, important that the reactor constructed for these studies have maximum optical access.

3.3 Short-Height Dilute Phase Flow Reactor

The central piece of equipment in this study was the dilute-phase flow reactor (DPFR). The concept and the detailed construction plans for the DPFR were described (Clay et al., 1985). Briefly, it is a vertically positioned 4-inch I.D. tube. The inner wall has sections of high-temperature ceramic with the option of one quartz (transparent) section. Hot gases having the desired temperature and free-oxygen concentration are admitted through a bottom section. The droplet injector is inserted through an exit section at the top of the reactor. The length of the reactor, i.e., the distance from the point of droplet injection to the bottom, is variable. For all the data reported herein, this length was essentially constant, 30 ± 4 inches (76 ± 10 cm). Hence this reactor is referred to as the "short-height" DPFR. Extension to the "full-height" DPFR is discussed in Section 10.

3.3.1 Equipment

The short-height DPFR was operated in two different configurations. The two are basically the same, except for the addition of two sampling-and-observation sections (SOS). A schematic representation of the DPFR in the first configuration and a photograph of the second configuration are shown in Figure 3-1 and Figure 3-2, respectively.

The DPFR system shown in Figure 3-1 consists of nine components: (A) gas metering system for fuel, burner air and diluents; (B) gas burner; (C) mixing section for burner and diluent gases; (D) flow-straightening section; (E₁) the optical observation section; (E₂) lower SOS (second configuration only); (F) the droplet injector; (G₁) flow straightener; (G₂) upper SOS (second configuration); and (H) the exit section. As shown in Figure 3-1, in the first configuration the needle tip of the injector extends into the quartz observation section. In the second configuration, the injector tip is viewed through a window in the upper SOS. A detailed description of many of these components can be found in Clay et al. (1985). A brief description of the essential parts follows.

3.3.1.1 Gas Metering System. Propane was the fuel gas. The diluent was air, oxygen, or nitrogen, or a mixture of air with one of the other two. This allowed wide variations of oxygen concentrations in the reactor gas, as described in Section 3.3.2.

Figure 3-1. Dilute phase flow reactor, first configuration. See Section 3.3.1 for letter definition.

3.3.1.2 Gas Burner. A schematic of the gas burner is shown in Figure 3-3. The burner consists of two sections, an upstream one for the premixing of propane with air and a downstream flame-holding section. The downstream end of the flameholding section, welded onto a side-arm of the reactor mixing section (see 3.3.1.3), is water-cooled through copper cooling coils, since it is the only

Figure 3-2. Short-height dilute phase flow reactor, second configuration.
A. Gas burner; B. Mixing section; C. Sampling and observation
D. Quartz reactor tube; E. Exit section; F. Black liquor drop-
let injector.

portion of the entire reactor system exposed to high-temperature gases without insulation.

Figure 3-3. NBS gas burner for the dilute phase flow reactor.

3.3.1.3 Mixing and Flow Straightening Sections. Both the mixing and the flow straightening section are stainless steel tubing, 10-1/8-inch O.D. 9.75-inch I.D.

The mixing section is 6 inches high. In addition to the side-arm for admission of burner gas is a second side-arm for injection of diluent gases, welded directly opposite the burner. The bottom of the mixing section is insulated by 2-inch-thick firebrick.

The flow straightening section is 8 inches high. Initially, the walls of both the mixing section and flow-straightening sections were lined with a moldable refractory, 2-7/8 inches thick, leaving a 4-inch diameter passage duct for gases. A ceramic-cloth partition was stretched between the two sections and a bed of alumina pebbles was placed on the partition. Some early tests were done with this arrangement. Subsequently, a modification was made, shown in Figure 3-1, to improve the mixing of burner and diluent gases. The modification consists of the addition of a conical refractory insert at the bottom of the flow

straightening section, narrowing the gas passage diameter from 4 to 1 inch over a vertical distance of about 3 inches. Thus the entire gas flow in the mixing section is forced through this narrow opening. A 4-inch diameter ceramic-cloth partition, serving as the floor for the pebble bed, was placed inside the flow-straightening section. This modification locates the bottom of the pebble bed 3 inches above the bottom of the section, allowing room for bed depths up to 5 inches. The top of the section is closed off by a flange made out of the same stock as the other three flanges in the mixing and flow-straightening sections.

3.3.1.4 Sampling and Observation Section (SOS). The two SOS used in the second DPFR configuration (Figure 3-2) are of slightly different designs. Both are made of stainless steel tubing, 5.5-inch I.D. x 6 inches long, and have flanges matching those of the lower section and of the exit sections of the reactor. Both are insulated to 4-inch I.D. The lower of the two SOS has three side arms, 90° apart, for insertion of thermocouples, sampling probes, etc. The upper SOS has two quartz windows, 3 inches in diameter, opposite each other for straight-through viewing, and an additional side arm of the same design as those in the lower SOS, at 90° to the windows.

3.3.1.5 Optical Observation Section. The optical observation section is simply a quartz cylinder of nominal 4-inch I.D. with a wall thickness of about 1/4 inch. The quartz cylinder fits onto a ceramic shelf at the top of the flow straightening section, with annular clearance for packing with high-temperature fabrics or gaskets. Three lengths of quartz cylinders are on hand: 18, 30, and 36-inch. Most of the work to date was done with the 30-inch (76-cm) section.

3.3.1.6 Exit Section. The exit section consists of two parts. The first part houses the droplet injector and directs the vertically flowing gas flow horizontally. A ceramic honeycomb flow straightener can be installed at the bottom of the section, where the quartz tube is supported, to provide a smooth transition for the gas flow. The second part of the exit section is an attachment, designed to duct the hot gas horizontally away from the reactor before discharging it into the laboratory hood. Both parts of the exit section are made of stainless steel with ceramic insulation, similar in design to other sections of the reactor. The stepper motor for the droplet injector (not shown in Figure 3-1) is

placed directly above the injector, i.e., above the first part of the exit section. Both the injector and the stepper motor are described in Section 2.2.

3.3.2 Operation and Performance

3.3.2.1 Flows. The DPFR can be operated with various flow velocities, temperatures and oxygen concentrations of the upflowing gases. These parameters can be changed by varying the burner and diluent flow rates. The volumetric flow-rate capability is set essentially by the combined flow capacity of the two large flowmeters for burner and diluent air, which is somewhat in excess of 20 scfm (566 std. Lpm). The actual flow rates in the work to date ranged from 7-16 scfm (200-450 std. Lpm), corresponding to linear flow velocities of about 5-14 ft/second (1.5-4.3 m/second) at operating temperatures.

The reactor gas compositions are widely variable. Two modes of operation have been used. The first, intermittent mode takes advantage of the blowdown capability of the pebble bed underneath the optical observation section. When the bed is preheated, typically to temperatures of about 2000°F (1100°C), the burner can be turned off for several minutes without temperature changes in the reactor. The choice of gas in this mode, therefore, is completely arbitrary, in principle. In practice, it was used mostly with air as reactor gas for accurate reproducibility of the oxygen concentration.

In the continuous mode, with the burner on, there are some limitations to the gas compositions, but the variability is broad enough to be more than adequate. The oxygen concentration can be varied from zero (stoichiometric, or substoichiometric burner operation with nitrogen as diluent) to about 25% (lean burner operation with oxygen as diluent). The actual range in the tests to date was 1.5 to 21%.

3.3.2.2 Reactor Temperatures. Numerous reactor temperature measurements were made with type-K thermocouples. Two rather different techniques were used: lateral insertion of fairly large thermocouples at various levels in the reactor and the vertical lowering of a fine-wire thermocouple, mapping axially the temperature profile in the optical observation section.

In the first reactor configuration without SOS (Figure 3-1), thermocouples with 28 gage wires were inserted through the walls into the mixing section and just

above the top of the pebble bed, i.e., at the top of the flow straightening section. The wires were shielded inside ceramic "spaghetti" tubes. While the mixing section can be run at least up to 2370°F (1300°C), i.e., near the limit of type-K thermocouples, actual temperatures to date were restricted to about 2190°F (1200°C). Temperature readings at the top of the pebble bed were about 180°F (100°C) lower. In view of the fact that the upper thermocouple probably incurred some radiant losses, these measurements indicated the gas temperatures at the bottom of the reactor to be between 2000-2100°F (1100-1150°C).

In the second DPFR configuration (Figure 3-2), metal-shielded thermocouples were inserted through the side arms of the two SOS. Even in the lower SOS, the recorded temperatures were up to 360°F (200°C) lower than those measured at the top of the pebble bed. This large difference can be ascribed to three factors: (a) some actual gas temperature drops between the top of the pebble bed and the location of the thermocouple about 3.5 inches (8.9 cm) higher; (b) radiant losses from metal-shielded thermocouples which are, no doubt, higher than for smaller (28 gage) thermocouples; and (c) conductive heat losses along the metal shield. Substantial conductive losses were easily demonstrated: when the thermocouples were inserted past the center of the reactor to a point near the opposite wall, the temperature reading increased. Temperatures measured in the upper SOS, of course, were even lower because of heat losses in the optical observation section, discussed next.

In order to (a) obtain temperature data in the quartz tube which does not allow lateral insertion of thermocouples and (b) minimize the heat losses associated with the above measurements, vertical reactor traverses were made with a fine-wire thermocouple [2-mil (50- μ m) wire, 5-mil (125- μ m) bead]. This was done by means of a 4-foot (100-cm) long ceramic holder, housing the leads for attachment of the fine-wire thermocouple outside (about 1.5 cm underneath) the holder. The holder was lowered into the reactor through the opening in the exit section normally used for insertion of the droplet injector.

The essential reason for taking the considerable trouble of obtaining fine-wire thermocouple data is that the correction for radiant losses is small, allowing good quantitative determination of gas temperatures. The equation used for that purpose was:

$$T_g = T_b + \frac{\sigma d_b \epsilon_b T_b^4}{k \text{ Nu}} \left(1 - \frac{\phi}{4}\right)$$

T_g = Gas temperature

T_b = Thermocouple bead temperature

d_b = Thermocouple bead diameter

ϵ_b = Emissivity of thermocouple bead

σ = Stephan-Boltzman Const.

Nu = Nusselt number $(2 + 0.5 \sqrt{\text{Re}})$

k = Thermal conductivity of gas

Re = Reynolds number

ϕ = Fraction of the solid angle around the thermocouple bead
occupied by the highly radiant pebble bed surface

This equation is commonly used in gas-flame studies except for factor ϕ . This factor is needed to take into account the fact that heat losses are lower near the bottom of the reactor.

Several sets of temperature measurements were taken along the vertical axis of the DPFR at various heights above the bottom of the reactor up to about 25.5 inches (65 cm), which was just below the point where the black liquor droplets were injected in droplet combustion experiments. The measurements were made in a series of tests which consisted of all four permutations of two sets of two critical reactor flow parameters: gas flow rates of about 10.5 and 15 scfm (300-425 std. Lpm); and gas temperatures $T_0 = 1904 \pm 18$ °F (1040 ± 10 °C) and $T_0 = 2057 \pm 18$ °F (1125 ± 10 °C) at the bottom of the reactor. Temperatures were recorded at six heights in the reactor, at about 4-inch (10-cm) intervals, starting with 1 cm above the bottom (pebble bed). The flow rates were chosen so that almost all tube Reynolds numbers were less than 2300 at the low rate and exceeding 2300 at the high rate. The results show that temperature differences ($T_0 - T$) between the bottom and the higher points in the DPFR decrease with increasing flow rates and increase with increasing T . Also, at high Reynolds numbers, the temperature drop $(T_0 - T)/\Delta h$ was found to be relatively small near the bottom but to increase with height.

Both the direct thermocouple readings and the corrected (gas) temperatures are plotted in Figures 3-4, 3-5, and 3-6. Figures 3-4 and 3-5 show the data at the

DPFR Fine Wire Thermocouple Data

Figure 3-4. Temperature profile for short-height DPFR, initial gas temperature 1904°F (1040°C).

DPFR Fine Wire Thermocouple Data

Figure 3-5. Temperature profile for short-height DPFR, initial gas temperature 2057°F (1125°C).

DPFR Fine Wire Thermocouple Data

Figure 3-6. Temperature profile for short-height DPFR at high gas flow rate.

same relatively low flow rates of 10.6 scfm (300 std. Lpm), but somewhat different initial temperatures. Figure 3-6 is for a higher flow rate, 15.1 scfm (425 std. Lpm) but has almost the same initial temperature 2049°F (1120°C) as in Figure 3-5. Inspection of these temperature profiles shows the above mentioned trends, especially the less severe temperature drop at the higher flow rate.

The conclusions from all temperature measurements are (a) temperature drops along the quartz observation section are quite severe, of the order of 20°F/inch (4°C/cm); (b) metal shielded thermocouples inserted through SOS sidearms are not suitable for quantitative measurements; (c) the 28 gage thermocouples, inside ceramic spaghetti, inserted laterally through reactor walls, give somewhat low readings but are adequate for routine monitoring; and (d) vertically lowered thermocouples are preferable. The last conclusion presents something of a problem, because vertical lowering of any measurement device is incompatible with the operation of the droplet injector. Also, it is known (indeed, was demonstrated on several occasions in this study) that only heavily shielded thermocouples can be used for any length of time in the presence of black liquor droplets/particles. The most reasonable approach, therefore, is to measure temperature profiles with vertically lowered thermocouples (without droplet injection) for several representative gas flow conditions and obtain simultaneous records for comparison with ceramically insulated thermocouples inserted only to the inner wall of the reactor. The latter technique can then be used to monitor temperatures during actual runs. This means, however, that any major change of reactor geometry or conditions will require a separate set of measurements with vertically lowered thermocouples.

3.4 Black Liquor Characteristics

Early tests with the short-height DPFR were done with 60% solids black liquor which was stored at room conditions. This included the development of droplet diameter measurement techniques and early in-flight tests. Since February 1986, mill kraft black liquor No. 30 at 65% solids, supplied by IPC, has been used. All subsequent experiments in the DPFR have used this liquor. Table 6-2 lists its chemical composition.

Special storage and handling procedures were used, including the refrigeration of black liquor under nitrogen. To minimize exposure of black liquor to the atmosphere, the storage container is opened for only a short period of time. In this time, the liquor is transferred into a flask for a brief heating period in a water bath. The heating reduces the liquor viscosity which allows it to be transferred to 20 cc hypodermic syringes. The syringes are then sealed and refrigerated until needed. Liquor remaining in the flask is discarded.

3.5 Diameter Data

In-flight studies of black liquor droplets/particles were done with a high-speed framing camera. In all the tests, the field viewed by the camera was 3.9 inches (10 cm) (horizontal) by 3.2 inches (8 cm) (vertical). This viewing area covers the entire cross-section of the reactor and provides sufficient magnification for good determination of droplet/particle shapes and velocities. It also allows diameter measurements. In the case of initial droplets, the measurement is somewhat less accurate than from the video records. As the droplets expand, the accuracy improves, of course.

All in-flight droplet studies to date have been done with a camera rate of 500 frames per second. The method of obtaining in-flight droplet diameter and velocity is simple. A standard reference length is filmed, along with the droplets, from which a magnification factor is obtained for measurements on the viewing screen. The droplet velocity is obtained by counting the number of frames of film used by the particle to move through a certain known distance. Three sets of determinations were made at three locations in the short-height DPFR; at the top, at midheight and near the bottom.

3.5.1 Top Section of DPFR

High-speed photography of the top section was centered 1.2 inches (3 cm) below the needle tip of the droplet injector and it extended 1.6 inches (4 cm) below the center point. Thus, it included the lower 0.4 inch (1 cm) of the injector and a vertical height of 2.8 inches (7 cm) below the needle tip. The main purpose of high-speed photography in this section of the reactor was (a) to observe the process of detachment from the needle and initial trajectories of black liquor droplets and (b) to measure their velocities (see Section 3.6). Measurement of

droplet diameters was of secondary importance because it can be done more accurately by methods discussed in Section 2.2.

The process of black liquor droplet detachment from the needle is more abrupt than in the case of analogous preliminary experiments with glycerol. No long umbilical cords formed which would have caused the droplet to linger on the needle tip before final detachment. This is advantageous, because it decreases the chances of droplet drying and distortion before detachment. Another observation was that droplets became spherical immediately after detachment. A third observation was that the initial droplet trajectories were vertical. This was gratifying because the complex aerodynamic interaction of the upward flowing reactor gases with the downward flow of the droplet-injector assisting gas flow may well have introduced undesirable lateral velocity components. Finally, these records supplied additional information on the effect of the assisting-gas flow velocity, discussed in Section 2.3. In particular, the adverse effect of very high velocities of the assisting gas became evident. When these velocities are too high, the droplets become small and of nonuniform sizes, under which conditions they often do move laterally.

3.5.2 Center Section of DPFR

In high-speed photography of the center section of the DPFR the camera was centered at 16 inches (40 cm) below the injector. At this height [indeed, at any height lower than the segment extending 3.2 inches (8 cm) below the injector], there is a basic limitation of optical observation techniques used to date. While the initial droplet diameters are provided by the VCR system simultaneously with the high-speed droplet/particle diameter measurements at lower observation stations, there is not one-to-one correspondence between the droplets at injection and droplet/particles measured by high-speed films. The procedure adopted in these studies, therefore, was to relate the properties of droplets and particles observed by high-speed photography (shapes, sizes, and velocities) to average initial diameters from VCR measurements.

Qualitative observations at the center portion showed that most falling particles were still nearly spherical and were almost always falling vertically near the center of the reactor. Moderate expansion of particles was observed, sufficient for a correlation of particle diameters and velocities (Section 3.6). However,

no systematic measurements of droplet diameters with variations of reactor-gas properties were made at this height.

3.5.3 Bottom Section of DPFR

In view of the above results, the most extensive set of data was obtained in the lower portion of the DPFR, centered at 29 inches (74 cm) below the point of droplet injection. In all runs, the reactor temperatures were nearly the same, about 1740°C (950°C) in the lower SOS. The upward flow velocities of reactor gases varied from 8.3-12.8 ft/second (2.5-3.9 m/second). There was modest variation of original droplet diameters, d_0 , and major variation of oxygen concentration in the reactor gases. The data were taken in a series of 14 runs, each lasting about 10 seconds, during which period about 30 to 50 black liquor droplets were released from the injector. Simultaneous with high-speed photography, VCR records were obtained of the injection process, yielding initial droplet diameters.

The analysis of high-speed records revealed that most of the downward falling particles were again nearly spherical, allowing reasonable diameter measurements. Table 3-1 lists the average values of the initial droplet diameters, d_0 , and the corresponding average values, d , of particles in each of fourteen tests. Each of these average values is the arithmetic mean of at least ten individual readings. The individual readings are closely grouped in the case of initial droplet diameters, with somewhat higher scatter of the d values. For example, in the first line, all individual d_0 values are between 1.6 and 1.8 mm, and all d values are between 2.3 and 3.2 mm. The example is typical of the rest of Table 3-1.

Table 3-1 shows that the average linear expansion, d/d_0 , is about 1.5, with substantial scatter. There is no noticeable effect of oxygen concentration. Another effect which may be expected a priori is that of initial droplet diameters. A smaller droplet/particle should have a longer residence time between injection and observation. This is not apparent from Table 3-1.

The above measurements show that expansion during the drying stage is significant. Diameter expansion factors of 1.5 translate into a volumetric expansion factor of 3.4 and an area expansion of 2.2. The expansion will influence droplet trajectory.

Table 3-1. Initial black liquor diameter, and expanded diameter after 28 inches (72 cm) of downward travel.

Gas, O ₂	Initial d ₀ , mm	Expanded d, mm	Ratio, d/d ₀
1.5	1.7	2.6	1.5
2.2	1.6	2.1	1.3
5.1	1.7	2.5	1.5
8.4	1.7	2.4	1.4
9.4	1.3	2.2	1.7
9.5	1.7	2.2	1.3
9.7	1.6	2.5	1.6
9.8	1.6	2.7	1.7
9.8	1.7	2.7	1.6
10.1	1.5	2.1	1.4
10.3	1.6	2.9	1.8
16.7	1.4	2.4	1.7
16.9	1.6	2.0	1.3
20.9	2.0	3.1	1.6

m/second) 1740°F (950°C)

3.6 Velocity Data

Experimental downward particle velocities, U_p , relative to an outside observer, were obtained from measured travel distances and times determined by the camera framing rate. Velocities of particles relative to the gas, slip velocities, are $U_s = U_p + U_g$, where U_g is the upward gas velocity. The velocity U_s , of course, is a more fundamental quantity than U_p , because it is required for determination of particle Reynolds Numbers, drag coefficients, residence times, heat transfer rates between the gas and the particle, etc.

The experimental values of U_p and U_g in the top, center, and bottom segments of the DPFR are given in Sections 3.6.1, 3.6.2, and 3.6.3, respectively. Since the conclusions drawn from these data depend on correlations between experimental and calculated velocities, it is convenient to present also the calculated values in the same Sections. The latter were obtained by a computer program which calculates particle velocities and distances from the injection point by balancing the gravitational force against buoyant and drag forces due to upward gas flow. The program is described in Appendix 4. Since the calculated velocities are

very weak functions of temperature, all calculations were made for gas temperatures of 1560°F (850°C) with virtually no sacrifice of accuracy. The initial density of black liquor droplets, required for calculations, was assumed to be 1.3 gm/cc.

3.6.1 Top Section of DPFR

The high-speed films from which the velocities were obtained are described in Section 3.5.1. The segment of the reactor over which the data were taken, and calculations made, consists of the first 2.8 inches (7 cm) below the injection point. Thus, the U_p values started at zero and showed rapid acceleration over the viewed segment. The experimental velocities given in Table 3-2 are the final values, at 2.8 inches (7 cm), obtained from the last few frames before the disappearance of the droplet. The experimental residence times were determined directly from the total number of frames for a given droplet.

Table 3-2. Velocities and residence times at the top of DPFR.

d, mm	U_g	U_p (exp)	U_s (exp)	U_s (calc)	U_t (calc)	t_R (exp)	t_R (calc)
1.7	4.36 (1.33)	4.00 (1.22)	8.36 (2.55)	7.93 (2.42)	29.2 (8.91)	0.094	0.124
2.1	5.15 (1.57)	3.54 (1.08)	8.69 (2.65)	8.75 (2.67)	36.1 (11.00)	0.11	0.123

exp = experimental calc = calculated

t_R - Particle residence time, seconds

U_g - Upward gas velocity from measured volumetric rates and local temperature

U_p - Particle velocity relative to laboratory coordinates.

U_s - Particle velocity relative to gas (slip velocity).

U_t - particle terminal velocity relative to gas.

The agreement between the experimental and calculated U_g values is seen to be very good, probably fortuitously so, considering the limitations of reading accuracy of droplet locations on the film. The comparison is also satisfactory for residence times, since the uncertainty of the detachment time of a droplet from the needle tip is at least 10 msec. Table 3-2 also gives the computed terminal (settling) velocity, U_t , which U_g would approach at long times if the droplet remained physically unchanged. In this section of the DPFR, the droplets are still accelerating.

An important aspect of the experimental and calculated results in the top segment of DPFR is that they give the basis for a good definition of initial conditions. This is required for calculations of residence times at lower segments of the DPFR when there are no high-speed data in the top segment. This will be discussed in Sections 3.6.2 and 3.6.3.

3.6.2 Center Section of DPFR

Whereas the calculations in Section 3.6.1 were based on the assumption that there was no change in either the original diameter or the density of the droplet, this can no longer be done in the center or lower segments. The fact alone that droplet expansions were observed in the high-speed camera records necessarily implies density decreases. In addition, there may or may not have been mass losses due to vaporization.

Table 3-3 gives the data for four individual particles, all from a test with average initial diameters $d_0 = 1.6$ mm. The reactor velocities were also constant, 3.05 m/second. The format is similar to that in Table 3-2, with three differences. First, the ratio d/d_0 is given, because it is a parameter necessary for calculation of velocities and residence times. Specifically, for spherical particles, expansion without drying leads to particle densities of $\rho_0(d_0/d)^3$; with complete drying of black liquor with 65% solids, there is further decrease of density to $0.65 \rho_0(d_0/d)^3$. The second difference is that there is no experimental determination of particle residence times. The experimental arrangement does not provide continuous observation of particles by the high-speed camera from the injection point. The third difference, also due to the lack of continuous recording, is that the calculation of U_s is not straightforward, but requires some assumptions, as discussed below.

An obvious aspect of Table 3-3, seen immediately by inspection, is the close agreement of the experimental U_s with the terminal velocity, U_t , calculated on the assumption of no drying. It is pertinent to note here that neither of these two quantities depends in any way on the values of the initial droplet diameter, d_0 . The experimental U_s is read directly from the film and U_t is calculated only from the measured diameter of the expanded particle and the corresponding calculated density. The agreement of these two, therefore, offers prima facie

evidence that the data are consistent with the concept of expanded particles, with little or no mass loss, settling against the upward gas flow.

Table 3-3. Droplet velocities and residence times 15.7 inches (40 cm) below droplet injection.

	Experimental			Calculation A			Calculation B		
	1.6	6.92 (2.11)	16.9 (5.16)	15.0 (4.57)	16.8 (5.11)	0.39	12.7 (3.88)	12.7 (3.88)	0.50
	1.4	7.25 (2.21)	17.2 (5.26)	15.7 (4.78)	19.0 (5.81)	0.37	14.1 (4.31)	14.8 (4.51)	0.43
	1.6	6.92 (2.11)	16.9 (5.16)	15.0 (4.57)	16.8 (5.11)	0.39	12.7 (3.88)	12.7 (3.88)	0.50
	1.6	7.25 (2.21)	17.2 (5.26)	15.0 (4.57)	16.8 (5.11)	0.39	12.7 (3.88)	12.7 (3.88)	0.50
Average:	1.55	7.02 (2.14)	17.1 (5.21)	15.1 (4.62)	17.3 (5.28)	0.39		13.2 (4.04)	0.48

Calculation A - no drying assumed.

Calculation B - complete drying assumed.

Conditions: $d_0 = 1.6$ mm, $U_g = 10.0$ ft/sec (3.05 m/sec).

See Table 3-2 for term definition.

The calculated U_s values, on the other hand, depend both on the value of d_0 and on an assumption regarding the history of the droplet diameter before it comes into the viewing field of the camera. Observations in the top segment of DPFR (Section 3.6.1) had shown that droplets do not undergo expansion until at least 2.8 inches (7 cm) of travel from the point of injection. The subsequent expansion history is not known. The most conservative choice (i.e., one giving the lowest calculated U_s value), therefore, was to break up the calculation: up to 2.8 inches (7 cm) of travel with no expansion and thereafter with the expanded diameters. The U_s values so calculated are seen to be lower than the experimental values (or U_t), falling short of terminal velocities by an average 13%. In view of experimental errors and calculation assumptions, the agreement is reasonable.

Based on the assumption of no drying, the agreement of calculations, with the experiment implies that low velocities will be predicted if any drying is assumed.

Indeed, Table 3-3 shows that even terminal velocities of dry particles having the observed diameters are significantly lower than experimental U_g values. The t_R values in Table 3-3 are also the result of two-stage calculations: up to 2.8 inches (7 cm) without expansion and the remaining 13 inches (33 cm) of travel with full expansion to the d/d_0 value. The residence times computed for the two stages are additive. It may be of interest to note that the time to travel the first 2.8 inches (7 cm) never varied much. For all droplets in Table 3-3 it is 0.14 second; and for all droplet diameters and gas velocities used to date in the DPFR it varied only between 0.10 and 0.15 second.

The fact that the calculated residence times are rather short supports the inference that little drying of droplets could have taken place. Thus, all indications are that in this segment of the DPFR the droplets merely expanded by a linear factor of about 1.5 without other changes.

3.6.3 Lower Section of DPFR

The lowest section of the DPFR in which high-speed photography was used was centered 29 inches (74 cm) below the droplet injector. Droplet diameter data obtained from these photographic records were discussed in Section 3.5.3.

The results are shown in Table 3-4 in the same format as the analogous data presented in Section 3.6.2; i.e., the experimental U_g and calculated U_t are based only on direct velocity and diameter measurements in the viewed section, while the calculated U_g and t_R were made in two stages as described in Section 3.6.2, based on d_0 values from separate VCR records.

Table 3-4 consists of two parts. The first line is based on an overall average of experimental data of 14 runs, listed in Table 3-1. These original data show d_0 variations from 1.3 to 1.8 mm and variations of d from 2.0 to 3.1 mm. The second part of Table 3-4 gives the results of several individual tests.

Inspection of the first line (experimental averages) appears to show a contradiction: even on the assumption of no drying (calculation A), the calculated U_t is lower than the observed U_g . In fact, these results illustrate the problem of measurement accuracy which would have to be very high to give confident numerical agreement of this type of data. For example, if the measured d/d_0 were 6% lower

(i.e., if the measured value of d were 2.32 rather than 2.46 mm), U_t would exceed the measured U_s , removing the contradiction. The same would be true, of course, if the measured U_s were 6% lower. Experimental errors of that magnitude, due to two separate measurements, are certainly to be expected. On the other hand, experimental errors of 40% would have to be postulated to bring calculation B into agreement with the experiment, which is far less likely. The reasonable conclusion, therefore, is that even at this observation station, little or no vaporization of particles took place.

Table 3-4. Droplet velocities and residence times near bottom of DPFR.

Experimental			Calculation A			Calculation B		
d_o , mm	d/d_o	U_s	U_s	U_t	t_R , second	U_s	U_t	t_R , second
1.62 ^a	1.52 ^a	19.4 (5.91 ^a)	16.6 (5.07)	18.4 (5.60)	0.56	13.7 (4.19)	13.8 (4.20)	0.66 0.66
1.7	1.5	17 (5.1)	16 (4.8)	19 (5.9)	0.49	13 (4.1)	14 (4.4)	0.57
1.6	1.3	17 (5.3)	17 (5.1)	21 (6.5)	0.49	15 (4.5)	16 (4.8)	0.57
2.0	1.6	20 (6.0)	18 (5.4)	21 (6.4)	0.51	15 (4.6)	16 (4.8)	0.61
1.7	1.6	20 (6.1)	17 (5.2)	18 (5.6)	0.62	14 (4.2)	14 (4.2)	1.05
1.4	1.7	19 (5.8)	14 (4.3)	14 (4.3)	0.82	11 (3.4)	11 (3.4)	>5

Velocity units = ft/second (m/second)

^aAverage of 14 experimental tests shown in Table 3-1.

See Table 3-2 for term identification.

$U_g = 10$ ft/sec (3.06 m/sec)

Inspection of results from individual tests in Table 3-4 provides further illustration of the correctness of the main conclusion: limited drying, if any, after 0.6 second residence in the reactor. On the basis of calculation A, terminal velocities are seen to exceed U_s , providing the initial diameters are not too small and the measured expanded diameters not too large (expansion ratios not exceeding 1.5 or 1.6). Large expansion ratios, especially when combined with small d_o values, lead to results which can be explained only by invoking inadequate

measurement accuracy. The fault, most likely, is with the assignment of d_0 which, even for a single line in Table 3-4, is a calculated average of several individual particles (Section 3.5.3). However, inspection of the columns pertaining to calculation B, again, shows that the assumption of complete drying is not at all realistic, the terminal velocities being always substantially lower than the experimental U_s .

A final word is in order about the two-stage calculations which produced the U_s and t_R values in Tables 3-3 and 3-4. Since the height in the reactor at which droplet expansion begins is unknown, it is possible that the assumption of expansion (immediately below the top segment of the DPFR) was made at too early a stage. Therefore, calculations were also made on the assumption that the transition between the two stages takes place 7.9 inches (20 cm) below the injector, i.e., about half-way between the top and the center section. The differences in the computed U_s and t_R values are in the expected direction, but not significant enough to warrant the addition of another set of numbers in the tabulation. For example, in the first row of Table 3-4, the alternative assumption increases the computed U_s value from 16.6 to 16.9 ft/second (5.07 to 5.15 m/second) (i.e., from 90 to 92% of U_t), and decreases t_R from 0.56 to 0.53 second.

3.7 Qualitative Observations

In addition to the downward falling droplets and particles discussed in Sections 3.5.1, 3.5.2, and 3.5.3, the high-speed films show upward moving particles at all locations in the DPFR. It is clear that most of these particles had reached the bottom of the reactor, where they either ignited or shattered (or both). In either case they would become sufficiently light aerodynamically to be entrained upward. The upward moving particles usually had irregular shapes and moved in random trajectories, sometimes hitting the reactor walls and sticking to them. They also had widely different velocities. A few of them had gas flames on top; these, evidently, happened to be caught by the camera during the brief combustion of the volatiles. When filmed in total darkness, some particles glowed, indicating combustion of char. Measurements on any of these particles would have served no useful purpose, because neither the residence times nor the effective initial diameters were known. Extension to the full-height DPFR will expand the study range.

In addition, a very few particles were seen to enter the view at low downward velocities, decelerating further, igniting, and reversing the direction of motion (upward). Again, measurements on these would not be useful, because the data in section 3.5.3 and 3.6 clearly show that average droplets reached the bottom of the short-height DPFR before ignition. It is, therefore, probable that in these isolated observations of ignition the particles were abnormally small.

3.8 Particle Temperature Measurements

Black liquor particle temperature measurements during burning can be used to identify the controlling mechanism under certain conditions. A task in this project, therefore, is the measurement of black liquor particle temperatures under controlled conditions in the IPC single-particle reactor. Two different techniques, currently under development at NBS, were used. Both are nonintrusive and are based on optical emission intensity measurements. This section reports the progress to date on this task.

3.8.1 Measurement Techniques

One of the two optical techniques is the ratio pyrometry of solid surfaces, based on continuum emission (Planck function). The second line-intensity technique is for gas temperature measurements from atomic line intensities and is based on the assumption of Boltzmann distribution of energy levels of an atomic species. General descriptions of both can be found in the literature. Specifically, recent work at NBS has led to (a) the development of instrumentation and (b) demonstration of the applicability of these two techniques to engineering reactors. These recent developments serve as the basis for the present task.

One pertinent development at NBS is the application of ratio pyrometry, with time resolution of 50 to 100 Hz, to laboratory-scale fluidized-bed combustors and to a coal gasification pilot plant. The apparatus for these measurements was a simplified version of the arrangement shown in Figure 3-7. The optical fiber bundle had only two branches (instead of four) leading into two narrow bandpass filters in the near infrared, between 800 and 1050 nm. The detectors were silicon diodes. Data were taken with a dual channel stripchart recorder (Macek and Bulik, 1984; Macek et al., 1985).

Figure 3-7. Four-color temperature measurement system.

The other pertinent study is the ongoing development of a variant of the line-intensity technique for application to systems where some background emission is inevitable. It uses the full 4-channel system shown in Figure 3-7. The four channels are used for time-resolved intensity measurements of two atomic lines and the corresponding background continua at two wavelengths near each line, for correction. Two potassium lines, at 767 nm and 404 nm, have been used for determination of gas temperatures in methane flames, seeded with potassium, on a laboratory burner. In addition, work is in progress now to adapt the same technique for temperature measurement in actual recovery boilers (Charagundla and Semerjian, 1986).

Regarding the application to combustion of single black-liquor particles, the ratio pyrometry may reasonably be expected to yield surface temperatures (a) during the volatiles burning stage (see Figure 3-8) and (b) during the subsequent char burning stage as long as the temperature is high enough for measurement. In addition, the preignition surface temperatures may be measurable if they are high enough, which is dubious. For gas temperature measurements by the line-intensity technique the best, and perhaps the only chance is during the flaming combustion. It is questionable whether gas emission intensities are sufficiently high for recording and measurement even during the char-burning stage, and quite unlikely that they are so during the preignition stage.

Figure 3-8. Representation of a burning droplet.

In addition to emissions from the surface of the particle and from the surrounding gas, particulate aerosol (soot) should be expected in the combustion zone near the surface. This may be helpful for ratio pyrometry measurement, but will probably contribute undesirable luminous background for gas emission measurements.

3.8.2 Preliminary Tests in Flame

Preliminary to the temperature measurements of black liquor particles in the IPC single-particle reactor, spectroscopic emission measurements were made at NBS with black liquor particles burning in the combustion products of a methane/air gas burner. The burner plate, 3 inch (7.6 mm) in diameter, had a number of holes which produced a steady flame having approximately flat-flame characteristics. Black liquor droplets were suspended on a Nichrome wire several inches above the burner plate. Thus, with lean operation of the burner, droplets were held in hot, upward moving laminar gas streams composed of N_2 , CO_2 , H_2O , and free O_2 .

Since black liquor in addition to sodium also has significant amounts of potassium, the purpose of the gas-burner experiments was to observe potassium line emissions in the presence of continuum emission originating from both the black liquor particle and the Nichrome wire. This was done by the recording of optical multichannel analyzer (OMA) spectra over two wavelength bands centered near the two potassium lines: 390 to 420 nm and 750 to 780 nm, i.e., near the blue and red ends of the visible spectrum, respectively. The light-gathering system for these experiments consisted of a quartz fiber bundle, 0.125 inch (3 mm) in diameter, with collection optics at one end trained at the burning particle and a lens at the other focusing onto the OMA spectrometer slit.

Two representative OMA spectra of burning black liquor particles are shown in Figures 3-9 and 3-10. Because the 404 nm potassium line is the much weaker of the two, the spectrum shown in Figure 3-9 had to be taken with a much higher gain of the sensor elements; i.e., the intensity scales in the two figures are widely different. It can be seen that the relative contribution of the continuum background is negligible in Figure 3-10, but quite strong in Figure 3-9. This is so despite the fact that the absolute continuum intensity is higher at the longer wavelength.

Figure 3-9. Potassium emission lines for a premixed flame with and without the presence of a black liquor droplet.

Figure 3-10. Potassium emission lines for a premixed flame with and without the presence of a black liquor droplet.

The above results indicate that in single-particle experiments with black liquor the line intensity measurement is very promising for the red potassium line and may also be possible for the blue line. The plans for experiments in the IPC single particle reactor were made accordingly. Two separate measurement systems will be used, all the components of which are on hand. One system is for ratio pyrometry (see Section 3.8.1). The second system is the one shown in Figure 3-7. The filters to be used in this four-color system have very narrow band passes, centered at 404, 415, 750, and 767 nm for the recording of the two potassium lines and the corresponding nearby continua.

3.8.3. Tests with IPC Single Particle Reactor

A two-color ratio pyrometer (Section 3.8.1), an existing NBS instrument, was used to measure temperatures of burning black liquor droplets. It consists of (a) a bifurcated flexible fiber; (b) two interference filters for transmission at 850 ± 20 nm and 1000 ± 20 nm; (c) two silicon photodiodes with amplifiers; (d) a dual-channel stripchart recorder and (e) standard emission sources for in-situ calibration.

The black liquor droplets were burned on wires suspended in the IPC Convective Single Particle Reactor (Section 6.1.1). The fiber optic probe viewed the particle through the optical trench. An example trace of the flame intensities at the two different wavelengths is given in Figure 3-11. The corresponding temperatures, based on the Planck relationship and on-site calibration, are also listed. Although it is not possible to derive much process information from these preliminary tests, they do prove the validity of the technique. More extensive work with this technique will be a part of an IPC Ph.D. thesis conducted by Katherine Crane Kulas.

Figure 3-11. Intensity traces from the NBS two-color pyrometer of a burning single particle of black liquor.

4.0 PROCESS FLOW REACTOR SYSTEM

Process studies which emphasize the chemical composition of solid, liquid, and/or gaseous products are the focus of the IPC process flow reactor system. The system has been constructed in three stages.

The first stage was the Central Units with gas upflow. Its four modules are the air delivery, in-flight reactor, char collector, and analog control panel and annunciator. Figure 4-1 shows the schematic of the Central Units. The detailed design and equipment specifications are given in the first DOE progress report (Clay et al., 1985). The Central Units were under construction when the first report was issued.

The second stage was the addition of the gas treatment package. Its modules are incineration, water quenching, and gas scrubbing. Figure 4-2 is a schematic of the gas treatment package. It was installed approximately one year after the Central Units were installed.

The third stage is the addition of the bed burning furnace. There are two main modules: the external electrical heater panels and the interior metal retort. A conceptual drawing of the furnace is shown in Figure 4-3. It will replace the Pyrex char collection vessel for the Phase 2 work. The bed burning furnace is currently under construction at the vendor's site. Start-up is expected in March 1987. Simultaneous with the char bed burning furnace addition, the air delivery system will be converted over to the downflow mode.

4.1 Central Units Assembly/Checkout

The Central Units (CU) were constructed by Xytel, Inc., Mt. Prospect, Illinois. Xytel had previously been responsible for the detailed design of the CU. The CU were assembled and wired at Xytel as much as possible. It was inspected by both IPC and NBS personnel. No power up or hot tests were conducted at Xytel. The CU were disassembled in large modules and shipped to IPC. They arrived on January 15, 1985.

Figure 4-1. IPC central units isometrics. a. Reaction section with heater. b. Sampling/observation section. c. Electric air heater. d. Gas/solids separator. e. Char collection vessel.

Figure 4-2. Gas treatment system main components for the IPC system.

Figure 4-3. Conceptual isometric of IPC bed burning furnace.

The installation and three performance tests at IPC were completed by the end of February. A significant number of problems, especially electrical, surfaced during the initial checkouts but were overcome.

The detailed design of the CU has previously been reported (Clay *et al.*, 1985). The four major components of the Central Units will be summarized below. This is the configuration used for both the initial residence time tests (Section 6.4) and the trajectory observations (Section 6.5).

4.1.1 Air Delivery Module

The air delivery module supplies inlet gas (air, N₂, etc.) into a pair of electrical heaters and then into the base of the in-flight module. The flow can range from 1 to 15 scfm (28 to 424 std. Lpm). The first-stage is a 4.5 kW Watlow air heater designed for a maximum outlet temperature of 1000°F (538°C). The second-stage is a 11.1 kW custom-built air heater designed for maximum temperatures of 2300°F (1260°C). There are six Super Kanthal elements in the main part. The part surrounding the gas/solids separator has a small Kanthal built-in heater rated at 2.2 kW. The design outlet temperature of the second-stage heater is 1800°F (982°C).

4.1.2 In-flight Reactor Module

The in-flight reactor module is directly above the second-stage heater. Three 36-inch-long sections are separated by two 6-inch-long sample and observation sections (SOS). In addition there is a third 6-inch-long support section between the bottom SOS and the top of the second-stage air heater. The heated length from the top of the in-flight reactor to the base of the second-stage air heater is 13 ft 8 in (4.17 m).

Each 36-inch-long section consists of a 4-1/8 inch ID fused alumina inner liner. A 1/2-inch fiber insulation blanket surrounds and separates the inner liner and the 5-1/2 inch ID 310SS metal housing. (See Section 4.2.2.2 for later modifications.) Three 10.5 kW ATS clamshell heaters encase the three metal housings. There is approximately a one-inch gap between the metal housing and the encasement heater elements. The gap is sealed at both ends of each furnace. The maximum ATS element temperature is 1800°F (982°C).

The SOS have a castable alumina/silica fiber refractory inner liner which has a 4-1/8 inch ID. Strip electrical resistance heaters surround the outside of the SOS metal housings. Outer insulation covers these heaters and the metal housing. (See Section 4.2.2.3 for later modifications.)

Hot gases produced in the in-flight section were vented into a large duct directly over the top of the top encasement heater. The hot gases were blended

with a large volume of ambient air and vented through a roof mounted fan. This arrangement was satisfactory for only short-term single-droplet tests.

4.1.3 Char Collector

The char collection vessel hangs directly below the second-stage air heater. The Pyrex vessel has a 6-inch ID and a 36-inch length. A metal plate at the base includes a port for N₂ introduction to inert the atmosphere where char is collecting. The falling char particles can be easily observed. In addition, placing a mirror at the base provides a full view of the in-flight reactor interior.

4.1.4 Analog Control Panel and Annunciator

A single NEMA-1 enclosure houses the switches, controllers, and annunciators. The controllers for the encasement heaters and the SOS heaters are LFE time proportioning controllers. The second-stage air heater main controller is an LFE current proportioning controller. The smaller built-in heater is manually controlled via a rheostat. The power to the first-stage air heater is also manually controlled via a second rheostat. The gas flowrate LFE controller is current proportioning.

All heaters have a high temperature limit switch set at a higher level than the required process measurement. There is a flow limit switch on main gas flow. In order for the system to operate gas flow must exceed 1.0 scfm (28.3 std. Lpm).

The annunciator panel is a RIS Microalarm System. All high temperature and low flow alarm limits indicate with a light and a buzzer.

4.1.5 Central Units Performance Testing

Performance testing consisted of measuring the gas temperature at the entrance and exit of the in-flight reactor. Black liquor feeding was not done during these tests. Table 4-1 shows data from the three performance tests.

The design flow and temperature are 13 scfm (368 std. Lpm) at 1800°F (982°C). The entering gas temperature exceeded this target. The exit gas temperature, as measured in the center of the top heater module, was significantly below target.

During these tests only five of the six high temperature Super Kanthal heaters were operable in the second-stage air heater. In addition, the 1/2-inch fiber insulation was in place between the alumina inner liner and the 310SS metal housing. As will be seen later (Section 4.2.4.1.1) with all six elements working and with the insulation removed, slightly higher gas exit temperatures are possible. The target exit temperature of 1800°F (982°C) will probably only be reached or exceeded with internal liquor combustion.

Table 4-1. IPC flow reactor system performance test results.

Upward Gas Flow, scfm std. Lpm		Gas Temperatures			
		Entering Reactor,		Center of Top Heater Module,	
		°F	°C	°F	°C
10	283	1790	977	--	--
13	368	1835	1002	1680 ^a	916 ^a
15	424	1730	943	1665 ^a	907 ^a

^aCorrected for radiation/conduction errors via aspirated thermocouple.

4.2 Flow Reactor System Upflow Configuration - Phase 1

Following the initial residence time tests and the trajectory observations, additional modules were added to upgrade the Central Units into the Phase 1 process flow reactor system. There were also a number of modifications made to the original modules to improve their performance. The essence of the upgrade was to enable black liquor droplet feeding into the top of the in-flight reactor and to safely remove the generated toxic gases. The configuration described in this section was used for the in-flight test groups 1-3 (Sections 6.6.1, 6.6.2, and 6.6.3).

4.2.1 System Overview

The upflow configuration of the flow reactor system used in Phase 1 provides continuous feeding of black liquor droplets at realistic droplet injection temperatures. The three essential functions added for this purpose were continuous black liquor feeding, gas treatment, gas analysis, process safety, and computer-based data acquisition. In this configuration, continuous operation can be achieved and sustained during a normal 8-hour working day.

Figure 4-4 shows a schematic of the process flow reactor system components used in test groups 1-3. All tests to date have been in the gas upflow mode. The

conversion of this system to the gas downflow mode will be discussed in Section 11.1. Table 4-2 lists nominal operating conditions which have been used.

Figure 4-4. IPC Phase 1 process flow reactor system in upflow mode.

Table 4-2. Nominal operating conditions for the IPC process flow reactor system in the gas upflow mode used during Phase 1 tests.

Black Liquor Feed	Flow	1.3 lb solids/h (15 g liquor/min)
	Temperature	200 to 240°F (93 to 115°C)
	Solids	62 to 68%
Gas Characteristics	Velocities	0.7 to 4.3 ft/sec (0.2 to 1.3 m/s)
	Temperatures	1375 to 1675°F (746 to 913°C)
Longest Sustained	6 hours with liquor feed	
Operating Period	10 hours including times without liquor feeding	

The flow rate of the black liquor solids is approximately one-seventh of the target 10 lb solids/h specified in the original design (Clay *et al.*, 1985).

The droplet injector is the main capacity limit. Its upgrade to handle the higher flows will be discussed in Section 11.3. The flow rate listed above produces reasonably uniform droplets and char quantities more than adequate for the analytical tests required in Phase 1. The higher flows will be needed from the second half of Phase 2 until project completion. Simultaneous with higher black liquor solids flows, the gas temperature should increase above present limits due to the heat release upon combustion.

The remaining subsections within Section 4.0 will describe the process flow reactor system components used in Phase 1 test groups 1-3. First, modifications made to components of the original Central Units to improve their performance will be detailed. Second, the modules added to the Central Units to upgrade the system will be described. Third, the overall performance of the modules functioning as the Phase 1 process flow reactor system will be reported.

4.2.2 Modifications To Central Units Modules

Following the initial tests described later in Sections 6.3-6.5, a number of equipment changes became necessary. Some of the changes were necessary to enhance performance during the in-flight studies. Other changes were required to maintain satisfactory operation.

4.2.2.1 Gas-Solids Separator. The function of the gas solids separator is to admit heated air into the base of the in-flight section and then to rapidly remove reacted char particles from a heated environment. The original design (Clay et al., p. 83, 1985) accomplished these objectives for only short test periods. Char particles would build up on the lower ledge and burn on the Nextel/Nichrome Wire composite. This reduced the number of particles caught in the char collection vessel and severely damaged the separator.

The redesign was to make the separator in the shape of a 5-inch ID by 12-inch high cylinder. The composite structure of an inner layer of 6 mesh Nichrome V wire covered with one layer of Nextel B ceramic fabric was retained. In addition, the roof of the chamber surrounding the separator had severely dropped. A three-legged support of 310SS 1/8-inch x 1-inch angle with upper and lower rings was placed around the separator to prevent further damage. Both the composite and the surrounding refractory had significant yellow sulfur deposits in all the damaged areas.

Following group 1 tests (Section 6.6.1) the Nextel was relocated to the outside of the steel legs. Burning char particles were still corroding away the Nextel fabric. This minimized direct contact if burning particles impinged upon the Nichrome wire. The separator is shown in Figure 4-5 in position within the second-stage air heater housing as it has existed since group 1 tests.

Figure 4-5. Gas-solids separator. Redesigned configuration.

4.2.2.2 In-Flight Reactor Module. Early tests (Section 6.3) showed that reaching the target maximum temperature 1800°F (982°C) over the entire reactor would be difficult without in situ liquor solids combustion. In order to reach the highest possible temperatures throughout the reactor several modifications were made following group 1 tests (6.6.1).

First, the 1/2-inch refractory fiber felt insulation between the 310SS housing and the alumina inner lining was removed in all reactor modules. Second, steps were taken to minimize the leakage of air. All the gasketing between the main metal housings for the reactor modules and the SOS was replaced. The original graphoil gaskets burned through, failing in a number of critical areas. The screw-secured ceramic support spacers cracked in all locations. These were replaced with 14 gage 309SS plates cut to size. Disks of No. 882 Babcock & Wilcox mill-board and ceramic paper were used as necessary spacer material and compression gaskets. The V-groove clamps were replaced with bolts that firmly secured modules together.

4.2.2.3 Sample and Observation Sections (SOS). A significant decrease in gas temperature occurred across each of the SOS (Section 6.3). One reason for this was inefficient external heater design. A new heater was designed for the mid-SOS location. The Watlow heater completely surrounds this SOS. There are openings for all three pipe extensions. It has a rating of 3.6 kW compared to the original tubular heater of 2.5 kW. The original inner silica/alumina molded refractory liner had also significantly deteriorated. Following group 1 tests it was replaced with an all alumina moldable sheet made of Zircar type DM refractory. The inner diameter of 4 1/8-inch was retained.

The top SOS was replaced with an optical SOS. The quartz windows are 3-1/2-inch ID. Initial tests showed that burning particles collected in the access ports and that fume deposits readily collected on the cooler quartz windows. Gas purging near the reactor end of the optical extension did not prevent the fume coating. The windows are effective for only short test periods. One of the quartz windows was later removed and replaced with spring loaded refractory discs which provide pressure relief should over-pressurization occur. The second quartz window has also been replaced by a sliding gate which allows a particulate sampling probe to be inserted into the center of the in-flight section. The top SOS in its present configuration is shown in Figure 4-6.

TOP SOS SECTION

Figure 4-6. Top SOS modified for solids sampling.

When liquor droplet injection was initiated into the flow reactor a feed SOS section was added directly above the top reactor module. Figure 4-7 shows the details of this unit. Since it is near the top, there are no burning particles in the access ports. Fume deposition still occurs, however, and frequent manual cleaning of the windows is required.

4.2.3 Auxiliary Component Design

In addition to the major reactor components described above, there are several auxiliary systems which are needed for the reactor to operate efficiently and safely.

4.2.3.1 Gas Treatment Package. In order to prevent the emission of hazardous gases (H_2S , SO_2 , CO , and others) a flue gas treatment system was installed following the flow reactor. The major components are an incinerator, a gas quench, a scrubber, and an induced draft fan (Figure 4-2). This system was assembled and installed by MEI Systems Inc., of Appleton, Wisconsin.

Figure 4-7. Feed SOS located on top of the top encasement heater. The optical ports enable video records of droplet formation.

The gases leaving the reactor are routed into a Brule Incinerator which operates at a temperature of 2000°F (1100°C) to oxidize any remaining combustible material in the gas stream. The inside dimensions are 1 ft 8 inches (508 mm) ID x 6 ft 8 inches (2.0 m) interior length with a volume of 14.5 foot³ (0.4 m³). The nominal flowrates into the incinerator are 150 scfm (4.2 std m³/min) of air, 3 scfm (0.084 std m³/min) of natural gas, and 50 acfm (1.4 m³/min) from the flow reactor at 1750°F (954°C). The incinerator discharge is designed to be 770 acfm at 2000°F (1100°C). The nominal gas residence time for these conditions is approximately one second. A controller is used to adjust the air and natural gas flowrates to maintain the temperature at 2000°F (1100°C). A flame detector is used in the incinerator to prevent accumulation of natural gas. An orifice plate flame arrester with an opening of 0.75 inch (19 mm) is located at the inlet of the flow reactor gases into the incinerator.

The hot gas leaving the incinerator is cooled from 2000°F to 100°F (1090 to 38°C) in a quench system. This is achieved by direct contact with a water spray of 2.1 lb/min (9.5 kg/min). A compartment is provided for the separation of

gas and water, and a drain seal pot is used to maintain the system vacuum while removing the excess water. The gas flow of 175 acfm ($4.95 \text{ m}^3/\text{min}$) at 100°F (38°C) then goes to the scrubber.

The Croll Reynolds scrubbing system is designed to remove SO_2 from the gas stream before discharge to the atmosphere. It also removes particulate material not removed by the quench. The scrubber is designed to use an alkali solution to remove SO_2 , but water alone has been adequate for all tests run to date because of the low black liquor flowrates. The gas is first contacted with the solution in a venturi scrubber and then passes through the solution storage tank, 3 ft (0.9 m) ID x 3 ft 4 inch (1.0 m) in height. The normal tank liquid holding capacity is 175 gallons (0.66 m^3). The gases exit through a 10 inch (254 mm) diameter by 4 ft 10 inch (1.47 m) high packed column which has the tank solution fed at the top to provide additional gas/liquid contact.

Gas is drawn from the flow reactor and through the flue gas treatment system by a Robinson Industries size 22.5 x 1/4 induced draft fan with a 5 HP (3.7 kW) motor. It has a nominal capacity of 400 acfm ($11.3 \text{ m}^3/\text{min}$). An automatic controller operates a bypass valve and maintains the vacuum at the outlet of the reactor at the desired setpoint (typically about 0.10 inch H_2O). In the event of a power failure an emergency draft ejector driven by city water pressure is used to prevent accumulation of gases in the system.

4.2.3.2 Black Liquor Feed System. The feed system is used to heat and deliver black liquor from the storage tank to the injector at the top of the reactor (Figure 4-8). The black liquor supply is stored in a jacketed 70 gallon (0.26 m^3) tank and is heated with steam whenever necessary. Once the liquor has been heated to 180°F (82°C) a mixer is started to maintain a uniform batch. A Moyno pump with a capacity of approximately 5 gpm (19 L/min) draws liquor from the bottom of the tank and circulates it through a steam heat traced pipe, returning most of the liquor to the storage tank. During test periods a portion of the circulating liquor is diverted through a Brookfield Model TT-100 continuous viscosity meter before it is returned to the storage tank.

A side stream of black liquor is drawn off by a Nichols-Zenith metering pump and passes through a Micro-Motion meter which measures both density and flowrate.

Figure 4-8. Black liquor feed and metering system for the IPC flow reactor.

Both the pump and the density/flow meter are electrically heat traced. The liquor then flows to a heat exchanger system which adjusts the black liquor's temperature before it is injected into the flow reactor. The first heat exchanger is tubular, 1/4-inch O.D. x 3/16-inch I.D. x 38 inch long (6.4 mm x 4.8 mm x 0.96 m). The second is the droplet injector itself. The heating fluid in both is an ethylene glycol solution. The glycol also cools the injector as it is heated by the flow reactor gases. The glycol first passes in the outside injector channel, picking up heat, and then passes to the inside channel heating the liquor in a counter current pattern.

A third exchanger then either heats or cools the glycol for temperature control. A controller provides either steam or water to this heat exchanger to achieve the desired temperature setpoint of the ethylene glycol solution as it leaves the injector. The exit temperature of the glycol from the injector is assumed to be close to the droplet temperature.

4.2.3.3 Injector System. A continuous stream of uniform spherical droplets of black liquor is provided to the reactor by the injector system. The black liquor is fed through a narrow stainless steel tube with a vibrating driver device located at the top. The physical movement of the tube at nominally 1800 Hertz causes the black liquor to break off in discrete droplets. With the exception of the vibrator, the injector is almost identical to the NBS injector discussed in Section 2.2. One minor system difference is the preparation of co-current flow of heated air or nitrogen and water vapor. It is produced by controlled water injection into a hot gas stream. The injector has also been modified to allow use of 1/8-inch OD injection tubes.

The additions to the injector to support the higher drop generation rates are shown in Figure 4-9. As described in Section 4.2.3.2 an ethylene glycol solution is used to cool the injector system. By varying the size of the stainless steel injector tube the size of the droplets formed can be changed. Uniform droplets in the range of 2.0 to 4.0 mm diameter have been produced. At larger sizes the droplets have been inconsistent.

4.2.3.4 Instrumentation and Control. A large number of instruments have been installed on the process flow reactor for data acquisition and control. This

equipment is listed in Tables 4-3 and 4-4. Much of this instrumentation is type-K thermocouples to monitor heater temperatures. Other major equipment includes flowmeters for the gas and black liquor, pressure gages, and gas analysis equipment (Section 4.2.3.6). Except for the thermocouples all of the meters produce an output signal of either 0-5 volts or 4-20 ma to provide compatibility with the data acquisition system (Section 4.3.3.5).

Figure 4-9. Vibrating system components used with the black liquor flow injector to achieve high droplet release rates.

Eleven automatic control loops are used to maintain the reactor operating conditions as needed. A microprocessor-based PID controller manufactured by LFE Corporation is used for each loop. Six of these are used to control heaters, one to control the gas feed rate, one to control the black liquor feed rate, one to control the black liquor temperature, one to control the system pressure and one to control the incinerator temperature. In addition alarms and limiting devices are installed to prevent excess temperatures or unsafe conditions.

4.2.3.5 Computer and Data Acquisition System. A computerized data acquisition system is used to collect and store information on the operating conditions of

Table 4-3. Flow reactor instrumentation.

Sensor	Output Signal	Measurement
FT51	0-5 V	Black liquor flowrate
PI55	0-5 V	BL feed pressure
TI51	4-20 ma	BL temperature
SG51	4-20 ma	Density of BL
VT50	4-20 ma	Viscosity of BL
FT21	0-5 V	Gas feed flowrate
PIC101	4-20 ma	Reactor outlet pressure
DPT201	4-20 ma	DP incinerator
DPT202	4-20 ma	DP incinerator
DPT301	4-20 ma	DP scrubber
FE201	0-5 V	Air flow to incinerator
FE202	0-5 V	Natural gas to incinerator
O ₂	0-5 V	Reactor gas oxygen
H ₂ O	0-5 V	Reactor gas water
CO	0-5 V	Reactor gas carbon monoxide
CO ₂	0-5 V	Reactor gas carbon dioxide
SO ₂	4-20 ma	Reactor gas sulfur dioxide

Table 4-4. Flow reactor thermocouples.

Thermocouple	Type	Location
TE124	K	BL injector tip
TE115	K	Top SOS internal
TE103	K	Upper heater
TE105	K	Upper heater
TE116	K	Second SOS internal
TE121	K	Second SOS heater
TE107	K	Middle heater
TE109	K	Middle heater
TE117	K	Third SOS internal
TE122	K	Third SOS heater
TE113	K	Lower heater
TE111	K	Lower heater
TE114	K	Lower support
TE118	K	Bottom SOS internal
TE123	K	Bottom SOS heater
TE101	K	High amp heater
TE23	K	Gas to second stage air heater
TE21	K	Gas preheater
TE203	K	Gas to incinerator
TE201	K	Incinerator
TE202	K	Gas from quench
TE301	K	Scrubber tank
TE50	K	Viscosity meter
TE52	K	Black liquor feed
TE53	K	Heat exchanger
TE56	K	Steam to injector
TE57	K	Steam to injector
TE58	K	Steam generator

the reactor during tests. The system includes an ISAAC 2000 data acquisition unit manufactured by Cyborg Corporation and an IBM XT Personal Computer. The thermocouples and low voltage signals from other sensors are wired to the ISAAC data acquisition system which converts the signals from analog to digital input (Figure 4-10).

The ISAAC unit is instructed to begin operation by a command from a basic program on the PC. The ISAAC automatically collects the data once a minute and stores it in its own 128 kilo-byte memory until it is instructed by the PC to transfer the data. This arrangement allows the PC to be used for other tasks during the test runs. Once the data has been transferred to the PC, the most recent values are displayed on the screen. Figure 4-11 is an example of the screen display. When a test has been completed, the data is installed in a Multistat™ spreadsheet (Davell Custom Software) where it can be reduced and analyzed.

4.2.3.6 Gas Cart and Gas Chromatograph. A complete system for analyzing the composition of the gas in the reactor has been assembled. This unit is assembled on a single cart and has the capability to condition and deliver a specified flowrate to each individual analyzer. Oxygen, water vapor, carbon monoxide, carbon dioxide, and sulfur dioxide concentrations are continuously determined and read by the data acquisition system. Figure 4-12 is a photograph and Figure 4-13 is a flow schematic of the system.

The gas conditioning enclosure was custom designed and built by Beckman Industrial Corp. Two vacuum pumps draw the gas from the reactor through filters and deliver it to the analyzers. The gas stream sent to the H₂O and SO₂ analyzers is held at a temperature of 250°F (120°C) and a vacuum of 15 inches Hg (51 kPa) to prevent condensation of these components. A similar flow path and port are also available for connection to the HNU gas chromatograph. Two water cooled condensers are used to remove water vapor from the samples for the O₂ and CO/CO₂ analyzers. Valves and flowmeters are provided to set the correct flowrate to each analyzer. An air backflush system is available to maintain a clean collection line. Standard gases are also mounted directly on the cart so the analyzers can easily be calibrated.

Figure 4-10. Data acquisition system for IPC flow reactor. Signal identification: Instrument identification (see Table 4-3 and 4-4) X.X (device number, channel number) I-100 Analog input. I-130 Analog to digital converter. I-160 Multiplexers. I-140 thermocouple preamplifiers.

IPC - Black Liquor Flow Reactor - Viewing Data - Test Number 80

Black liquor feed

Flowrate (g/min)	FT51	23.9	Pressure (kPa)	PI55	712	
Density (g/mL)	SG51	1.41	Viscosity (cp)	VT50	136	
Temperature (C)	TE50	98	T151	47	TE52	122
					TE53	129

Gas flowrate (sLpm) FT21 113

Reactor temperatures (C)

TE115	670	TE116	--	TE117	681	TE118	587
TE103	1371	TE107	975	TE111	985	TE101	1022

Gas analysis (%)

AI O ₂	5	O ₂	16.9	H ₂ O	3.1
CO	0	CO ₂	3.1	SO ₂	22 ppm

Incinerator/scrubber

Temperature (C)	TE203	184	TE201	1047	TE202	51	TE301	32
Pressure (Pa)	PI101	-27	DPT201	209	DPT202	66	DPT301	-136
Flowrate (sLpm)	FE201	4937	FE202	84				

Last time 12:43:13 press any key when finished

Figure 4-11. Data acquisition screen display from the ISAAC system.

A HNU Model 301 Gas Chromatograph with an automatic sampling system can also be connected directly to the Gas Cart. This is shown in Figure 4-14. With both a flame ionization detector (FID) and a photoionization detector (PID) the GC has the capability to detect both hydrocarbons and reduced sulfur compounds. Because of the low black liquor flowrates and the relatively high gas flows it has not been used to analyze the dilute gas from the tests thus far.

4.2.3.7 Evaporator System. In order to concentrate large black liquor quantities, an evaporator system has been constructed as shown in Figure 4-15.

Black liquor in the feed tank is heated with internal steam coils until it can be stirred. A Moyno pump with a nominal capacity of 30 gpm (114 L/minute) pumps the liquor through a flowmeter and then to a shell and tube heat exchanger. The four-pass exchanger with approximately 16 ft² (1.5 m²) of heating surface is heated via condensing steam. The hot liquor flows into a flash tank where water vapor forms which then travels to a water cooled condenser.

Figure 4-12. Gas analyzer cart used for gas sample conditioning and analysis. A-conditioning system, B-SO₂ analyzer, C-CO/CO₂ analyzer, D-O₂ analyzer, E-H₂O analyzer, F-H₂O sample vacuum control unit.

Figure 4-13. Flow schematic of the gas analyzer system.

Figure 4-14. Gas chromatograph for reduced sulfur and hydrocarbon gas analyses.

Figure 4-15. Evaporation system for preparing large quantities of concentrated liquors.

The concentrated liquor is then returned to the original feed tank. To improve the capacity of the system a new heat exchanger is being provided by Alfa-Laval. This is a spiral type exchanger with 40 ft² (3.7 m²) of heating surface. It should increase the heat transfer capacity and reduce the pressure drop on the black liquor side. The unit is 2 ft (0.6 m) O.D. x 1 ft (0.3 m) high.

4.2.3.8 Solids Sampling. In order to analyze the drying rate in the reactor it is necessary to have data on the liquor solids concentration over the length of the reactor. Black liquor samples are collected at three SOS in addition to the char sample collected at the bottom of the reactor. A simple system has been used and provides consistent results. A metal boat with a nominal capacity of 4.4 mL was constructed from a 2.75 inches (70 mm) length of a 3/8-inch pipe split lengthwise and welded to a long handle.

The sampling device is first cooled by insertion into a liquid N₂ dewar. It is then filled with liquid nitrogen. The boat is inserted into an SOS for approximately eight seconds and then removed. For this length of time the boat remains cool and quenches the black liquor so that no further drying occurs. Even after the liquid nitrogen vaporizes, the heat capacity of the metal boat still provides a heat sink. Generally three samples are collected at each SOS, providing a total sample of 1.5-2.0 grams at each location.

4.2.4 System Performance - Phase 1

4.2.4.1 In-flight Module. The in-flight module is the most important section of the reactor system, since it is here that the black liquor drying and burning initiation occurs. This section is also the biggest problem area for achieving consistent performance during tests because it is here that partially dried black liquor impinges on the reactor walls, collects, and in some cases plugs the gas passage.

4.2.4.1.1 Gas Flow and Velocity. All of the Phase 1 work on the process flow reactor has been performed with the gas flowing upward, counter-current to the black liquor droplet flow. The inlet gas first passes through a preheater which raises the temperature to about 390°F (200°C) before it enters the second stage air heater where the gas is heated to a nominal temperature of 1740°F

(950°C). The hot gas enters the core of the reactor, travels up the length of the reactor and then goes to the gas treatment system.

The gas flowrate has ranged from 1 to 6 SCFM (28.3 to 170 std. Lpm) during Phase 1 but the majority of the tests have been in the range of 4 to 6 SCFM (113 to 170 std. Lpm). This corresponds to an average velocity of 3.30 to 4.95 ft/second (1.0 to 1.5 m/second) at (910°C). This flowrate range was found to provide the best operating conditions and the fewest plugging problems.

A radial velocity profile within the in-flight module has been determined at 4 and 6 SCFM (113 and 170 std. Lpm) for both 77 and 1290°F (23 and 700°C) heater setpoints. At room temperature the velocity profile is relatively flat and approximates a theoretical turbulent flow profile (Appendix 1). At 1290°F (700°C) however, the velocity profile has a completely different shape with maximums at the center of the tube and also near the reactor walls, and a minimum at a radial distance of approximately one inch. Velocity profiles at 1290°F (700°C) are shown in Figure 4-16. This type of profile can be explained by natural convection currents being set up when the hot walls of the main heater sections raise the temperature of the gas near the walls above the average gas temperature.

Although the normal operating temperature is much higher than 1290°F (700°C), the shape of the curve is probably similar at 1670°F (910°C) in that it has maximums at the center and near the wall. The higher temperature would be expected to increase the velocity near the wall more than it would at the center. This effect could eliminate the central velocity peak and result in an inverted velocity profile. The higher velocity near the walls would have a tendency to retain black liquor particles near the center of the reactor and thereby reduce the amount of material striking the walls which can lead to plugging the gas passage.

4.2.4.1.2 Temperatures. The velocity profiles were determined using a hot-wire anemometer, but it was also necessary to know the temperature profile of the reactor in order to complete the calculations. A temperature profile was calculated earlier by using heat transfer correlations along with the measured temperatures of the metal retorts. The gas temperature profiles which were used to determine the velocity profile are plotted in Figure 4-17.

VELOCITY PROFILE — MID SOS 700 C (1290°F) HEATER SETPOINT

Figure 4-16. Reactor velocity profile.

In addition to the radial temperature profile the reactor has a temperature profile in the vertical direction (Figure 4-18). This is mostly due to the differences in temperature between the heater sections and the SOS. The resulting variation in the gas phase temperature is only about 72°F (40°C) from section to section and 108°F (60°C) over the entire reactor. The differences in the

wall temperatures are much greater than this [about 1780°F (970°C) in the heater sections vs. 1200°F (650°C) in the SOS] and as a result the heat transfer by radiation to the particle can vary significantly. The calculations and additional temperature profiles are included in Appendix 2.

TEMPERATURE PROFILE — MID SOS 700 C (1290°F) HEATER SETPOINT

Figure 4-17. Reactor temperature profile.

Figure 4-18. Vertical reactor temperature profile.

4.2.4.1.3 Gas Phase Components. Tests have been performed with oxygen levels in the feed gas ranging from 0 to 21%. The resulting reactor oxygen concentration, measured at the mid SOS, has ranged from 2 to 19%. Because the reactor is operated under a vacuum, oxygen infiltration occurs and raises the oxygen content, especially when the feed gas is pure nitrogen at low flow rates.

Because the amount of black liquor collecting on the walls of the reactor is less with a high oxygen level and because the O_2 concentration did not strongly influence char formation, all of the tests in groups 3A and 3B were performed

with 100% air feed. The reactor oxygen content never fell to less than 15% during these runs, mainly due to the low black liquor flowrates.

The gas cart was not fully operational before test groups 3A and 3B. Typical gas concentrations during test group 3B were 1 to 2.5% carbon dioxide, 100 to 600 ppm carbon monoxide, and 4.4 to 5.7% water vapor.

4.2.4.1.4 Quad Jet System. An attempt was made to eliminate the problem of the reactor plugging by introducing a tangential flow of air around the inside walls of the SOS. The intent was to create a relatively flat radial velocity profile. Four separate air jets were brought into the reactor and aligned at right angles to the gas flow. The jets were directed nominally 6° off the center line to create a tight tangential swirling motion (Adams, 1985). It was hoped that this circular flow of air would prevent the black liquor flow from striking the walls and accumulating to the point that the reactor plugged. This system was not successful, apparently because the turbulence created by the air jets resulted in more particles striking the walls of the reactor. The abovementioned velocity profiles at high temperature were measured subsequent to the quad jet installation. As previously noted a relatively large trough already existed at the center.

4.2.4.2 Black Liquor Feed Conditions. The range of black liquor feed conditions is listed below. During Phase 1 we were unable to achieve higher flowrates and still maintain good droplet formation. Because the viscosity is measured in the main pump loop at a temperature which does not correspond to the feed temperature the viscosity at the point of injection was estimated from the measured values and previously determined temperature-viscosity relationships.

Black Liquor Feed Conditions

<u>Variable</u>	<u>Range of Values</u>
Flow rate	16 to 23.5 g/min
% Solids	59.6 to 68.9%
Temperature	212 to 282°F (100 to 139°C)
Estimated viscosity	10 to 90 cp

4.2.4.3 Gas Treatment Package. The gas leaving the reactor is treated by the Gas Treatment Package to eliminate pollutants. This system has operated extremely

well during all tests with little or no attention. The gas is first sent to the incinerator to burn any remaining combustibles. The incinerator is normally operated at 1890-2040°F (1030-1115°C). Then the gas is quenched with a water spray to reduce the temperature [typically to about 122°F (50°C)]. The gas is cooled to about 100°F (37°C) and pollutants are removed in the scrubber system.

The gas is drawn from the reactor and through the treatment system by an induced draft fan located after the scrubber. A controller adjusts a bypass valve in order to maintain a set vacuum level in the reactor. Usually the reactor is kept at about -0.10 in H₂O (-25 Pa) although the pressure has been reduced at times in order to alleviate oxygen infiltration during some tests.

4.2.4.4 Safety. Several features have been built into the reactor to maintain safe operation. Maintaining a slight vacuum in the reactor prevents the gases from escaping the reactor and contaminating the laboratory. A carbon monoxide meter is used to monitor the laboratory atmosphere and signal when dangerous levels of carbon monoxide occur. In the event that the inlet gas flow is lost, nitrogen will purge the reactor and a water driven eductor will continue to draw gases from the reactor. A spring-loaded disk has been built into the top SOS in order to provide a safe system pressure relief outlet.

Because of the high reactor temperatures there is always a danger of burns. As much as possible the high temperature sections have been covered with perforated metal shields to prevent access. All heaters have been provided with control systems to limit the temperature and a back-up thermocouple and alarm to shut off the heater in the event that the controller fails. Standard electrical wiring procedures have been followed to insure that all electrical equipment is safe.

4.2.4.5 Mechanical and Corrosion Problems. Because of the harsh conditions in the reactor some of the original equipment has not held up and has either been modified or replaced. In many areas of the reactor there has been an accumulation of sulfur deposits, which along with the high temperature has resulted in the breakdown of ceramic insulating material. The preferred insulating material in contact with the process is almost all fibrous or fused alumina.

4.2.4.5.1 Second-Stage Air Heater. The original design of this heater provided for an air distribution system that would reduce turbulence in the gas flow. Operation of the reactor eventually revealed that black liquor char could accumulate and burn through the ceramic fiber producing an uneven flow distribution. A new design was installed which is less susceptible to char collection (Section 4.2.2.1).

4.2.4.5.2 SOS, Support and Main Heater Sections. The original insulation in three SOS has been replaced with Zicar type DM moldable sheet. The original material (Johns Manville Cera Form board) was subject to attack by the black liquor. Large sulfur deposits were apparent on the degraded insulation. The new material has a high alumina content (90%) and has held up much better in this environment.

The insulation in the support section has been replaced with a piece of 4-inch alumina tube, the same material used in the main heater sections. This material has shown virtually no wear in the reactor and is more resistant to sulfur and liquor deposits. The alumina plates which were used to support the tubes in the main heater sections cracked as a result of physical and thermal stress. They were replaced with plates fabricated from 309 SS. This material is showing some signs of corrosion but it has an adequate wear life for our application.

4.2.4.5.3 Flow Straightener. The gas flow straightener immediately above the droplet injector has been modified. Because of fume and particulate matter in the reactor the narrow openings of the flow straightener eventually plugged. The flow straightener was a Corning Celcor ceramic unit with 300 cells per square inch. To reduce the pressure drop to an acceptable level 1/4-inch (6.2 mm) holes were drilled through the unit.

4.2.4.6 IPC Phase 1 System Photographs. Figures 4-19 through 4-22 show the process flow reactor system installed in the South Research Building at IPC.

Figure 4-19. In-flight module of IPC process flow reactor (center). Discharge pipe to incinerator (left).

Figure 4-20. Base of in-flight module. From top to bottom: lower SOS, 2nd stage air heater, and Pyrex char collector.

Figure 4-21. IPC process flow reactor system. Right to left: Pyrex char collector, pipe from in-flight module, incinerator, quench, scrubber.

Figure 4-22. Incinerator and controls.

Figure 4-23. Gas quench, scrubber, and ID fan.

5.0 PROCESS TEST APPROACH

The IPC process flow reactor, described in Section 4, was designed and constructed to facilitate continuous laboratory-scale burning of black liquor droplet streams. The process test data and their analysis will be presented in Sections 6 and 7. This section will describe the general approach to process testing, liquor selection used in this contract, and liquor exchange with other DOE funded researchers.

5.1 Test Methods

The study of black liquor combustion is facilitated by the relatively large droplet size, i.e., order of magnitude of 10 mg. With this relatively large size both single droplet and droplet stream studies are possible. Process testing in this contract uses both single particle reactors as well as the previously described process flow reactor to study the burning phenomenon.

Single droplet studies are first used to characterize chemical changes during pyrolysis (one of the main steps in the volatiles burning stage) as a function of temperature. The main emphasis areas are carbon loss and fixation as char, total sulfur loss, and hydrocarbon and reduced sulfur gas release.

During single droplet studies the droplet hangs from a wire and hence is stationary. Optical records of an entire burn are then easily recorded. Tests under pyrolysis conditions define total mass loss, rate of mass loss, and the volumetric increase. Tests under oxidizing conditions define times for each of the four burning stages (Section 1.8), rate of mass loss, and the volumetric increase. Sections 6.1 and 6.7 describe the test equipment. Limitations of single droplet studies include interference of the suspending wire, lack of droplet-droplet interaction, restrained movement, inability to reliably determine intermediate compositions, inability to relate process conditions to burning characteristics, and the lack of multiple droplet averaging of an inherently stochastic phenomenon.

Droplet streams produced in the IPC process flow reactor allow aggregate behavior to be studied. The chemical and physical states of droplets at specific

times in the burning process can be determined. The changes are measured on multiple droplet samples and hence the necessary averaging is achieved. There is also full freedom of movement for the particle.

The overall objective of droplet stream studies conducted in the IPC process flow reactor is to understand the effect of process variables on the burning characteristics of black liquor droplets. The variables addressed in this report relate only to the in-flight processes, i.e., effectively only through the volatiles burning stage. Gas temperature, velocity, and oxygen concentration were varied. Droplet variables studied included size, solids content, temperature, and viscosity. Liquor composition changes have not yet been studied but these will be. The burning characteristics are studied by measuring changes in the droplets at several points in their flight. Specifically, the change in elemental analysis and in the type of inorganics present are determined. Aggregate characteristics of particles recovered from the char collector such as bulk density, particle specific swollen volume, moisture content, and the amount of carbon fixed are also measured. Samples collected at the SOS provide intermediate drying data between the initial droplet and the collected char.

Process flow reactor tests, after start-up and preliminary tests, are organized into test groups. Each test group has approximately 7 to 12 tests with typically 2 or 3 independent variables being simultaneously studied. In general, these groups are meant to be full factorial tests. In several cases, however, all of the planned tests were not achievable because of operational considerations.

Analysis of the test data will eventually be done in the context of an overall burning model of black liquor combustion. This effort, however, goes beyond the context of the present contract. The modelling effort has just been initiated and includes substantial input from other research efforts, both supported at IPC and that of others. At the present time the data are analyzed for internal consistency and consistency with other information (both laboratory and commercial) that has been made available to the authors. Standard statistical methods are used to identify significant effects between independent and dependent variables.

The intermediate drying data collected at the SOS is an exception to the above, i.e., it is analyzed in the context of a process model. Based on the thesis work of Mark Robinson (1987) an attempt has been made to analyze high temperature drying in the context of an external heat transfer controlled model. The dynamic velocity and particle size studies of NBS (Section 3) are used in conjunction with the model to translate the drying data into results with applicability broader than just the two experimental systems. This effort is covered in Section 7.

5.2 Liquor Selection

Several test liquors are used throughout this work. The majority are liquors produced in kraft pulp mills. Two source mills have been used to date. There will be at least one more mill source used on the present contract effort.

The preliminary tests were done with kraft mill black liquor (No. 31) already at IPC (Sections 6.4 and 6.5). The source mill was a north central mill with a normal wood furnish of 35% hardwood and 65% softwood. The combined average pulp kappa number was 18 for the batch digesters. The liquor was collected at the discharge of the multiple-effect evaporator, i.e., solids content nominally 50%. Liquor oxidation is not practiced at this mill but the Na_2S is low because of the relatively long storage times. The chemical analysis and burning characteristics are given in Table 6-2.

One of the main criteria for selection of the second liquor was that it be a mill oxidized liquor. There would then be no sodium sulfide present in the liquor to either react with the liquor organics or be oxidized to either sodium thiosulfate or sodium sulfate. For extended storage periods changes in liquor characteristics should then be minimized.

The second mill source was a north central mill with a normal wood furnish of 57% hardwood and 43% softwood. The combined average pulp kappa number was 16 for the continuous digesters. Three liquor collections (No. 30, 33, and 41) have been made at this mill. Liquors 30 and 33 were collected at the discharge of the multiple-effect evaporator at nominally 50% solids content. Liquor 41 was collected from the liquor supply to the recovery boiler nozzles at nominally

68% solids. Liquor 41 had make-up and recycle saltcake in it. Liquors 30 and 41 have been used in this contract. The chemical analysis and burning characteristics for liquors 30 and 41 are given in Table 6-2.

The third liquor to be tested in this contract will be from a kraft mill pulping southern pine. The liquor will be unoxidized and collected after the concentrator but before any recycle or make-up chemical are added.

5.3 Exchange of Liquors University of Maine -

Orono (UMO) and University of Florida - Gainesville (UFG)

The UMO and the UFG have DOE funded projects that address black liquor droplet formation and black liquor characterization, respectively (Fricke, 1985 and Stockel, 1986). Specific liquor samples have been exchanged with these institutions for property measurements. Liquor 33 was collected for use by the University of Maine in a surface tension measurement study. This study is complete and has been reported elsewhere (Stockel, 1986). Samples of liquor 41 have been sent to UMO for rheology study. Identification of changing liquor characteristics with time is the objective of these measurements. The rheological study is not yet completed. Sample exchange with both institutions will continue as appropriate.

6.0 PROCESS TEST RESULTS

Black liquor combustion research at IPC focuses on process chemistry and physical changes which occur during burning. The reactor systems chosen for these studies include both the process flow reactor (Section 4.2.4) and two single particle reactors. The single particle reactors provide environments in which the particles can equilibrate for pyrolysis or gas release studies. The process flow reactor system provides realistic free-falling conditions. Single particle burning studies will be discussed first followed by work in the process flow reactor system. Finally, results of hydrocarbon and reduced sulfur gas-release studies with single particles are presented.

6.1 Equilibrium Pyrolysis Tests

6.1.1 Objectives and Approach

One of the fundamental processes that the black liquor particles undergo in the volatiles burning stage is pyrolysis. The extent of pyrolysis and subsequent mass loss is highly dependent upon particle temperature. At the present time it is not possible to either measure or calculate particle temperature in the IPC flow reactor system. One possible way to estimate such a temperature is from particle composition. The equilibrium pyrolysis tests were designed to produce chars of different composition based on exposure to known temperatures.

The specific objective of the equilibrium pyrolysis tests was to produce char particles in a N_2 atmosphere at six specific temperatures. Five char particles were produced in the convective single particle reactor (SPR). Figure 6-1 is a schematic of the SPR. The test conditions are listed in Table 6-1.

The SPR is purged with N_2 to ensure that the O_2 content is less than 0.5% before each pyrolysis test. Since the primary mode of heat transfer is convection in the SPR the gas temperature is an accurate measure of the final particle temperature. After the test a separate N_2 quench from the lower half of the reactor minimizes air oxidation of the hot char when the particle is removed. In some cases white ashing was observed; these particles were discarded. The upper temperature limit, 1470°F (800°C) is fixed because of this problem.

Figure 6-1. IPC convective single particle reactor SPR.

Table 6-1. Test conditions for equilibrium pyrolysis tests in the convective single particle reactor.

N ₂ flow	3.5 scfm (100 sLpm)
Velocity	4.4-8.2 ft/second (1.3-2.5 m/second)
Gas temperature	570-1470°F (300-800°C)
Particle	40 mg (~ 3.8 mm diameter) at 78.4 % solids content Liquor No. 31

Each particle and corresponding char particle was weighed. The average mass loss for a group of five particles was measured at each condition. The five char particles were thoroughly ground, mixed, and analyzed for total carbon, total organic carbon, total sulfur, and sodium. The analytical procedures are given in Appendix 6. The combined samples of all five particles for one temperature were still relatively small, 120-160 mg, and may have contributed to some analytical inaccuracies.

6.1.2 Results

Figure 6-2 shows the mass loss data as a function of temperature. Rapid change seems to stop at about 1110°F (600°C). Thirty percent of the original solids mass was lost. The continued mass loss may be due to minor amounts of O₂ reacting with the char.

Sulfur loss is already substantial at 570°F (300°C). Figure 6-3 shows a continued steep rise between 660 and 750°F (350-400°C). An apparent maximum of nominally 60% total sulfur loss at approximately 930°F (500°C) was measured. Above this temperature sulfur capture mechanisms appear to become operable.

The lost organic carbon data are shown in Figure 6-4. The major organic carbon loss period is between 750 and 930°F (400-500°C). The continued mass reduction may be due to slight oxidation. In order to better understand the carbon transition approximately 20 grams of black liquor solids were charred in a covered crucible at various temperatures in a muffle furnace. The carbon components were divided into four groups: SOC (soluble organic carbon), TIC (total inorganic carbon), FC (fixed carbon), and LC (lost carbon). The analytical test for fixed carbon was developed on this project (Appendix 6). Fixed carbon is highly condensed, either in an aromatic or free carbon form. Figure 6-5 shows the changes in each of these groups as a function of temperature. Carbon fixation ceases by 930°F (500°C) in a N₂ atmosphere. Nominally 55% of the original carbon is fixed. The absolute percentage may be different for small particles and higher heating rates compared to the relatively large batch pyrolyzed at relatively moderate heating rates.

A comparison of the carbon and sulfur plots shows that sulfur release precedes organic carbon loss as particle temperature rises. In order for complete pyrolysis of liquor 31 to be achieved in the flow reactor, particle temperatures must equal or exceed 930°F (500°C).

Three of the char samples were analyzed for BET surface area. Samples of the 750, 1110, and 1470°F (400, 600, and 800°C) chars were analyzed by Micromeritics Instrument Corporation. The values reported were 1.64, 2.29, and 0.60 m²/g, respectively. The standard deviation is approximately 0.01 m²/g. The data are consistent with increasing surface area up to the melting point of the inorganics

Figure 6-2. Mass loss during equilibrium pyrolysis tests in the SPR.

Figure 6-3. Sulfur loss during equilibrium pyrolysis tests in the SPR.

after which it decreases. The nominal melting point of the reduced inorganics is 1370°F (740°C). The carbon surface area free of the inorganics would typically have higher values.

Figure 6-4. Lost plus fixed carbon measured in chars from equilibrium pyrolysis tests.

Figure 6-5. The transition of carbon during thermal degradation of kraft black liquor solids. SOC - soluble organic carbon, FC - fixed carbon, LC - lost carbon, TIC - total inorganic carbon.

6.2 Single Particle Burning Tests

Techniques have been developed at IPC to measure certain burning parameters of single liquor droplets. The two basic parameters are volumetric expansion and burning times. The specific swollen volume in high temperature environments of both N_2 and air are measured. The burning times for three of the burning stages are measured.

The droplets are suspended on a wire in the single particle reactor (SPR) shown in Figure 6-1. The procedures used are described in Appendix 6.

Three kraft mill black liquors have been used in the course of this work; two at IPC and one at NBS. Table 6-2 lists their respective compositions. The results of the burning tests are given in Table 6-3.

Table 6-2. Characterization and composition of kraft mill black liquors used for tests at IPC or NBS. Chemical analysis basis is weight percent of oven dried solids (ODS) at 221°F (105°C).

Liquor No.	31	30	41
Liquor Type	Kraft	Kraft	Kraft
Mill	A	B	B
Wood	Hwd/Sft (35/65)	Hwd/Sft (57/43)	Hwd/Sft (57/43)
Oxidized at mill	No	No	Yes
HHV, Btu/lb	6580	5850	5540
Sulf. ash, % NaOH	33.3	36.9	36.9
RAA, % Na ₂ O	3.0	3.0	1.3
C	38.6	--	35.7
H	2.70	--	3.25
O	31.7	--	34.3
Na	19.3	19.8	19.8
K	1.8	2.6	1.4
S	4.2	4.6	4.6
Cl	0.3	0.29	0.8
Na ₂ CO ₃	3.6	10.3	8.0
Na ₂ SO ₄	0.7	3.2	5.9
NaOH	3.5	4.2	1.7
Na ₂ S	0.34	0.32	0

Complete burning in air of a nominal 2.3 mm diameter (9 mg) particle for any of these liquors requires at least 5-6 seconds. These data are consistent with the prior tests (Section 1.7) when proportioned with droplet mass. These times are far greater than the in-flight residence time available in the process flow reactor. As will be shown in section 6.4 an estimated residence time for liquor 31 in the IPC process flow reactor is 1.4 seconds. Based on these burning studies particles should be quenched in the char catcher somewhere within the volatiles burning stage in the gas upflow mode. Smaller particles and higher gas temperatures undoubtedly will increase the burning rate. The liquors range in swelling potential from moderately high to moderately low.

Table 6-3. Burning test results for kraft mill liquors used for tests at IPC or NBS. Solids levels from actual tested levels may differ.

[Pyrolysis: 930°F (500°C) in N₂ nominal droplet size 40 mg]
[Combustion: 1470°F (800°C) in air nominal droplet size 9 mg]

Liquor No.	31	30	41
Solids, %	71.8	75.0	67.4
Swol vol pyr, cc/g-s	138	104	68
Swol vol comb, cc/g-s	42	26	14.9
Time to ign, second	0.9	1.1	1.4
Time ign, -max vol, second	1.4	2.2	2.0
Time max vol-smelt, second	2.5	1.6	2.3
Time total, second	4.8	4.9	5.7

Liquors 31 and 41 were used in IPC tests while liquor 30 was used in NBS tests. Both liquors 41 and 30 were from the same mill but collected at different times. Liquors 30 and 31 were collected at the evaporator outlet, while liquor 41 was collected at the black liquor header in the recovery boiler. The solids were adjusted to keep the droplet on the wire.

With the liquor chemical and burning characterization complete the remainder of this section discusses in-flight testing in the IPC process flow reactor system.

6.3 Start-up Tests

The start-up tests were conducted on the central units of the IPC process flow reactor system. The equipment configuration is shown in Figure 4-1. No automatic liquor injection equipment was in place. The gas flow was upward. The top encasement heater had a refractory plate with a two-inch hole covering its exit to prevent excessive radiation loss.

Temperature profiles at two different gas flow rates were the first measurements made. A sixteen foot (3 meter) long one-sixteenth of an inch sheathed type-K thermocouple with an exposed bead was used. A 1/4-inch stainless steel tube [4 inches (100 mm) long] was loosely wired to the thermocouple sheath as a radiation shield. The thermocouple tip with surrounding shield was held in the center of the in-flight section by a four pronged nichrome wire spider. The thermocouple was inserted into the top encasement heater at the gas discharge end. Temperature measurements were made at the center of each of the three encasement heaters and at the three SOS. The exit temperature from the second-stage air heater was measured by the one-sixteenth inch sheathed type-K thermocouple used for heater control. This thermocouple extends approximately one-quarter inch (6 mm) into the center duct of the in-flight section.

Start up temperature profiles for the second stage-air heater, the lower encasement heater, and the top encasement heater are shown in Figure 6-6. These conditions yield a rapid heatup. Figure 6-7 shows heatup profiles for the gas and the top encasement heater. Steady state is achieved in nominally 3 hours or less at higher gas flow rates.

Figure 6-6. IPC flow reactor heatup curves with gas flow at 5.5 scfm (156 std. Lpm). Heater setpoints 1815°F (990°C). Second-stage air heat setpoint 1800°F (982°C) + second-stage heater, Δ middle/heater, x upper heater, O lower heater.

DOE REACTOR HEATUP
Test 2 Air Flow 5.5SCFM 2NDSTHTR SP1800F HTR 6P 1815F

Figure 6-7. TPC flow reactor heatup curve for top encasement heater and flowing gas. The upper line is the gas temperature. Gas flow 5.5 scfm (156 std. Lpm). Heater setpoints same as Figure 6-6.

Table 6-4 lists the steady state values measured for two target average temperatures and two flow rates. The average temperature is a weighed value over the length of the in-flight section based on length at temperature. Calculational details are in Appendix 2.

During all of these tests the lower SOS heater was not properly functioning. The top and middle SOS were heated with the original one-quarter inch tubular heaters. Improved temperature profiles were obtained in later tests (Section 6.6) with improved SOS heaters and measurement/calculation techniques.

Table 6-4. Temperature profiles in IPC process flow reactor.

Gas upflow, scfm (std. Lpm)	8 (226)	12 (340)
Temperatures, °F (°C)		
Top heater	1540 (838)	1549 (843)
Top SOS	1515 (824)	1521 (827)
Middle heater	1537 (836)	1542 (839)
Middle SOS	1533 (834)	1533 (834)
Lower heater	1524 (829)	1526 (830)
Lower SOS	1501 (816)	1508 (820)
Second-stage air heater exit	1654 (901)	1634 (890)
Average reactor	1548 (842)	1549 (843)

The system limits with the present configuration and no internal combustion are listed in Table 6-5.

Table 6-5. System limits determined during start-up of the IPC process flow reactor system.

Upward gas flow	14 scfm (495 std. Lpm)	
Gas Temperature(no combustions)		
Average	1665°F	(900°C)
Encasement heater center	1680°F	(915°C)
Second-stage air heater exit	1895°F	(1035°C)

Higher gas flows (up to 20 scfm, 565 std. Lpm) can be obtained but temperatures fall. Slightly higher gas temperatures (+ 63°F, + 35°C) were obtained later when the 1/2-inch insulation between the the metal housing and the alumina liner was removed (Section 4.2.2.2).

6.4 Initial Residence Time Tests

The initial residence time tests were conducted in the central units system shown in Figure 4-1. The only addition was the use of a manually operated dual switch stopwatch to record the visually observed time of fall.

The objective of this first test series was to measure the residence time, particle expansion, and extent of pyrolysis of a typical mill kraft liquor (No. 31). Table 6-2 gave information on this liquor. These tests also defined practical operating limits of the reactor during black liquor particles injection. The three tested independent variables were gas flow rate, gas temperature, and initial droplet mass. Nitrogen was used as the gas in all of these tests. Twenty-nine successful tests were conducted. Table 6-6 shows the independent variable levels chosen.

Manual injection of liquor particles was used for these tests, since the liquor injection method was still under development. Liquor No. 31 at 78.4% solids was manually formed into small beads of the required size. Their mass was weighed to the nearest milligram on an analytical balance. Once formed, the particles were placed in covered glass dishes at room temperature until use. The particles were transferred one at a time into the top of the reactor through the 2-inch opening with a laboratory spatula.

The residence time was read directly from the stopwatch. When a particle fell from the spatula into the reactor the stopwatch was started via a switch at the top. When the second observer saw the particle hit the base of the char catcher the stopwatch was stopped via a second switch at the base. Blank tests determined that the observers' lag time was nominally 0.02 second. Not all of the particles made it to the base; this was the first indication that wall impact occurred.

The collected char samples were analyzed for specific swollen volume, carbon loss, and sulfur loss. The analytical procedures are listed in Appendix 6. The average values and ranges of the reduced data for all twenty-nine tests are listed in Table 6-7. Note the large reported data ranges, especially the specific swollen volume. The data from each test represent averages of approximately 10 samples per test. The measured values for each test are shown in Appendix 8.

Table 6-6. Values of independent variables for residence time tests.

Test	N ₂ Flow, scfm	Average Gas Temperature,		Particle Initial Mass, mg	Particle Initial size, mm
		°F	°C		
4	12	1550	844	12	2.5
5	8	1552	844	12	2.5
6	12	1550	844	30	3.4
7	8	1552	844	30	3.4
8	12	1341	727	30	3.4
9	8	1335	724	12	2.5
10	12	1341	727	12	2.5
11	8	1335	724	30	3.4
13	6	1320	716	10	2.4
14	2	1323	717	10	2.4
15	2	1323	717	5	1.9
16	6	1522	828	10	2.4
17	6	1522	828	5	1.9
18	2	1526	830	10	2.4
19	2	1526	830	5	1.9
20	14	1617	881	15	2.7
21	14	1617	881	30	3.4
22	2	1605	874	15	2.7
23	2	1605	874	30	3.4
24	14	1664	906	15	2.7
25	14	1664	906	30	3.4
26	2	1638	892	15	2.7
27	2	1638	892	30	3.4
28	12	1553	845	12	2.5
29	12	1553	845	30	3.4
30	12	1609	876	15	2.7
31	2	1615	879	5	1.9
33	2	1639	893	5	1.9
34	2	1639	893	2	1.4

Table 6-7. Residence time tests: reduced data averages and ranges for all twenty-nine tests.

Variable	Units	Average	Range
Residence time	seconds	1.5	1.2-2.0
Expanded diameter	mm	4.9	3.1-6.3
Specific swollen volume	cc/g-solid	8.3	1.7-27
Sulfur loss	% of initial S	11	0-41
Fixed and lost carbon	% of initial C	12	0-60

6.4.1 Residence Time

The volumetric expansion which occurred when the black liquor particle was exposed to the high temperature environment did significantly increase the residence time. The calculated residence time for a 3.4 mm droplet with no

expansion (see Appendix 4) is 0.9 second. The measured average and 95% confidence limit for 3.4 mm particles was 1.4 ± 0.1 second. As will be shown below, both expansion and wall impingement account for this increase.

Statistical analysis of the data identified significant independent and dependent variable interrelationships. Multiple linear regression was the basic approach used for this identification. Some first order interactions and logical nonlinear terms were also tested. Student's t-test at the 95% level was the criterion for identifying variable significance. Details of the statistical methods used are given in Appendix 7. The pertinent results will be summarized below.

The residence time varied significantly with four variables. Table 6-8 lists the regression formed equation's variables, coefficients, and intercept. Figure 6-8 is a comparison of the actual residence time with the predicted time based on the regression fit. The higher the absolute value of the t-value for a given variable, the greater its significance. With an overall equation r^2 of 0.78 there is still a significant amount of unexplained variation.

Table 6-8. Significant variables which relate to droplet residence time.

Variable	Units	Coefficient	t-value ^a
Swollen volume	cc/g-solids	2.59E-02	5.6
Temperature 2nd-stage			
N ₂ heater outlet	°F	-6.97E-04	-3.3
N ₂ flow	scfm	1.43E-02	2.3
Initial droplet wt.	mg	-8.50E-03	-2.4
Regression equation intercept 2.94 seconds			
Regression equation $r^2 = 0.76$			

^at-Value greater than 2.06 indicates 95% significance level for 25 d.f.

The strongest dependence is on the swollen volume; larger final swollen volumes imply longer residence times. Since the swollen volume is continually changing during flight, it is not unusual that the final swollen volume does not explain all the variation. Swollen volume provides an empirical sensing of the residence time through changes in particle size. The last variable listed, the initial droplet weight, shows decreasing residence time with larger values as expected.

These two variables are coupled through particle temperature. Larger particles will fall faster and also will not reach as high particle temperatures as smaller

ones. Hence the expansion should be less. The remaining two variables indirectly indicate changes in particle temperature. The strongest temperature dependence was with the second-stage N₂ heater outlet. This is typically the highest temperature and is the last heated section seen by the particle. Higher temperatures imply lower residence times. Higher temperatures also imply increased heat transfer, both convective and radiant. During expansion the outer layers can char more rapidly and hence limit the expansion as has been shown by Miller (1986). The outer char layer is also generally nontacky and hence would have less of a tendency for longer times through wall impact. Higher N₂ flows promoted longer residence times. Note that this is the least significant variable. Longer residence times were achieved at higher N₂ upward flows. The predicted difference in residence time between 2 and 14 scfm, based on the above coefficient is nominally 0.2 second. The residence time appears to be more dependent on particle size changes and possible wall impacts than on aerodynamic considerations alone.

Figure 6-8. Comparison of predicted residence time, via Table 6-8, with the actual residence time values.

6.4.2 Specific Swollen Volume

The swollen volume had a significant effect on the residence time. Miller (two in 1986) has shown that both process and compositional variables influence the

swollen volume. Data from the residence time tests were analyzed to define specific influences for this flow reactor system. A statistical procedure similar to that for the residence time analysis was used. The significant variables along with the multiple regression equation are given in Table 6-9. Figure 6-9 is a comparison of the regression fit with the actual swollen volume data.

Table 6-9. Significant variables which relate to specific swollen volume.

Variable	Units	Coefficient	t-value ^a
Expanded diameter	mm	5.85	8.8
Residence time	second	12.9	7.6
N ₂ flow	scfm	-0.543	-6.0
S/Na ₂ molar ratio	fraction	-55.1	-4.2
Temperature top SOS	°F	-0.0161	-4.0
Temperature lower heater	°F	0.0125	3.54
Inorganic char carbon	%	0.466	2.69
Regression equation intercept -25.2 cc/g-solids			
Regression equation $r^2 = 0.95$			

^at-Value greater than 2.06 indicates 95% significance level for 25 d.f.

Figure 6-9. Comparison of the predicted specific swollen volume, via Table 6-9, with the actual measured values.

The strongest dependence is on the expanded diameter. This is not surprising, since it is used to first calculate the swollen diameter which is then normalized by the initial mass of the solids. Its absolute value, however, does play a role in droplet trajectory and hence residence time. In this regard it is interesting to note that d^2 and d^3 values did not correlate as well as d . Increasing both the expanded diameter and residence time implied larger specific swollen volumes. Higher N_2 flows gave lower swollen volumes. One possible explanation is that higher gas flows past the particle increase heat transfer to it, and hence increase surface charring. Char formation on the surface then limits swelling. The small influence that N_2 flow had on the residence time may be because of the counter influence to yield smaller swollen volumes.

The two temperature influences on specific swollen volume shown in Table 6-9 appear to be contradictory. They are consistent with the work of Miller (1986). Essentially the trends suggest that lower initial temperatures (top SOS) and high final temperatures (lower heater) are conducive to higher swollen volumes. This temperature profile would fix char later and hence allow the volume to grow unconstrained.

The remaining two variables relate char chemistry to the swollen volume. Low sulfur retention in the char and high inorganic carbon (Na_2CO_3) imply high swollen volumes. Since the in-flight module could only accomplish limited charring, these trends apply to early pyrolysis. In general, inorganic carbon will form and sulfur will be released as char is formed. One possible explanation is as follows. Expansion is driven by gases generated during pyrolysis (Miller, 1986). Reduced sulfur gases are one of the major early components. The extent of expansion increases with either a lower temperature pyrolysis or a greater degree of pyrolysis (Miller, 1986). Both are conducive to higher rates of sulfur release, i.e., lower S/ Na_2 ratios in the collected char (Brink, 1970). If the temperature of the expanded surface was high enough to develop molten salts, then a sulfur capture mechanism may have been operable (Cantrell, 1986). Molten conditions were not obtained by most particles during these tests. The higher inorganic carbon results from a greater degree of pyrolysis caused by a higher average particle temperature. This implies that the added surface area provides faster particle heatup. As was seen in Section 6.1 carbon fixation is essentially complete by 930°F (500°C). Since complete carbon fixation was not reached, particle temperatures were less than 930°F (500°C).

If the expanded diameter is not used in the regression fit the only two significant variables identified are the S/Na_2 molar ratio and the residence time. They had the same trends as before. The r^2 with only these two variables was 0.71.

6.4.3 Sulfur and Carbon Loss

The in-flight section provides sufficient residence time to initiate the charring processes. Drying is essentially complete and pyrolysis began as evidenced by sustained swelling. Although N_2 was used as the upward flowing gas, air infiltration at the lower flow rates was suspected. This was quantified during later tests. With O_2 present some limited gasification undoubtedly occurred. The char samples looked friable, black, and very light but they were not completely pyrolyzed. Comparison of the values listed for sulfur and carbon loss in Table 6-7 with the equilibrium sulfur and carbon loss reported in Section 6.1 shows that only partial charring occurred. At higher black liquor flows more complete charring should occur if there is a significant increase in heat transfer rates to the particles. Despite this limitation during the present tests, some useful information on carbon and sulfur loss was obtained. This is listed below.

Since the mass of the droplet hangs dynamically as it falls through the in-flight section, a tie element is needed to correctly assess carbon and sulfur loss. Sodium was chosen as the tie element. Particle temperatures remained on average low during these tests, so the assumption of no Na vaporization is reasonable. The sulfur and carbon contents of the collected char were expressed as molar ratios of S/Na_2 and C/Na_2 .

The percent of original sulfur lost was calculated for each sample. This parameter correlated better than either the char sulfur content or the S/Na_2 ratio with other test data. A significant predictive relationship for the percentage of lost sulfur was not possible. Three test variables, however, were significant in the direction of their influence on the percentage of lost sulfur. The specific swollen volume was the most significant; its t-value was 3.3. Higher swollen volumes were simultaneous with greater sulfur loss. The temperature of the upper heater had a t-value of -2.4; lower temperatures implied increased sulfur loss. The last significant variable identified was the percent fixed plus lost carbon based on the original total carbon content. Higher carbon loss implied higher sulfur loss. Its t-value was 2.3.

Fixed plus lost carbon is synonymous with organic carbon degradation either through volatilization or conversion to Na_2CO_3 and char carbon. The lost organic carbon (fixed plus lost) is expressed as a percentage of the initial carbon content in the original sample. As can be seen in Table 6-7 there was less organic carbon loss than sulfur loss. These results are reasonable in light of the extended pyrolysis data of Section 6.1 which show that sulfur volatilization occurs ahead of organic carbon loss. Three variables from this test set showed significant trends with the lost organic carbon data. The temperature of the lower SOS was the most significant; its t-value was 3.5. A higher temperature produced greater organic carbon loss. Higher N_2 upward flow reduced the amount of organic carbon loss. The t-value for this relationship was -2.7. In general higher N_2 flow should cause better heat transfer, higher particle temperatures, and increased organic carbon loss. The swollen volume is also decreased at higher N_2 flows. This could imply a lower extent of pyrolysis or rapid char formation on the expanding surface.

There is an apparent discrepancy between these results and those for swollen volume. Air leakage into the reactor at the lower N_2 flows may also be another explanation for this relationship. However if this were the sole explanation the swollen volumes should have decreased when the N_2 flow decreased. The opposite trend was found. It does not appear possible to completely sort out the basic relationship between N_2 flow and carbon loss with just this group of tests. Particle residence time showed a positive correlation with carbon loss; the t-value was 2.1. This trend is reasonable. The last significant variable was the S/ Na_2 ratio with a t-value of -2.0. Lower char sulfur contents implied larger carbon losses. This trend is reasonable based on the data of Section 6.1.

6.4.4 Summary

The initial residence time tests demonstrated that particle residence times are between 1.2 and 2.0 seconds, depending on test conditions. This is sufficient time to essentially complete drying and initiate the volatiles burning stage. Particle changes in specific swollen volume, sulfur content and carbon content were measured. The dynamic increase in specific swollen volume was the major identifiable reason for longer residence times than had been anticipated (Clay *et al.*, 1985). The influence of upward flowing N_2 was minimal. The three measured particle characteristics were interrelated to both process and composition dependent variables.

The influence of heat transfer to the particle as implied by temperature and N₂ flow rate was the most significant overall trend. The early in-flight processes are dominated by heat transfer to the particle as it dries and pyrolyzes. Another significant yet hard to quantify variable was wall impact. Virtually all particles impacted the wall. Most bounced off and were retained only a short time. The extent of wall impact and subsequent retention depended upon conditions.

6.5 Trajectory Observations

6.5.1 Objective and Approach

The residence time tests implied that particle trajectories often included wall impact. This had only been directly observed on a limited and random basis. A group of tests was conducted to specifically observe particle trajectories in the in-flight reactor module.

Five trajectory tests were successfully completed. These tests used the black liquor droplet injector as described in Section 4.2.4.2. A small heat traced and pressurized reservoir supplied the black liquor. Another new feature added prior to these tests was the injection of 4 air jets (each at about 1% of the main gas flow) perpendicular to the main flow and set 6° off center. This quad-jet arrangement was to test the sensitivity of particle trajectory to the velocity profile. Conceptually, the quadjet should break up the parabolic upward velocity profile, minimizing particle movement toward the walls (Adams, 1985). The two test variables were upward air flow at 4 levels between 0-12 scfm (0-340 std. Lpm) and temperature at nominally 4 levels between 1200 and 1740°F (650-950°C).

Mill black liquor No. 31 was used in all trajectory tests at 66.5% solids content. The injector tip was 0.84 mm I.D./1.27 mm O.D. Trajectory observations were made via a mirror placed at an angle in the base of the Pyrex char catcher. With careful observation one can view the complete particle flight. The location of particle ignition and the type of product impinging on the mirror were noted.

6.5.2 Results

The general patterns of wall impingement are shown in Figures 6-10 and 6-11. It was encouraging to see such a wide range of product composition. A significant number of particles hit the wall under all conditions. When the air flow was 4

scfm (113 std. Lpm) or less and the temperature was above 1525°F (830°C) the majority of particles hit but did not stick on the walls. The quadjet was tested at each condition. No significant change in percent reaching the bottom was noted. It appears that regardless of the velocity profile once the char expansion is underway it inevitably hits the wall. Feed and reactor conditions must be adjusted to minimize permanent sticking. Figures 6-12 and 6-13 show views of the interior through the mirror as single and multiple particles are injected, respectively.

Figure 6-10. Vertical location for ignition in the IPC in-flight module.

6.6 In-flight Tests

6.6.1 Test Group 1

6.6.1.1 Objective and Approach. The objective of test group 1 was to evaluate the effect of gas phase O₂ content and black liquor injection temperature on the chemical and physical properties of the produced chars. A complete factorial with three levels for each variable plus two replicates was planned.

Figure 6-11. Product characteristics at base of IPC in-flight module for four temperature conditions.

Figure 6-12. View of IPC in-flight module interior during operation. Single droplet released.

Figure 6-13. View of IPC in-flight module interior during operation. Multiple droplets released.

The base operating conditions for the reactor were as follows:

Liquor feed: 1.0 to 1.3 lb solids/hr (12 to 16 g/m)
liquor 41 at 65% nominal solids
2 mm nominal droplet size (tip 0.84/1.27 ID/OD)

Gas feed: 4 scfm (113 std Lpm) gas upward flow
1615°F (880°C) average target gas temperature

Once the reactor reached the steady state target temperature, liquor droplets were injected. Tests started when consistent droplets were visually observed through the feed SOS. Normally this was only a few seconds after liquor injection started. The char collected in the Pyrex char catcher at the reactor base. Sufficient char for analysis purposes was usually produced within 15 to 30 minutes.

The char catcher would be from one-quarter to one-half full. The N₂ purge into the char catcher base quenched and inerted the char. At the end of each test the char was manually transferred into plastic bags which were purged with N₂.

The actual test levels for O₂ and liquor injection temperature are listed in Table 6-10. The O₂ level was set by either using N₂, air, or the required metering

of the two. The actual O₂ level in the reactor was not measured during these tests. The O₂ level for the 10% and 21% inlet cases was slightly less, due to partial combustion. There was some air infiltration due to the slight negative pressure in the reactor and hence, at the intended 0% O₂ level, some O₂ probably existed.

Table 6-10. Test group 1 actual independent variable levels.

Test	Oxygen, % volume	Temperature of Liquor,		Feed Solids, % ODS ^a
		°F	°C	
47	0	199	93	67.4
50	0	207	97	64.8
51	21	200	94	64.8
52	0	215	102	64.0
53	21	217	103	64.0
54	21	217	103	64.0
56	10	221	105	64.0
57	10	239	115	64.0
58	10	203	95	64.0
59	21	219	104	64.0
60	21	241	116	63.6

^aODS oven dried solids at 221°F (105°C).

6.6.1.2 Results

The average and range of each chemical and physical char property measured are listed in Table 6-11. The properties of the initial liquor are also listed for comparison. Comparison of these data with those in Section 6.1 shows that the char is only partially pyrolyzed. It is also interesting to note that moisture still remains in the char even though pyrolysis has begun. This is a good indication that particle temperature gradients exist and that there is overlapping of the burning stages for the tested conditions. Despite the fact that pyrolysis was only partially complete substantial sustained swelling occurred. The swollen volume increased on average over 8 times and the char bulk density decreased over 15 times. The factors controlling the swelling process (Miller, 1986 and 1986) appear to be mainly operable during the latter phases of drying and the early phases of pyrolysis.

Table 6-11. Average physical and chemical properties of test group 1 product chars.

	41	Product Char	
		$\pm 95\% \text{ CL}^a$	Range
Fixed carbon, % ODS ^b	0	4.42 ± 1.41	2.65-10.27
Moisture, % ODS	64.4 ± 0.7	1.53 ± 0.45	0.55-2.71
Swollen volume, cc/g-solid	Approx. 1.2	9.8 ± 2.2	4.2-16
Bulk density, g/L	~1300	83 ± 17	27-113
(All values, % ODS)			
C	35.7	31.3 ± 1	27.4-33.0
H	3.25	2.59 ± 0.22	1.85-3.10
O	34.3	35.5 ± 0.4	34.5-36.4
S	4.56	4.5 ± 0.3	3.8-5.2
Na	19.8	22.3 ± 0.8	20.2-24.6
K	1.4	2.93 ± 0.12	2.74-3.28
Na ₂ CO ₃	7.97	27.8 ± 3.3	22.8-38.0
Na ₂ SO ₄	5.87	8.08 ± 1.11	6.71-11.7
Na ₂ SO ₃	0.96	1.66 ± 0.38	1.01-2.80
Na ₂ S ₂ O ₃	8.19	4.64 ± 0.54	3.27-5.71
Na ₂ S	0	0.85 ± 0.41	0.14-2.15

^aCL confidence limit.

^bODS oven dried solids at 221°F (105°C).

Most of the chemical shifts were as expected. Table 6-12 lists the percent change of the major components. Based on the change in Na the average solids mass loss was 11%. The major elements lost were C, H, O, and S. It is interesting to note that there is on average a higher carbon loss than sulfur loss. Liquor 41 is an oxidized liquor. Its sulfur content may be more stable than the liquor tested in Section 6.1 (31) which is an unoxidized liquor. A substantial percentage (70%) of the sulfur in an oxidized liquor is as Na₂S₂O₃. Sodium thiosulfate showed a 50% loss during these tests. It apparently decomposes rapidly at relatively low temperatures. Literature data (Kubelka, 1957) support this contention. The reactions are claimed to be:

The present data support the reaction products. They do not support the reaction stoichiometry. Na₂S was found in the product char. In the cooler regions

of the reactor yellow deposits presumed to be sulfur were found during an inspection following this test group. The low mass loss, sulfur loss, fixed carbon values, and visual observation support the hypothesis that only relatively low particle temperatures were achieved. Sulfide formation via the sulfate-sulfide cycle is ruled out since temperatures producing molten conditions did not exist. Sulfide formation and elemental sulfur release via Na_2SO_3 decomposition is one of the early in-flight sulfur release processes in the particles.

Table 6-12. Average percent change in chemical components during char forming processes of test group 1.

	Average $\pm$ 95% CL	Range
Carbon loss, %	22.2 ± 4.9	9.3-33.8
Hydrogen loss, %	33.2 ± 7.6	12.6-46.5
Oxygen loss, %	11.2 ± 3.3	2.0-20.5
Sulfur loss, %	11.9 ± 6.3	0.1-32.8
$\text{Na}_2\text{S}_2\text{O}_3$ loss, %	49.2 ± 7.2	34.6-67.9
Na_2CO_3 gain, %	208 ± 27	170-288
Na_2SO_4 gain, %	23.2 ± 14.7	-1.7-71.9
Na_2SO_3 gain, %	52.7 ± 32	3.1-151
S ⁼ /S, %	7.7 ± 3.7	1.5-20.0
Fixed Carbon/ Organic carbon, %	12.7 ± 4.4	7.2-31.7
Solids mass loss, %	10.9 ± 3.4	2.0-19.5

The two main independent variables in this test group, O_2 content and liquor temperature, did produce significant variation in some of the measured char properties. They could not, however, explain the majority of the observed variation. During these 11 tests the feed solids changed from 67.4 to 63.6%. Feed solids content effectively became a third independent variable. Unfortunately, the unplanned variation in feed solids had a significant trend with liquor temperature, see Table 6-10. Higher feed solids were present when higher liquor temperatures were tested. This trend makes it difficult to separate the two variables. All measured values for each test are listed in Appendix 8.

Significant effects of the three independent variables on char characteristics were evaluated with Student's t-test (Hogg, 1969). Single and multiple dependencies were tested. The relationships which were significant at the 95% level (t-values > 2.2) are listed in Table 6-13.

Table 6-13. Char characteristics which had a significant relationship with one of the three independent variables.

Char Characteristic	Indep. Variable	t-value ^a
Swollen volume	Liquor temperature	+2.3
	Feed liquor solids	-2.4
Swollen volume confidence limits	Liquor temperature	+2.7
	Feed liquor solids	-2.9
C/Na ₂ percent lost	Liquor temperature	+2.2
CO ₃ /Na ₂ percent gain	Gas phase O ₂ level	-2.2
SO ₄ /Na ₂ percent gain	Feed liquor solids	+4.5
SO ₃ /Na ₂ percent gain	Feed liquor solids	+4.2
	Liquor temperature	-2.6
S ₂ O ₃ /S percent in char	Liquor temperature	+2.2

^aInitial absolute t-value = 2.2. See Appendix 7 for statistical methods.

The listed t-values are for the single independent variables' relationship with the char characteristic. No multiple relationships were significant. Increased liquor temperature produced larger and more variable swollen volumes, greater carbon loss, less Na₂SO₃ in the char and a higher percentage of the char S as Na₂S₂O₃. Lower liquor solids produced higher and more variable swollen volumes, and more Na₂SO₄ and Na₂SO₃ in the char. As noted above variations caused by feed solids and liquor temperature may not be completely separable. Fortuitously, changes in both of these variables consistently changed liquor viscosity, so that at least cancelling effects should not be present. The suggested implication is that lower liquor viscosities enable the particle to proceed further in pyrolysis, i.e., more swelling and more decomposition products. Lower O₂ levels produced higher Na₂CO₃ levels in the char. It should be noted that other char characteristics, listed in Appendix 8, have no significant relationship with the three independent variables.

The r² values for the above relationships are all less than 0.70. This indicates that changes in char characteristics can not be significantly explained with only the three independent variables. Since the r² values are low, quantitative relationships predicting char characteristics from only the independent variables were not feasible to develop.

6.6.2 Test Group 2

6.6.2.1 Objectives and Approach. The objective of test group 2 was to evaluate the effect of gas upflow velocity and gas average temperature on the chemical and physical properties of the produced chars. A complete factorial with three levels for each variable was planned.

The base operating conditions for the reactor were as follows:

Liquor feed: 11.4 lb solids/hr (16 g liquor/min)
 63.8% solids, liquor No. 41A
 2 mm nominal droplet size (tip 0.84/1.27 mm ID/OD)
 223 $\pm$ 7°F (106 $\pm$ 4°C)*
 Gas O₂ content: 10.7 $\pm$ 2.5%*

*Average $\pm$ 95% confidence limits.

Tests were started in the same manner as those for test group 1 (Section 6.6.1.1). The actual test levels for gas flow and gas average temperature are listed in Table 6-14.

Table 6-14. Test group 2 actual independent variable levels.

Tests	Gas Average Temperature,		Gas Flow	
	°F	°C	scfm	(std. L/min)
64	1485	807	2.0	57
65	1486	808	1.0	28
66	1668	909	6.0	170
67	1668	909	2.0	57
68	1668	909	1.0	28
69	1486	808	3.0	85
70	1310	710	1.0	28

The gas flow is measured and controlled via a mass flowmeter prior to entering the preheater. The gas average temperature is a weighted temperature average of the calculated gas temperature in each of the in-flight modules. Appendix 2 contains the details of these calculations. Only seven of the planned nine test

conditions produced collectable char samples. Only one test was done at 6 scfm (170 std. L/min) and only one test was done at 1310°F (710°C). The uncompleted tests had variable combinations which resulted in significant wall impingement, plugging, and/or uncollected char particles.

The metered gas flow for all of these tests was N₂. Since there was nominally 10% O₂ measured in the reactor, there had to be air leaks.

6.6.2.2 Results. The average and range of each chemical and physical char characteristic measured are listed in Table 6-15. The properties of the initial liquor are also listed for comparison. As was the case with the test group 1 data (Table 6-11), these chars are only partially pyrolyzed.

Table 6-15. Average physical and chemical characteristics of test group 2 product chars.

	Feed Liquor 41A	Product Char	
		Average + 95% CL ^a	Range
Fixed carbon, % ODS ^b	0	5.75 ± 3.14	2.67-12.3
Moisture, % ODS	63.8 ± 0.7	5.13 ± 2.96	1.44-8.57
Swollen volume, cc/g-solid	Approx. 1.1	11.0 ± 2.7	8.0-16.5
Bulk density, g/L	1400	107 ± 19	85-144
(All values, % ODS)			
C	35.7	31.8 ± 1.2	29.3-32.9
H	3.25	2.48 ± 0.54	1.90-2.71
O	34.3	35.6 ± 0.7	34.8-36.7
S	4.6	4.15 ± 0.16	3.98-4.41
Na	19.8	22.0 ± 1.0	21.0-24.2
K	1.4	2.33 ± 0.37	1.87-2.98
Na ₂ CO ₃	7.97	26.4 ± 6.1	20.7-39.9
Na ₂ SO ₄	5.87	7.65 ± 0.97	6.80-9.79
Na ₂ SO ₃	0.96	0.99 ± 0.22	0.68-1.38
Na ₂ S ₂ O ₃	8.19	4.13 ± 0.74	2.81-5.22
Na ₂ S	0	0.25 ± 0.05	0.14-0.29

^aCL confidence limit.

^bODS oven dried solids.

The char moisture content and bulk density averages are significantly higher than those from the test group 1 data. Also, the range of the moisture content is wider. The remaining characteristics are similar.

Table 6-16 lists the percent change of the major components. Based on the change in Na the average solids mass loss was 9.8%, with the range being from 5.7 to 18.2%. Component mass loss changes were first expressed on a Na₂ basis prior to calculating the percent loss to eliminate the influence of total mass loss.

Table 6-16. Average percent change in chemical components during char forming processes of test group 2.

	Average $\pm$ 95% CL ^a	Range
Carbon loss, %	19.5 $\pm$ 6.0	14.0-32.8
Hydrogen loss, %	46.5 $\pm$ 15.0	29.5-76.1
Oxygen loss, %	18.3 $\pm$ 9.6	5.8-34.0
Sulfur loss, %	17.8 $\pm$ 5.6	11.8-27.7
Na ₂ SO ₃ loss, %	54.3 $\pm$ 9.2	42.1-71.9
Na ₂ CO ₃ gain, %	196 $\pm$ 53	144-310
Na ₂ SO ₄ gain, %	17.0 $\pm$ 9.7	5.7-36.5
Na ₂ SO ₃ gain, %	-6.5 $\pm$ 22.0	-35.7-31.8
S ⁼ /S, %	2.4 $\pm$ 0.5	1.4-2.9
Fixed carbon/organic carbon, %	15.3 $\pm$ 9.5	6.8-35.9
Solids mass loss, %	9.8 $\pm$ 3.6	5.7-18.2

^aCL confidence limit.

The two main independent variables in test group 2, gas flow and gas average temperature, did produce significant variation in some of the measured char characteristics. Only a few, however, were consistent with thermal degradation of black liquor solids. The significant effects were evaluated with Student's t-test (Appendix 7). The relationships which were significant at the 95% confidence level (t-values > 2.45) are listed in Table 6-17. Component changes were evaluated on a Na₂ basis.

The gas average temperature has the dominant influence. The implication is that heat transfer to the droplet is quite important in determining the extent of mass loss in the early in-flight processes. Decreased moisture content and increased sulfide formation occurred with rising gas temperatures. The influence of increased residence time is shown via changes in the upward gas

flow. Increasing gas upflow velocities produced high char swollen volumes. All three of these trends are consistent with our current understanding.

Table 6-17. Char characteristics which had a significant relationship with one of the two independent variables for test group 2.

Dependent Variables	Measured t-Values of Significance Two Independent Variables	
	Gas	Gas
	Upflow	Temperature
<u>Reasonable</u>		
Char. moisture		-5.4
Char S ⁼ /Na ₂		+4.0
Char swollen volume	+3.1	
<u>Unreasonable</u>		
Char O/Na ₂		+6.7
Char H/Na ₂		+5.8
Char S/Na ₂		+2.8
Char SO ₄ ⁼ /Na ₂		-2.6

Note: An absolute t-value of 2.45 or greater implies a 95% confidence level for significance. See Appendix 7 for statistical methods.

The last four trends, however, are not consistent with current understanding. The data show increasing levels of O, H, and S as the temperature rises. All three of these should decrease as the volatiles are lost. The Na₂SO₄ level is shown to decrease. This too is counter to the findings of test group 1 that show an increase should occur because of the decomposition of Na₂S₂O₃.

During tests at the two lower temperatures (i.e., 1290 and 1470°F, 700 and 800°C) agglomerates formed in the in-flight module. There was also a significant amount of wall impact. The particles on the wall would detach and fall into the char collection vessel. The agglomerates or at least particles with significant time on the walls were undoubtedly in the collected product char samples.

The unreasonable results can be explained with the assumption that longer wall impacts and more agglomerates form at lower gas temperatures. With the effectively longer residence time, the extent of reaction and the amount of volatiles lost increases. The lower temperature test samples had both high moisture and high solids mass loss. This can be explained by a burning outer surface and a wet, still drying, inner core which is consistent with agglomerate formation.

A clear indication of the burning difference between test groups 1 and 2 is shown in Fig. 6-14 through 6-16. The data presented in these figures for test group 1 are all in dots. For test group 1 as the average moisture content decreases the solids mass loss increases, the amount of fixed carbon increases, and the amount of sulfide formed increases. This is consistent with the understanding that as the particle temperature increases the residual moisture is driven off. At very low average moisture contents the particle temperature reaches the point where pyrolysis begins. The degree of pyrolysis increases as the average moisture content decreases.

Figure 6-14. Solids mass loss as a function of the product char moisture content.

The test group 2 data in these same figures (6-14 through 6-16) are not all consistent with this premise. The 1650°F (900°C) tests indicated by the upward pointing triangles are consistent. Test group 1 was with a similarly high average gas temperature of 1615°F (880°C). Other tests in test group 2 were not consistent. The major difference was that their average gas temperature was lower, 1290 and 1470°F (700 and 800°C). The difference in gas temperature clearly enhanced simultaneous drying and pyrolysis. In the case of these tests the lower temperatures caused agglomerate formation which then enabled surface

burning while the inner core was still drying. The lower the temperature the higher the extent of pyrolysis for a given average moisture content, e.g., the 1290°F (700°C) test.

Figure 6-15. Fixed carbon formation as a function of the product char moisture content.

6.6.3 Test Group 3

6.6.3.1 Objectives and Approach. The objective of test group 3 was to evaluate the influence on burning of three black liquor variables: droplet size, solids content, and flowrate. A complete factorial with three levels for each variable was planned plus one additional test.

This test group had to be repeated because of very poor droplet formation with test liquor No. 41A. Since both groups of tests (3A and 3B) were completed and analyzed, both groups of results will be presented. Test group 3A represents a wide and sometimes uncontrolled particle size distribution, while test group 3B has good droplet size distribution. Liquors No. 41A and No. 41B are essentially the same (Section 5.2 and Table 6-19).

Figure 6-16. Sulfide formation expressed as the molar ratio of S^{2-}/Na_2 as a function of the char moisture content.

The base operating conditions for the reactor were as follows:

Liquor feed:	Liquor No.	3A	3B
		41A	41B
Injection temperature, °F		264-282	228-250
		°C	129-139
°C		129-139	109-121
Gas Flow:	scfm (std. Lpm)	4 (115)	4-6 (115-170)
Gas Temperature:	°F	1675-1679	1670-1675
	°C	913-915	908-912
Gas Oxygen Content:	%	21	17-19

The gas flowrate was at the lower value for test group 3B for all but tests 89, 90, and 91. Tests were started in the same manner as those for test group 1 (Section 6.6.1.1). The actual test levels for black liquor droplet size, solids content, and flowrate are listed in Table 6-18.

The droplet size was changed mainly by varying the injector tip size. The droplet size as a function of the measured injector droplet diameter for test group 3B data is shown in Figure 6-17. The relatively large amount of scatter (compared to the NBS data in Figure 2-3) is caused by the wide range of solids and injector temperatures used. The injector temperature selection was based on visual observation to achieve good droplet formation.

Table 6-18. Test group 3 actual independent variable levels.

Test Group 3A	Droplet Size mm, avg $\pm$ CL	Solids, %	Black Liquor	
			Flowrate,	
			g liquor/min	lb solids/h
73	6.2 $\pm$ 1.8	66.8	23.4	2.0
74	Not measurable	66.8	23.4	2.0
76	6.8 $\pm$ 1.8	66.4	23.4	2.0
77	6.6 $\pm$ 1.3	63.2	23.4	1.9
78	6.7 $\pm$ 1.3	61.1	23.4	1.8
79	5.8 $\pm$ 1.1	60.4	23.4	1.8
80	6.5 $\pm$ 1.4	64.8	22.4	1.9
81	5.2 $\pm$ 1.3	64.8	22.4	1.9
82	Not measurable	64.8	22.4	1.9
Test Group 3B				
83	2.8 $\pm$ 0.2	68.9	23.5	2.1
84	4.2 $\pm$ 0.6	68.9	23.5	2.1
85	2.5 $\pm$ 0.0	68.9	23.5	2.1
86	2.0 $\pm$ 0.3	59.6	16.1	1.3
87	2.9 $\pm$ 0.7	59.6	16.1	1.3
88	3.8 $\pm$ 1.3	59.6	16.5	1.4
89	2.2 $\pm$ 0.3	62.0	16.5	1.4
90	3.0 $\pm$ 0.6	62.0	16.5	1.4
91	3.6 $\pm$ 0.6	62.0	16.5	1.4
92	2.7 $\pm$ 0.3	62.0	16.5	1.4

The variation in solids was achieved by evaporating water from the liquor held in the feed tank prior to a test. For test 3A liquor 41A was initially heated to 215-220°F (102-104°C) for about 6 hours to raise the solids from 63.8 to 69%. Poor droplet formation began after this procedure. The liquor was dramatically higher in viscosity. Despite using high injector temperatures and reducing the solids level, good droplet formation was not achieved in test group 3A. The liquor apparently had undergone reactions which resulted in higher viscosity.

The flow rate variation was achieved by changing the speed of the Zenith positive displacement metering pump. Highly variable signals from the mass flow meter prevented a closed loop control of black liquor mass flow.

Figure 6-17. Relationship between injector tip inner diameter and the diameter of the formed droplet.

6.6.3.2 Results. The average and range of each chemical and physical char characteristic measured are listed in Table 6-19. The chars are only partially pyrolyzed.

Table 6-19. Average physical and chemical characteristic of test group 3 product chars.

	Test Group 3A			Test Group 3B		
	Feed Liquor	Product Char		Feed Liquor	Product Char	
	41A	Average $\pm$ 95% CL ^a	Range	41B	Average $\pm$ 95% CL ^a	Range
Fixed carbon, % ODS ^b	0	3.20 $\pm$ 1.00	1.59-5.15	0	3.59 $\pm$ 1.71	1.22-9.16
Moisture, % ODS	60.4-66.8	4.31 $\pm$ 1.87	1.94-8.33	59.6-68.9	5.28 $\pm$ 1.50	2.31-8.30
Swollen volume, cc/g-solid	Approx. 1.1	-- ^c	-- ^c	Approx. 1.1	4.47 $\pm$ 2.06	1.25-10.2
Bulk density, g/L	-- ^e	81.5 $\pm$ 12.3	58-103	1400-1460 ^d	121 $\pm$ 17	84-175
Higher heating value, Btu/lb-solid	5540	5151 $\pm$ 187	4830-5480	5453	5154 $\pm$ 188	4660-5450
(All values, % ODS)						
C	35.7	32.8 $\pm$ 0.67	31.1-33.9	35.5	32.7 $\pm$ 0.95	29.6-34.1
H	3.25	2.64 $\pm$ 0.18	2.16-2.85	2.95	2.68 $\pm$ 0.26	1.83-3.00
O	34.3	35.1 $\pm$ 0.49	34.7-36.7	34.9	35.2 $\pm$ 0.19	34.8-35.5
S	4.6	4.5 $\pm$ 0.09	4.3-4.7	4.6	4.6 $\pm$ 0.2	4.3-5.4
Na	19.8	21.7 $\pm$ 0.88	20.2-23.4	19.8	21.7 $\pm$ 1.20	20.6-26.1
K	1.4	2.82 $\pm$ 0.08	2.64-2.97	2.5	2.64 $\pm$ 0.17	2.43-3.14
CL	0.8	0.65 $\pm$ 0.19	0.49-1.26	0.5	0.54 $\pm$ 0.10	0.32-0.85
Material balance, % closure	99.8	100.2 $\pm$ 0.5	99.6-101.3	99.6	100 $\pm$ 0.5	98.7-101.2
Na ₂ CO ₃	7.97	20.9 $\pm$ 2.1	17.1-26.1	11.54	18.6 $\pm$ 3.31	14.0-27.8
Na ₂ SO ₄	5.87	7.60 $\pm$ 1.0	5.84-9.30	6.10	6.69 $\pm$ 0.49	5.06-7.45
Na ₂ SO ₃	0.96	1.30 $\pm$ 0.48	0.60-2.28	0	0.86 $\pm$ 0.30	0.30-1.46
Na ₂ S ₂ O ₃	8.19	4.65 $\pm$ 0.43	3.79-5.13	5.74	4.64 $\pm$ 0.51	3.50-5.90
Na ₂ S	0	0.33 $\pm$ 0.18	0.10-0.63	0	0.14 $\pm$ 0.06	0.05-0.32

^aCL - 95% confidence level.

^bODS - oven dried solids at 221°F (105°C).

^c--Not available, initial size too variable.

^dFrom micromotion sensor.

^eNot measured.

The listed physical and chemical characteristics indicate that product char was very similar between the two tests. The variation and wide range of conditions in the liquor independent variables account for the wide range for each observed property.

It is very interesting to note that at least in the early burning stages the large difference in initial droplet size and its distribution did not overshadow the other variables. For test group 3A the average initial droplet size was 6.3 ± 0.5 mm. For test group 3B the average initial droplet size was 3.0 ± 0.6 mm. This represents a nine fold volume reduction in the initial droplet size between test group 3A and 3B. Large changes in composition would have been expected based on such large mass differences.

The initial droplet size was so variable for test group 3A that it was not possible to estimate a reliable average initial droplet mass. The result is that swollen volumes are not available for test group 3A. It is encouraging that on average the material balance on both the feed and the product char samples have excellent closure.

Table 6-20 lists the percent change of the major components. Based on the change in the Na the average solids mass loss was 8.5% for both test groups 3A and 3B. Component mass loss changes were first expressed on a Na_2 basis prior to calculating the percent loss to eliminate the influence of total mass loss.

The characteristic changes of the early burning stages are noted again in these samples. The largest organic losses occur with the carbon and hydrogen. Sodium carbonate shows a very large increase followed by an increase in Na_2SO_4 . A large loss in $\text{Na}_2\text{S}_2\text{O}_3$ was again seen. Only a slight amount of Na_2S was measured in these tests. Some of the formed Na_2S may have been oxidized during sample collection or analysis.

Based on the data in Table 6-20 there are differences between test groups 3A and 3B. Test group 3A had higher losses of Na_2SO_3 and higher gains of Na_2CO_3 than test group 3B. This would suggest that test group 3A had undergone more

pyrolysis. The average bulk density and product moistures also support this premise. The average solids mass loss and the fixed carbon loss do not support this premise.

Table 6-20. Average percent change in chemical components during char forming processes of Test Group 3.

Compositional Changes, %	Test Group 3A		Test Group 3B	
	Average ± 95% CL ^a	Range	Average ± 95% CL	Range
Carbon loss	15.9 ± 5.1	6.9-26.2	15.6 ± 6.0	8.6-36.7
Hydrogen loss	39.2 ± 6.8	29.5-52.5	34.7 ± 9.9	14.7-64.9
Oxygen loss	16.6 ± 13.5	11.6-24.6	20.3 ± 4.0	12.2-31.3
Sulfur loss	9.7 ± 3.8	2.0-16.5	7.9 ± 6.8	-12.2-23.6
Na ₂ S ₂ O ₃ loss	47.9 ± 6.6	38.6-59.3	25.9 ± 9.6	1.2-43.3
Na ₂ CO ₃ gain	139 ± 17.4	108-177	46.0 ± 20	13.0-90.0
Na ₂ SO ₄ gain	18.0 ± 13.7	-3.4-43.9	0.16 ± 7.7	-22.9-10.4
Na ₂ SO ₃ gain	21.7 ± 41.0	-38.6-101	(Started at essentially zero)	
S ⁼ /S	2.98 ± 1.66	0.90-5.74	1.30 ± 0.53	0.48-3.0
FC/C	7.99 ± 2.58	3.88-13.3	9.22 ± 4.73	3.08-25.2
Solids mass loss	8.51 ± 3.70	1.98-15.4	8.52 ± 4.38	3.88-24.1

^aCL confidence limit.

One explanation for the above observations is that significant burning occurred on the reactor walls for test group 3A. Walls impact and subsequent burning would result in effectively longer residence times for the sample. The longer residence time would tend to compensate for the larger droplet size. More pyrolysis could also occur. Due to this apparent complication, only test group 3B results will be used to analyze the impact of the three independent test variables. Test group 3A was, however, analyzed in this regard and had similar but weaker trends than those from test group 3B.

The three independent variables caused consistent significant changes in a number of product char characteristics. A consistent significant influence is judged by Student's t-test (Appendix 7). Table 6-21 lists the significant influences.

Table 6-21. Measured t-values^a of significance. Three independent variables.

Dependent Variables	Three Independent Variables			Combination of Variables	
	Drop Diameter	Liquor Flow	Solids (Viscosity ^b)	Solids/ Diameter	Solids/ Temperature ^b
Char swollen volume	-5.0				
Char moisture	+4.3			-3.2/+6.7	
Gas O ₂ %		-5.4			
Char HHV			+2.5 (+2.2)		
Char CO ₃ /Na ₂			-3.7 (-4.2)		-2.4/2.9
Char K/Na ₂			-3.1 (-4.3)		-5.5/3.3
Char SO ₄ /Na ₂	-2.8				
Char CL/Na ₂	-2.2				
Char S ⁼ /Na ₂				+2.8/-3.2	

^at-Value of 2.26 or greater implies a 95% confidence level for significance.
See Appendix 7 for statistical methods.

^bTemperature is injected droplet temperature.

The black liquor viscosity at injection is included in parentheses with the black liquor solids. Note the very similar influence of these two. The viscosity actually measured was that in the feed tank recirculation line. This value was corrected to the injector temperature based on an experimentally measured $1/T(\text{absolute})$ vs. $\ln(\text{viscosity})$ relationship. Viscosity is thought to be the controlling property which influences the burning characteristics. The solids content is the way in which the viscosity was actually varied between tests. This concept will be discussed in more detail below.

The two dominant variables are the drop diameter and the solids content. As the drop diameter increases the extent of reaction is decreased, i.e., lower swollen volume, higher moisture content, and lower Na₂SO₃ content. The dependence of final char moisture and swollen volume is shown in Figure 6-18. Significant permanent swelling, i.e., about 2 cc/g-solid, begins at moisture contents of between 6 and 7%. From a practical viewpoint the particle is essentially dry at these levels. The particle size at which this level occurs will undoubtedly vary with the thermal environment of the particle. The trend of the fourth significant variable, the NaCl content, is not at first consistent with this premise. This point will be discussed later in conjunction with the K loss.

Figure 6-18. Char moisture and final swollen volume as a function of the initial drop diameter.

The reduction in gas phase oxygen with an increase in liquor flow is consistent with an increase in overall combustion as more solids are fed while maintaining a constant air flow rate.

Higher liquor solids and correspondingly higher liquor viscosities, showed a lower extent of reaction, i.e., higher high heating values and lower Na_2CO_3 . Finally, lower initial solids and higher droplet injection temperatures resulted in higher K levels in the final char. Lowering of the K level suggests at first an increase in the extent of reaction. More on this point below. Figures 6-19 and 6-20 present the data for the two most significant variables. Viscosity is used instead of solids content, since this is thought to be the controlling property.

Three variables produced significant trends in four combinations of two variables each. The absolute t-values are shown in Table 6-21. Lower initial solids and larger droplets resulted in higher char moisture contents. Higher initial solids and smaller diameter droplets produced larger quantities of Na_2S . Lower initial solids and higher droplet injection temperatures produced more Na_2CO_3 . Finally, lower initial solids and higher droplet injection temperatures resulted in more potassium being left in the char.

The results of the single variable dependencies listed in Table 6-21 imply that larger and more viscous droplets have a lower extent of reaction. Both of these conditions reduce the rate of heat transfer to the droplet interior. Larger diameters have less effective surface area per unit mass. Higher viscosities reduce the thermal conductivity and also hinder bulk vapor or liquid transport between the surface and the droplet interior. This situation increases temperature gradients within the particle and encourages surface burning while the inner core is still drying.

Visual observations made during this test group showed glowing particles, sometimes flaming. Since the volatility of potassium and chloride is relatively high compared to most inorganics, their decrease as either the size or the diameter increases can be explained by surface burning.

The interpretation of the significant two-variable combinations requires additional discussion. It is encouraging that where one of the two variables was a

Figure 6-19. Char Na_2CO_3 variation with initial liquor viscosity.

me a conclusion from the initial test group are listed below. Between the black and white stages and either the char bed or furnace wall. The black stage represents the largest stage and the early stages. The black stage represents the largest stage and the early stages. The black stage represents the largest stage and the early stages.

MOLAR RATIO K/Na IN FINAL CHAR

The three test groups are listed below. Between the black and white stages and either the char bed or furnace wall. The black stage represents the largest stage and the early stages. The black stage represents the largest stage and the early stages. The black stage represents the largest stage and the early stages.

Figure 6-20. Char K variation with Initial Liquor viscosity.

Test Group 3B

significant single variable the trend is the same. The injection temperature in combination with the solids level is significant. Higher injection temperatures imply a higher extent of reaction, i.e., more Na_2CO_3 formation. This also implies that less K is lost as the injection temperature is raised. With the higher temperatures the droplet will be less viscous, enhancing internal mixing and reducing the surface burning tendency.

The solids content in combination with the droplet diameter is also significant. Higher initial solids and smaller diameter droplets will decrease the char moisture content and increase the amount of Na_2S in the final char. The trend with diameter is understandable for char moisture. The trend with solids implies that initial moisture levels are more important than viscosity effects in determining final char moisture levels. The implication of the solids trend with Na_2S is that surface composition is more significant than bulk. Smaller particles also imply more Na_2S . This is to be expected since the surface is a greater fraction of the smaller particles.

Test group 3 results have shown that physical properties of inlet droplets have a significant influence on the early burning stages of black liquor. When the viscosity of the liquor is dramatically increased (in the case of test group 3A, inadvertently) the droplet formation process itself is significantly changed. The droplet size, solids content, and viscosity strongly influence the extent of particle burning. The size and viscosity, in particular, influence particle temperature gradients which determine the burning pattern. These two black liquor variables dominate the early in-flight processes.

6.6.4 Conclusions from In-flight Tests

The three test groups discussed earlier in this section studied the influence of key process variables on the early burning stages of black liquor. As presently practiced in the chemical recovery boiler, these early stages occur in flight between the black liquor nozzle and either the char bed or furnace wall. The major conclusions from the three test groups are listed below.

Moisture loss represents the largest single mass loss in the early stages. The initial droplet diameter, gas temperature, and initial droplet solids content

were the significant variables influencing the final char moisture content. Smaller diameters, higher gas temperatures, and higher initial solids lowered the final char moisture. Drying rate modeling and intermediate solids sampling during the early burning stages will be covered separately in Section 7.0. The other variables studied (gas phase O_2 content, liquor temperature, gas flowrate and liquor flow) did not significantly influence the extent of particle drying. Chemical changes in the solids begin to occur prior to complete moisture removal. Typically there would be between 1.5 to 5% moisture in the final char samples which had already begun to pyrolyze.

Solids mass loss during the early burning stages is mainly from thermal decomposition of organic components. There are, however, significant changes in the inorganic constituents despite the fact that the volatiles burning stage has just begun. The average percent losses of carbon, hydrogen, and oxygen (mainly organics) from the test groups ranged from 16 to 22%, 33 to 46%, and 11 to 20%, respectively. The average sulfur loss ranged from 8 to 18%. The specific gas components released during this period will be covered in Section 6.7.

The major inorganic transitions are the formation of Na_2CO_3 and the decomposition of $Na_2S_2O_3$. As organic decomposition proceeds the organically bound sodium is carbonated to Na_2CO_3 . The thermally unstable $Na_2S_2O_3$ decomposes to the more stable compounds Na_2S , Na_2SO_4 , and elemental sulfur. This reaction is significant since the tested mill liquor was oxidized and contained substantial quantities of $Na_2S_2O_3$. Many of the particles undergo surface burning which elevates surface temperatures to the gas temperatures. In these cases volatile inorganic components such as potassium and chlorides may also be lost.

Only a few of the independent variables significantly related to the chemical changes produced as solids were lost. The important variables were initial solids, initial droplet diameter, and initial droplet temperature. Higher solids imply lower Na_2CO_3 formation (lower degree of pyrolysis), increased K loss (high surface temperatures), more Na_2S formation (high surface temperatures), and less overall organic loss (lower degree of pyrolysis). Higher initial droplet diameters had lower swollen volumes, less Na_2SO_3 formation, and more Cl loss. Higher initial droplet temperatures imply increased carbon losses, increased Na_2CO_3 formation, and reduced K losses. The other test variables of gas flowrate, gas

O₂ content, and liquor flowrate were not significant. The effect of gas temperature was confounded by significant wall impingement at the lower temperature conditions and can not be discussed in this context. In Section 8.1.1 modeling of the mass loss during the entire volatiles burning stage will be discussed.

The observed chemical changes support the premise that initial droplet characteristics influence the early stages of black liquor burning. Thermal decomposition progress is directly related to the ability of the droplet to maintain good heat transfer characteristics during the drying stage. In general, lower viscosity initial droplets enhance the inner droplet heat transfer. With higher viscosity droplets, significant temperature gradients will develop. The surface temperature will rapidly rise, impeding external heat transfer to the droplet. In addition, the pyrolyzing surface produces a rigid char which hinders bulk fluid flow, hence heat transfer. During char formation voids are formed. These can effectively act as thermal insulators, further increasing the temperature gradients. The net result of sustained thermal gradients is overlapping of burning stages.

6.7 Pyrolysis Gas (Hydrocarbon/Reduced Sulfur)

6.7.1 Introduction

In order to understand the volatiles burning stage of black liquor combustion, tests were performed to analyze selected volatiles produced by pyrolysis of black liquor droplets at high temperatures, 570 to 2010°F (300 to 1100°C), in a nitrogen atmosphere. The gas produced was analyzed using the gas chromatograph described in Section 4.2.3.6.

6.7.2 Experimental Procedure

A furnace consisting of a mullite ceramic tube surrounded by electrical heating elements was used to heat the black liquor droplet (Figure 6-21). A nitrogen flow of 0.64 scfh (0.300 L/min) was fed into the reactor and the gas out of the unit was collected in an evacuated Teflon sample bag for 2 minutes. A black liquor droplet, suspended on a wire, was inserted through a 7/16-inch (11 mm) diameter opening. Testing with an oxygen meter showed that the above N₂ flow was sufficient to prevent oxygen from entering the reactor through this opening. The black liquor used was a mill liquor (No. 41A) at 67.4% solids. The black

liquor particles had a nominal size of 15 mg and were approximately 2.75 mm diameter.

Figure 6-21. Radiant single particle reactor used for hydrocarbon and sulfur gas release studies.

The gas sample was analyzed using the gas chromatograph mentioned above. This system will detect both hydrocarbons and sulfur compounds. The photoionization detector (PID) was used for H_2S . The remaining gases were detected with the flame ionization detector FID. The (FID) signal was connected to a Hewlett-Packard integrator. The experiment was run at seven different temperatures within the range listed above with three tests at each temperature. Test conditions are listed in Table 6-22. Before each test a standard gas containing methane, ethane, propane, and hydrogen sulfide was used to calibrate the GC.

6.7.3 Calculations

The retention time and height or area of each peak was measured and recorded from the strip charts for both detectors and the HP integrator for all 21 tests.

Table 6-22. Test condition for pyrolysis gas study.

Test Number	Temperature,		Mass, mg
	°F	°C	
4.1	577	303	15.2
4.2	568	298	15.6
4.3	572	300	15.1
5.1	842	450	15.1
5.2	833	445	14.4
5.3	838	448	16.0
3.1	1099	593	15.9
3.2	1103	595	15.6
3.3	1099	593	15.0
1.1	1364	740	14.8
1.2	1373	745	15.3
1.3	1368	742	15.4
2.1	1634	890	13.6
2.2	1634	890	14.3
2.3	1652	900	14.7
6.1	1908	1042	15.3
6.2	1913	1045	15.9
6.3	1917	1047	15.1
7.1	2003	1095	15.4
7.2	2007	1097	15.7
7.3	2012	1100	14.9

Analysis of the time data indicated that there are 11 time regions which corresponded to 11 chemical compounds (Fig. 6-22). From the retention times of the standard gases, the first 6 constituents were easily identified as methane, ethene, ethane, hydrogen sulfide, propene and propane. Other gases had been identified in prior work. The next components to appear on the GC are carbonyl sulfide, methylmercaptan, carbon disulfide, and dimethyl sulfide. The remaining constituents originally appeared to be two closely spaced peaks at 10.6 and 11.1 minutes, but are actually part of the broad peak of dimethyl disulfide.

All of the runs using the standard gases were examined. The height or area for each gas was recorded and used with the known concentration to calculate a response factor for all four standards for each of the seven runs (Table 6-23). The response factor (RF) was assumed to be equal for ethene and ethane and for propene and propane.

Figure 6-22. Gas chromatogram of the FID detector on the HP integrator. H₂S was monitored on the PID with a strip chart recorder.

Prior work with this GC system used a standard gas containing methane, methylmercaptan and dimethyl sulfide. Because both analyses contain methane as a standard gas, it was possible to convert the prior RF values to the present data. By assuming that the response factor was equal for carbonyl sulfide and methylmercaptan, and for carbon disulfide, dimethyl sulfide and dimethyl disulfide, all RF values for the 11 compounds were obtained (Table 6-23).

With these RF values and the height/area data the concentration of each constituent was calculated for each test. These values (ppm) were then converted to millimole per gram of initial black liquor solids (Fig. 6-23 to 6-25).

6.7.4 Results

In Fig. 6-23 to 6-25 the hydrocarbons, methane and sulfur compounds are plotted against temperature. Of all the components measured, methane was detected at the highest concentrations. It was also the only component to show increasing concentration with increasing temperature over the entire range of test conditions. Among the other hydrocarbons, ethene, ethane, and propene show maximum concentrations at temperatures of 1380, 1110, and 1110°F (750, 600 and 600°C), respectively.

Table 6-23. Retention times and response factor for GC used in pyrolysis gas study.

Chemical	Retention Time	Calculation Data				Height or Area
		FID	HP	Response Factor	Analyzer	
A Methane	0.35	0.35	0.26	8.65	HP	A
B Ethene	0.70	0.70	0.58	4.54	HP	A
C Ethane	0.85	0.85	0.73	4.54	HP	A
D H ₂ S	1.22			4.04	PID	H
E Propene	2.50	2.50	2.28	3.13	HP	A
F Propane	2.75		2.56	3.13	HP	A
G COS	3.70	3.65	3.44	9.46	HP	A
H CH ₃ SH			4.78	9.46	HP	A
I CS ₂	6.30	6.32	5.95	5.18	HP	A
J (CH ₃) ₂ S	7.35		6.90	5.18	HP	A
K (CH ₃) ₂ S ₂	10.6		9.97	5.18	HP	A
	11.10	11.15	10.3			

By assuming that the response factor was equal for carbonyl sulfide and methyl mercaptan, and for carbon disulfide, dimethyl sulfide and dimethyl disulfide. PID = Photoionization detector. FID = Flame ionization detector. HP = Hewlett-Packard integrator. H = Height. A = Area.

With these RF values and the height/area data the concentration of each component was calculated for each test. These values (ppm) were then converted to milligrams per gram of solids. Similarly, the sulfur compounds hydrogen sulfide, carbonyl sulfide, carbon disulfide, dimethyl sulfide and dimethyl disulfide show a maximum production in the temperature range 840-1110°F (450 to 600°C). Dimethyl disulfide had the highest concentrations of all the sulfur compounds and was measurable at all tested temperatures. Of all the components measured, methane was detected at the lowest temperature. The total carbon measured in the released hydrocarbon from each test was calculated along with the total sulfur measured (Figure 6-25). The total hydrocarbon had a maximum value of 54 mg C per g of solids at the highest temperature tested (1100°F, 600°C). This represents 15.5% of the organic carbon in the original sample. The maximum sulfur recovery was 31.8 mg S/g solids (70% of the original sulfur) at 1110°F (650°C).

Figure 6-23. Hydrocarbon gases vs. temperature.
Figure 6-25. Reduced sulfur gases vs. temperature.

These pyrolysis gas studies demonstrate that even for a single particle there is both a sulfur release and recapture mechanism. Below 1100°F (600°C) the release mechanism dominates. Above this level the recapture mechanism dominates. Earlier sulfur release studies (Brink, 1970) showed a similar sulfur maximum. One key difference was in the major sulfur component, i.e., Brink reported mainly H₂S. At present there is no clear reason for this difference. An explanation is being pursued.

In recovery boilers there will not be strict pyrolysis, i.e., thermal degradation in the absence of gaseous oxygen. Despite this fact, pyrolysis gas studies identify the reduced gaseous species next to the particle surface. When oxygen is present, oxidation of these gaseous species occurs. Because of the rapidity evolved water and the gases, oxygen is believed to be absent from the particle interior until the material is completely oxidized, hence pyrolysis proceeds in the particle interior as a more accurate representation of the particle burning studies. Since surface oxidation would raise the particle temperature, the maximum in the sulfur release

Figure 6-24. Methane vs. temperature.

Figure 6-25. Reduced sulfur gases vs. temperature.

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curve should appear at lower gas temperatures when oxygen is absent. With increasing particle temperature, especially above the melt point, more sulfur is retained as Na_2S .

The critical temperature for recapture is the temperature of the inorganics, not the gas temperature. The rates of capture appear to accelerate above the inorganics melt point. For a typical melt composition the inorganics melt point is 1345°F (730°C), close to the reported sulfur maximum in this study.

7.0 ANALYSIS OF DRYING RATES

7.1 Introduction

The in-flight module of the LPC process flow reactor system provides a unique opportunity to study black liquor droplet drying. Tests were performed to determine the drying rate of free falling black liquor droplets and how this rate is influenced by operating conditions. The results are not only reviewed by themselves but also in the context of an externally controlled heat transfer model. The data and model suggest a controlling mechanism for black liquor droplet drying.

7.1.1 Test Data

7.1.1.1 Experimental. During test group 3B intermediate black liquor samples were collected and analyzed for percent solids to study drying rates. The samples were collected at the SOS and at the base of the reactor, which correspond to distances of 43, 86, 136, and 180 inches (1.09, 2.19, 3.46, and 4.58 m) below the droplet injection point. During these tests the reactor was operating with upward flowing gas. The samples were collected in liquid nitrogen to prevent further drying of the liquor (see Section 4.2.3.8 for details). The conditions for these tests were listed in Table 6-18. For all of the tests the gas temperature and flowrate are constant. The most important variables for this series of tests were initial percent solids, initial droplet diameter and the distance of the particle down the reactor (Z). Z is directly related to residence time through the velocity of the particles. Other variables which could influence drying are feed temperature and viscosity.

7.1.1.2 Analysis. The drying rate was first studied as a function of Z, the distance the black liquor particle travels down the reactor. The analysis can be more easily performed if the percent solids is converted to a value which directly indicates water such as X (mg H_2O /mg solids) or X/X_o (mg H_2O /initial mg H_2O). X/X_o is plotted against Z in Figure 7-1 to 7-3. These graphs show that the drying rate is relatively constant until the particle is almost completely dry ($X/X_o < 0.2$), which generally occurs at $Z = 86$ inches (2.19 m) (mid SOS). This behavior, however, is not a strict constant rate period for drying. This will be discussed in more detail later.

Figure 7-1. Unaccomplished drying vs. distance from injection.

Figure 7-2. Unaccomplished drying vs. distance from injection.

Figure 7-3. Unaccomplished drying vs. distance from injection.

The relationship of $\ln(X/X_0)$ to Z also confirmed that the drying rate is relatively insensitive to the amount of water remaining in the drop. If the drying rate was proportional to X then $\ln(X/X_0)$ should be a linear function of Z . Only one of the ten tests showed such a linear plot.

In order to determine how drying is related to the initial droplet size, d , the evaporative flux was calculated as mg of H_2O removed divided by the initial drop surface area in mm^2 . This value is plotted as a function of drop diameter in Figure 7-4. The evaporative flux is approximately proportional to the droplet diameter, considering the evaporative flux over the entire reactor (total bar height in Figure 7.4). This is logical, since in all cases the final droplet is almost completely dried. Since the total amount of water removed is proportional to d^3 , then the evaporative flux will be directly proportional to d .

If only the drying which occurs before the top SOS is considered then, except for one series of tests (86-88), the evaporative flux is relatively constant (approximately $0.11 \text{ mg } H_2O/mm^2$). That is, before drying is complete the rate is proportional to the initial surface area of the droplet. In tests 86-88 the

drying rate is higher for the larger droplets, even in the first heater section. An explanation for this discrepancy is discussed in the next two paragraphs.

Figure 7-4. Droplet drying flux vs. initial droplet diameter. Test number shown on top.

An approximate correlation was developed to predict viscosity of the black liquor droplets at their initial feed temperature using viscosity values measured during these tests. This equation estimated the initial feed viscosity at approximately 80 cps for tests 83-85, 45 cps for tests 89-92 and for tests 86-88 the predicted viscosity was 10 cp. Although this correlation is based on limited data it is apparent that the initial viscosity of the black liquor was considerably less for runs 86-88 than for the other runs.

This difference in viscosity could explain the difference in the evaporative flux. With the higher viscosity droplets the internal movement of the liquor and vapor bubbles is somewhat limited, enhancing the formation of a stiff outer shell. This would mean the transfer of water through the outer shell and the transfer of heat in are the limiting factors. Drying rate would be proportional to the surface area. In the case of low viscosity black liquor droplets, not only does the larger drop show a higher evaporative flux but the smaller particle shows an

evaporative flux which is lower than average. If the droplets tended to form a hollow shell of uniform thickness, then the surface area developed would be proportional to the volume. The drying flux would then be related to d^3 , which is what is observed in Figure 7-4 for tests 86-88.

Based on the above data two equations can be developed to describe the drying rate in terms of the initial drop size, d , and the droplet position Z . For high viscosity droplets (> 20 cps) the result is

These equations describe the initial drying rate until the droplet is nearly dry ($X/X_o < 0.2$) which typically occurs at about $Z = 86$ inches (2.19 m). For an initial solids content of 65% the solids content where $X/X_o = 0.2$ is 93%. After this the drying rate is essentially zero.

7.1.2 Engineering Modeling

7.1.2.1 Background. The drying stage of black liquor burning has been the subject of a soon to be completed Ph.D. thesis at IPC (Robinson, 1988). A recent article covers low temperature drying (less than 392°F, 200°C) of black liquor droplets in air (Robinson, 1987). Robinson successfully modeled the drying process for the conditions studied. Since a similar approach has been attempted with the present drying data, a very brief summary of Robinson's findings will be discussed.

Black liquor drops dried in hot air form a surface skin and undergo repeated cycles of inflation and rupture. An externally limiting heat transfer model identified that the drying rates are insensitive to the increased surface area caused by inflation. As the drop dries, vapor bubbles nucleate in the moist drops, increasing the resistance to heat conduction. With a continuing heat

flux, the surface temperature then rises, reducing the driving force for heat transfer to the drop. The effect of the rising surface temperature is to reduce the temperature driving force offsetting the presumed increase in heat transfer due to surface expansion.

In the present work gas temperatures exceed the initial black liquor pyrolysis temperature. This means that the particle can proceed into the volatiles burning stage. As the surface temperature exceeds the minimum for pyrolysis, the particle surface begins to char, restricting further expansion and further reducing the heat flux to the particle. The expansion that occurs with pyrolysis is permanent. These differences need to be accounted for in adapting the low temperature model to the present high temperature data.

7.1.2.2 Results. The objective of the modeling work was to develop a predictive model for drying black liquor droplets in the in-flight module of the IPC flow reactor system. The model and method of solution have previously been discussed (Robinson, 1987). The important heat transfer equations are listed in Appendix 10. Particle velocities relative to the gas stream for residence time and heat transfer calculations were done via the same method as reported in Appendix 9.

Three process parameters were adjusted to develop the best model fit. The first parameter is the average droplet expansion for the initial 33 inches (0.84 m). Experimental data from the NBS short-height DPFR measured diameter expansion factors of 1.3 to 1.9 (Section 3.5.3).

The second parameter is the average droplet expansion for the remainder of its flight. The final swollen volume measurements for test group 3 also implied diameter expansions of 1.3 to 1.8 (Section 6.6.3.2). The final swollen volumes are somewhat less than actual in-flight swollen volumes. The product produced in these tests is only slightly pyrolyzed. As such, all the expansion is not permanent and the particles shrink when quenched. Test data for the average expansion over the last portion of the in-flight section is not available at this time.

The third parameter is the average solids content at which the surface temperature rapidly rises, reducing heat transfer to the droplet. Again, only the

final char moisture levels are available as an approximate cross check on this parameter. The assumed particle temperature varied linearly with solids from the inlet temperature to 570°F (300°C). This upper temperature is assumed to occur at average solids where the surface temperature rapidly rises. After this point the particle surface temperature is assumed to be the gas temperature.

A comparison of the fitted parameters with the measurements mentioned assist in describing the drying stage. The data and model comparisons are shown in Fig. 7-5 and 7-6. The distance down the reactor has been translated into a calculated residence time, consistent with the assumed droplet expansion. The wall impacts were assumed not to affect particle residence time as predicted by the model. The model with the appropriately chosen parameter values corresponds reasonably well to the data. The values used for the parameters are also consistent with the observed initial expansions, the presumed expansions that may have occurred in-flight, and the char solids content.

Figure 7-5. Comparison of drying model to measured test data for a high viscosity inlet liquor.

Figure 7-6. Comparison of drying model to measured test data for a low viscosity inlet liquor.

The main difference between these two figures is that the initial liquor solids and viscosity are different. The first breakpoint corresponds to the first 33 inches (0.84 m) of the in-flight module. At the second breakpoint the surface temperature begins to rapidly accelerate. The initially lower solids content liquor reaches a higher average solids content at the second breakpoint. Although breakpoint definition is more for model convenience than an actual phenomenon, there do appear to be three general rate regions. The continuing rise of the model after the final breakpoint is because the reactor walls are hotter than the reactor gas temperature.

By inspection the rates for the two cases appear quite similar in all three regions. Because of expansion differences between the two cases, however, the lower solids liquor has a slightly longer residence time. This is not a significant factor in explaining the higher solids level, since the last region has a very slow rate. The critical region is the second which ends when the surface temperature accelerates.

The parameter values that best fit the data imply that more swelling and more complete drying occur with the initially lower solids liquor. The increased swelling of lower initial solids droplets during drying enhances bulk mixing in the droplet which minimizes temperature gradients between the surface and the core. This produces on average higher solids contents prior to the surface temperature accelerating. Once the surface temperature has reached the gas temperature heat flux to the particle is dramatically reduced. Formation of vapor pockets in the particle also reduces heat conduction to the core. Viscosity is believed to be the main physical property that controls this phenomenon. Future tests will attempt to study the viscosity effect separately from a solids content change to verify this thesis. The lower solids droplets do require more time to dry.

8.0 RECENT RELATED RESULTS OF OTHERS

The research conducted on this contract represents only a portion of a fairly sizeable research effort in the black liquor combustion area. The results of our work in Sections 3 through 7 need to be combined with that of others before a summary of the current understanding of black liquor combustion can be presented (Section 9). The intent of Section 8.0 is to identify and recognize other contributions. It is not intended as an exhaustive and critical research review.

8.1 Recent Advances in Black Liquor Combustion

8.1.1 IPC Research

The IPC research effort, other than this contract, addresses aspects of the burning phenomenon best studied in single particle or more defined experimental systems. More recently an extensive mathematical modeling effort has been undertaken to place the research results into a structure consistent with the present recovery furnace. The modeling effort should work in concert with continuing experimental work to more effectively direct both efforts. Since the modeling effort is just beginning and has more direct relevancy to Phase 4 of this contract, only the experimental results which contribute significantly will be discussed.

Research in black liquor drying focused initially on the boiling point rise (BPR) as a function of solids content. The BPR enables the boiling point to be predicted under a wide range of conditions including during evaporation and drying in the furnace. Robinson (1986) developed the first consistent BPR data at solids levels above 85%.

Subsequent work (Robinson, 1987) studied the drying phenomenon at temperatures less than 340°F (170°C). In this work Robinson measured drying rates and photographically observed physical changes as droplets dried. His work covers solids content of 16 to 56%. Although Robinson's work indicates that drying tends to be controlled by external heat transfer to the droplet, the expansion that accompanies drying causes an internal heat transfer resistance. Robinson developed a model to describe this phenomenon for the conditions he studied. His

contribution to understanding drying at elevated temperatures is contained in Section 7.

Aspects of the volatiles burning stage which have been addressed include expansion during pyrolysis, total sulfur release, and the rate of mass loss. Miller (two in 1986) showed that expansion during pyrolysis (one of the processes occurring during the volatiles burning stage) was influenced both by process conditions and black liquor composition. Maximum swollen volumes under pyrolysis conditions occurred at 930°F (500°C). The largest compositional effect was the ratio of sugar acids to kraft lignin. A maximum in swelling occurred at nominally equal proportions. Swelling is caused by pyrolysis gases expanding a relatively pliable mass. The extent of swelling did not relate to the quantity of gas produced but to the dynamic rheological properties of the expanding surface.

Sulfur release during black liquor droplet burning (Cantrell, 1986) showed significant variation with both droplet size and initial solids content. Higher solids and larger sizes both resulted in less sulfur release from the droplets. Although Cantrell's study was done for complete burns under oxidizing conditions, it was presumed that most sulfur came off during the volatiles burning period.

The rate of mass loss during volatiles burning and identification of physical occurrences at various states of mass loss have been reported by Crane (1987). Initial droplet size is the dominant influence of mass loss. The oxygen content and temperature of the surrounding gas had only minor influences on the mass loss rate. Although no theoretically based model was developed for this complex stage, an empirical model with the above three parameters was established. This model serves as a guide to describing the volatiles burning stage.

Most of the char burning studies at IPC have been done in molten salt systems (Na_2CO_3 and Na_2S) with low concentrations of carbon. This work was directed by Cameron and has been reported elsewhere (Cameron et al. 1986). The sulfate-sulfide cycle was proposed as a primary mechanism for char burning under furnace conditions. Some single particle verification of this work is included in the later reference. Recently Aiken (1987) has reported on work which looks at char burning in environments with an excess of carbon. There is

consistency between the two experimental systems. The C/O ratio variation between systems produces variations in the CO/CO₂ ratio in the product gas. For the low C/O molten salt systems CO₂ is the dominant product. For the high C/O char bed system CO is the dominant product. Aiken's results showed that at high temperature the reactions tend to be mass transfer controlled, while at lower temperatures sulfate-carbon reaction rates can be limiting. At high temperatures mainly Na₂S is present, while at lower temperatures significant Na₂SO₄ can be present.

8.1.2 Other Work

Hupa (1985) has contributed significantly to the understanding of all burning stages. He worked with various mill liquor droplets in a radiant environment. The results included both times for the first three stages and measurements of final expansion as a function of selected compositional changes. Although burning times in Hupa's studies for all stages are longer than in the convective environment of the flow reactor, his data do present base liquor burning characteristics. Cooperative studies with Hupa are underway (on another project) to compare differences in the experimental systems.

Black liquor characterization (Fricke 1984, 1985) and droplet formation (Stockel, 1985 and 1986) work at the University of Florida (UFG) and the University of Maine (UMO), although not directly relating to black liquor burning, studies properties and parameters which are very significant in the drying effort. The jet break-up mechanism of droplet formation studied at UMO is analogous to that used in this project's droplet injectors. Their studies on surface tension have also suggested that this property is not one of the main controlling ones during the early in-flight processes. Surface tension is, however, expected to play a significant role in droplet formation. The rheological portion of the work at UFG addresses viscosity, which has in this report been tied closely to initial burning behavior. Their studies of the compositional and thermal treatment effects on viscosity are not only valuable to the present research but may contribute to its broader applicability.

Kubes (1984) and Milanova (1985) studied various parts of the volatiles burning stages. Kubes' focus has been mainly on expansion measurements and a measurement of pseudoactivation energies during this period. The expansion studies are less extensive but consistent with the work of Miller previously mentioned.

The activation energy studies, although not directly applicable to the present work, do identify that differences in liquor activities exist.

Milanova (1985) and Li and Van Heiningen (1985) have studied black liquor char burning. Milanova, in work with small TGA samples, identified what she called point of ignition. In reality it appears to be more closely related to the melting point of inorganics. In any event her work identifies that NaCl may be a significant parameter influencing char burning. Van Heiningen's work looks at char gasification at temperatures below the melting temperature of the inorganics. At this present time this work has not been closely studied in the context of this work.

9.0 CURRENT UNDERSTANDING OF BLACK LIQUOR BURNING

Although the present research and that of others is not yet complete, there has been significant advancement in the understanding of black liquor burning. Our current qualitative understanding of the phenomenon will be summarized in this section.

9.1 Drying

The early stages of black liquor burning, for conditions similar to recovery furnaces, are dominated by the influence of black liquor droplet characteristics. Heat transfer to and through the droplet is the controlling phenomenon. The three most dominant initial liquor effects are size, solids content, and viscosity. During drying the droplet swells and collapses in rapid succession, expanding its surface area and mixing the droplet contents. The extent of swelling and mixing determine the ability of the droplet to absorb heat. Volumetric expansions of 4 to 6 times the original have been noted.

When the droplet viscosity is increased, a reduction in swelling and mixing rates occurs, reducing heat flux to the droplet core. Bubble nucleation begins near the surface, creating voids which act as insulators. Since external heat flux to the droplet by the environment is initially unchanged, the surface temperature will rise. The increasing surface temperature then reduces external heat flux to the droplet. This situation effectively stops rapid drying of the liquor droplet above average solids levels of 90-95%. The surface progresses into the volatiles burning stage while the inner core is still drying.

A reduction in initial liquor viscosity improves inner droplet heat transfer, reduces inner droplet temperature gradient, and droplets reach higher average solids levels before surface burning. The influence of size is analogous to viscosity, with larger droplets developing larger temperature gradients. The influence of solids is first through viscosity, since they are exponentially related. Solids are, however, directly related to the extent of drying. Droplets with higher initial solids content dry faster and give chars with lower average moisture contents.

9.2 Volatiles Burning

When the surface temperature of the droplets exceeds approximately 400°F (200°C) thermal degradation (pyrolysis) of the solids becomes significant. The gaseous decomposition products will mainly be CO, CO₂, H₂O, hydrocarbons, and reduced sulfur compounds. The solid product will be highly aromatic char carbon, Na₂CO₃, and sodium salts of sulfur oxides in various oxidation states. During pyrolysis the particle undergoes permanent swelling as the generated gases expand the pliable pyrolyzing solids. Expansions during burning correspond to volumetric increases of 15 to 30 times the original volume. Both liquor composition and conditions to which the droplet is exposed influence the extent of swelling. The outer surface then rapidly increases in temperature, reaching and exceeding the melting point of the inorganics.

The droplet initial size and viscosity will affect the burning pattern in the early part of the volatiles burning stage. With increasing size or viscosity the outer surface can be fully molten while the inner core is still undergoing pyrolysis. If the particle remains intact while in flight, the pyrolysis gases will contact the molten outer surface. Such a condition is viewed favorably, since a major portion of the reduced sulfur gases would react and be retained in the droplet.

The extent of the swelling will depend on many factors. For recovery furnace conditions surface char formation should occur quickly, limiting the degree of expansion. The char surface is an effective buffer between the particle and the hot environment. The gas phase O₂ and the gas temperature have little effect on the rate of mass loss in this region. The dominant influence is from the initial particle size with only a secondary effect from the gas phase oxygen content. Particles with significant temperature gradients will have portions in the char burning stage while the remainder is completing the volatiles burning stage.

9.3 Char Burning

There is insufficient hydrogen and oxygen to completely volatilize all of the organic carbon present in black liquor solids. The remaining organic carbon is

referred to as char carbon. This carbon is dispersed among the char inorganics. For kraft char rapid burning rates occur when the inorganics are molten and there is an external oxygen source for the system, i.e., inlet air. Grace et al. (1986) have presented an extensive discussion of the main char burning mechanism.

Once the carbon has been fixed, oxygen must be added to form the volatiles, CO and/or CO₂. The proposed mechanism of Grace et al. (1986), the sulfate-sulfide cycle, transfers the oxygen from the air first to Na₂S to form Na₂SO₄. The Na₂SO₄ then is reduced to Na₂S by reaction with carbon, producing and releasing CO or CO₂. Our present understanding is that the cycle rate is controlled by oxygen mass transfer to the char. Under this condition the sulfur is mostly present as sulfide.

The ratio of CO/CO₂ produced during char burning influences the heat release. At 1880°F (1300°K) the relative endothermic heats of reaction with Na₂SO₄ for CO₂ and CO formation, respectively, are 506 and 1521 Btu/lb (1177 and 3539 kJ/kg). Aiken and Cameron (1987) in recent work have found that the CO/CO₂ ratio in the product gas was primarily a function of the initial system organic carbon and oxygen (both in the solids and in the gas) contents. For systems with low organic carbon (molten salt studies) the primary product is CO₂. Carbon monoxide is the primary product at high carbon contents such as particulate char beds of laboratory batch made char.

The physical size of the particle decreases during char burning. In forced convective environments, particles burn rapidly on the side closest to the impinging air flow. A zone of molten smelt forms, moving in the direction of the gas flow. As the zone moves the char structure gradually collapses. The burn is more homogeneous under stagnant or low oxygen conditions.

9.4 Smelt Coalescence

Toward the end of the char burn a very rapid collapse of the remaining structures signifies the start of the smelt coalescence stage. This occurs when the surface tension forces of the smelt exceed the structural forces of the char. The controlling parameter for collapse appears to be the carbon content. Smelt

coalescence is a stage primarily characterized by physical phenomenon. Although it occurs in a very brief time, typically only a few tenths of a second, it has a large influence on the particle's aerodynamic characteristics. Light fluffy char particles can be entrained, but if burned in-flight through the smelt coalescence stage, they will rain back on the bed.

Either toward the end of the char burn or at smelt coalescence the almost completely reduced particle can be reoxidized (i.e., Na_2S to Na_2SO_4) if there is sufficient oxygen. It is important to prevent this possibility, mainly by letting smelt percolate under the surface of an active char bed and moving toward the smelt spouts.

The four stages are shown pictorially in Figure 9-1.

DRYING

VOLATILES BURNING

CHAR BURNING

SMELT COALESCENCE

Figure 9-1. Four stages of black liquor burning.

10.0 FULL-HEIGHT DILUTE PHASE FLOW REACTOR (DPFR)

There are significant knowledge gaps in the current understanding. Some of these will be the subject of future work under the present contract. Sections 10 and 11 address the experimental changes which will be implemented in the near term future. Section 10 discusses the NBS system. Section 11 discusses the IPC system.

10.1 Objective

The results in the short-height DPFR (Sections 3.5 and 3.6) clearly demonstrated the desirability of extending the residence times of black liquor particles in reactor gases. The full-height DPFR will increase residence times and allow studies of black liquor droplets beyond the early in-flight stages. The full-height DPFR retains all the basic concepts of the DPFR described in Section 3.3, with a greatly increased reactor length. While the maximum height for observation of particles in short-height DPFR was about 3 ft (1 m), the full-height reactor more than triples this height to about 10.5 ft (3.2 m).

Before a description of the full-height DPFR, and its performance to date, the effect of the increased reactor height on the expected residence time will be demonstrated in Table 10-1. The velocities and residence times were calculated with the computer program used to obtain the analogous data in the short-height DPFR given in Tables 3-3 and 3-4. These estimates of residence times are realistic only up to ignition of particles, at which point the particle trajectories become erratic, usually turning upward and occasionally moving to the walls of the reactor (Section 3.7).

10.2 Equipment

A photograph of the full-height DPFR is shown in Figure 10-1. The lower parts of the reactor - consisting of the gas burner, the mixing section, the flow-straightening section, and the lower SOS - were described in section 3.3.1 as were the upper parts, consisting of the upper SOS and the exit section with the droplet injector. The reader is referred to these descriptions which will not be repeated here. In the full-height reactor, five sections are interposed

between the lower and upper SOS. Three of these are each 3 feet (0.92 m) long and the other two are additional SOS sections, each 6 inches long. Thus the total added height is 10.5 ft (3.2 m). These sections are partly interchangeable, allowing several modular arrangements. Two configurations, tested to date, will be described.

Table 10-1. Calculation of black liquor droplet/particle residence times in full-height DPFR 10.5 ft (3.2 m).

d_o , (mm)	d , (mm)	Calculation A			Calculation B		
		t_R	U_s	U_s	t_R	U_s	U_t
1.5	2.25	1.8	17.3 (5.27)	17.3 (5.28)	4.3	12.8 (3.92)	12.8 (3.92)
2.0	3.0	1.2	22.2 (6.77)	23.1 (7.04)	1.8	17.1 (5.23)	17.1 (5.23)
2.5	3.75	1.1	25.6 (7.81)	26.2 (8.00)	1.3	20.8 (6.34)	20.8 (6.34)

Velocity Units = ft/sec (m/sec)

t_R = particle residence time, sec

U_s = slip velocity

U_t = terminal velocity

Calculation A - no drying

Calculation B - complete drying

Assumptions: $T_g = 1562^\circ\text{F}$ (850°C)

$U_g = 10.6$ ft/second (3.25 m/second)

Droplet unexpanded for first 7.9 inches (20 cm) of flight

The first configuration is the one shown in Figure 10-1. The three 3-ft sections are ceramic tubes, 4-inch I.D. These are placed inside stainless steel tubes of the same length, 5.5-inch I.D., the ends of which have welded stainless-steel flanges designed to mate with SOS. The sections are surrounded by heater furnaces with temperature capability up to 1800°F (982°C). The top and the bottom SOS have windows to allow the viewing of the droplet injector tip and a short segment near the bottom of the reactor (see Section 3.3.1, short height DPFR, Configuration 2). The lower and the upper 3-ft sections are attached to these two SOS. The middle 3-ft section is separated from the lower and upper ones by the two additional SOS. These have three side-arms each to allow insertion of thermocouples, etc., as described in Section 3.3.1, but also have the capability of being heated by resistance heaters. In the second configuration of the full-height DPFR, the lowest of the 3-ft long sections is replaced by a transparent quartz tube of equal length (Figure 10-2). The arrangement near the bottom of

Figure 10-1. Full-height DPFR - first configuration.

Figure 10-2. Full-height DPFR - second configuration.

the reactor, thus, is almost the same as in Figure 3-2, except that the tip of the droplet injector, of course, is not in the SOS immediately above the quartz tube, but in the top SOS, about 7 ft (2.1 m) higher.

The gas-metering system, both for generation of reactor gases and for operation of the droplet injector, is the same design as that used to operate the short-height DPFR. It is described fully in Section 3.3.1. The entire photographic equipment (VCR and the high-speed camera with the accessories) has been transferred without change from the laboratory where it was used in the studies with the short-height DPFR to the high-bay area housing the full-height DPFR. A new exhaust system was designed and constructed to allow operation of the full-height DPFR with either positive or negative pressure inside the reactor. The system consists of an insulated flow duct attached to the exit section described previously, a silencer, and an induced-draft fan. The flow duct is equipped with an air-inlet port with vanes allowing variable air-intake areas. The I.D. fan can also be operated at continuously variable speeds up to 200 scfm (5.7 std. m³/min). These two variable features allow independent variations of total exhaust flow rates, and thereby temperatures into the I.D. fan, and the pressure in the DPFR. The latter is measured by a sensitive (Magnehelic) gage through a side arm in one of the SOS.

10.3 Performance

Performance characteristics of the full-height DPFR were tested mostly in the first of the two configurations (Figure 10-1), i.e., without the transparent quartz section at the bottom. The flowrate capability, of course, is the same as in the short-height DPFR and need not be discussed any more. The exhaust system was capable of handling negative pressures in the reactor at all flowrates. Temperatures were measured in two ways: by horizontal insertion of thermocouples through all four SOS and by the vertical lowering of a thermocouple from the top flange of the reactor to the lowest SOS. The characteristics and the limitations of the results obtained with the horizontally inserted thermocouples, discussed in Section 3.3.2, apply equally to the full-height DPFR.

The leads of the vertically lowered thermocouple are about 15 ft (4.6 m) long. They are shielded and insulated from each other by numerous ceramic "spaghetti"

segments, each 10 inches (25.4 cm) long. The lowest segment is provided with a wire ring, about 3.5 inches (8.9 cm) in diameter, supported by several radial spokes fastened onto the ceramic shielding. This arrangement allows sufficient flexibility for the device to be lowered through the droplet injector port from the top to the bottom of the reactor, with the thermocouple bead near the center axis of the reactor at all heights. Thermocouple traverses were made with unheated SOS, but with variation of furnace heater temperatures around the three 3-ft reactor sections.

The results of the temperature profile obtained in a test with the furnace heaters at a relatively low temperature of 1100°F (593°C) are shown in Figure 10-3. Two trends are quite clear. First the gas temperature, which is 1600°F (870°C) at the bottom of the reactor, approaches the heater temperatures near the top. This is true generally also with other heater temperatures. Second, heat losses at SOS locations are quite obvious. Again, this was the common feature of several tests with variations of three parameters: the initial gas temperature, the heater temperatures, and the gas flowrates. On the other hand, no effect of the pressure inside the reactor (positive or negative) was observed. The preliminary conclusion is that temperature drops are due largely to conductive heat losses, not to leaks of air into the reactor. In view of these results, it appears desirable to (a) heat the SOS and (b) operate the furnace heaters near the desired gas temperature.

The full-height DPFR has also been tested in the second configuration, with a transparent 3-ft observation section at the bottom (Figure 10-2). Only a few temperature checks were made, confirming the results which have just been discussed. In addition, to the above described heat losses, a large temperature drop along the length of the transparent section has been measured, as expected (see Section 3.3.2). This temperature drop does not appear to present a problem, because in the planned tests with the transparent observation section, virtually all of the droplet residence time will be spent in the upper, heated section of the reactor. The most important preliminary performance test in this configuration was the observation of droplet trajectories. The results of this test appear promising. As earlier in the short-height DPFR, most unignited droplets and particles were found to fall vertically to the bottom of the reactor and should, therefore, be measurable in the transparent observation section.

Temperature Profile in D.P.F.R.

Figure 10-3. Temperature profile, full-height DPFR.

11.0 FUTURE PROCESS FLOW REACTOR SYSTEM COMPONENTS

11.1 Down-flow Capability

One of the current problem areas of operational recovery boilers is particle entrainment in flue gas. These particles impact and adhere to heat transfer surfaces and under conducive conditions can block critical gas passages. The condition can worsen to limit or curtail operations. Identification of particle characteristics which promote this condition is needed. Since the original particles are small, typically perceived to be less than 1 mm, they exhibit low slip velocities. In order to document the burning characteristics, coflow testing of particles and gas are required. In the IPC process flow reactor system this can be accomplished in the downflow mode.

The downflow mode will be accomplished via several equipment changes. These are listed below.

- a. Add an air preheater and final heater at the top.
- b. Replace the original top with one that mates with the feed SOS and the final air preheater.
- c. Add a "Y" separator section between the base of the second-stage air heater and the Pyrex char catcher.
- d. Add the necessary ducting between the "Y" and the inlet to the incinerator for gas removal.

Figure 11-1 is a schematic of the process flow reactor system in the downflow mode. Since velocity profiles are slightly peaked toward the center and both the gas and the particles are traveling down, the particle-wall impact should be minimal. This will provide well defined residence times in a known environment. Intermediate samples at the three SOS and the final char/smelt sample will still be attainable.

11.2 Bed Burning Furnace Design

The char bed in present recovery boilers is essential for maintaining high reduction efficiency and low carbon levels in smelt. The physical and chemical character of the char bed plus the nature of the impinging air jets significantly

influence the bed's performance. The focus of Phase 2 work is to study char bed burning operations under a wide variety of conditions.

Figure 11-1. IPC process flow reactor in downflow mode.

The conceptual bed burning furnace design bases are listed in Table 11-1. The unit will be able to operate in either the continuous or semicontinuous mode. In the continuous mode feed char (and in some cases partially charred liquor) will rain onto the bed surface and smelt will flow out. Steady state operation will be attempted. In the semicontinuous mode a pile of char will be burned without additional char being added. Smelt will continually be removed. Burning rates in the semicontinuous mode will exceed that possible in the steady state continuous mode.

Table 11-1. IPC bed burning furnace design basis.

- Continuous and semicontinuous operation
- 1 ft² cross section
- Flexible bed and air port geometries
- Maximum temperature + 2000°F (+1100°C)
- Gas tight inner metal retort
- Modular electrical panel heaters
- Two-zone temperature control
- Continuous yet contained smelt runoff
- Optical and instrument access
- Manual sampling of bed and smelt
- Removable base

The maximum designed continuous burning rate is 12 lbs/hr-ft². In the semicontinuous mode the rate should reach and probably exceed 120 lbs/hr-ft². The latter burning rate is a nominal standard design value for commercial recovery boilers. The lower rate in the semicontinuous mode is a result of the nominal one square foot bed surface area available in the bed pan compared to the one-tenth square foot cross section of the in-flight section. The one square foot bed pan size was judged to be the smallest practical for realistic bed burning tests. At the higher rate the bed pan square footage would have been only 0.093 ft² (3.7 x 3.7 inches).

Figure 11-2 is a schematic of the bed burning furnace. The process is contained by a metal retort. The metal is Haynes alloy 556 (Cabot Corp). The inner parts are all removable for easy modification. These include the bed pan, the inner baffle and the air manifold, and inserted instrumentation. The height and angle of the bed pan are both adjustable.

The four large optical access ports on the front panel view the bed region and the zone above. The air manifold will have extensive pipes that extend through the insulation to the outside. Three levels are possible for the entry pipes. Other ports for instrumentation will allow the use of thermocouples, optical pyrometers, laser light scattering/extinction instruments, and others as identified. The two large circular ports on the rear of the unit allow insertion of

a high temperature borescope described in the next section. These ports can also be used for additional air introduction if needed.

IPC Bed Burning Furnace (Conceptual Isometric)

Figure 11-2. IPC bed burning furnace schematic.

The smelt flow from the bed pan will collect in a rectangular pan. This collection pan will be in an unheated extension of the metal retort. Smelt samples will be collected from the smelt flow as it exits the bed pan. Mild N₂ inerting will be done to prevent smelt oxidation.

Surrounding the metal retort are electrical panel heaters supplied by Therm Tec, Inc., Campbell, CA. These are capable of reaching element temperatures of 2190°F (1200°C). The heating elements are embedded in moldable refractory which is backed with 4-inch insulation. The heaters will be one inch from the metal retort

to maintain temperature uniformity. Heated panels are provided for the front, 2 "L" shaped side/back panels, and the entering top duct. The furnace will have 3 zone control. The top portion of all panel heaters will be on one controller. The bottom portion of the "L" panels will be on a second controller. The bottom portion of the front panel will be on a third. The entering pipe circular heater will be on a fourth controller. The top, bottom, and exit pipe will be insulated but unheated.

The maximum power delivery capability is as follows:

Lower front	2.8 kW
Top half	12.3 kW
Bottom half	9.3 kW
Top entering pipe	<u>3.6 kW</u>
Total	28 kW

The power supply will be with 240 VAC. The calculated ambient loss is equivalent to 12.2 kW (42,000 Btu/hr). Satisfactory steady state operation should be achieved with approximately 44% of the maximum designed power.

Corrosion testing of the Haynes 556 alloy in a pure smelt environment showed significant attack can occur. The metal surface lost 2% after 3 hrs. at 1725°F (940°C) in a typical smelt (75 Na₂CO₃ - 25 Na₂S molar percentage). The system was inerted by a N₂ purge. When air was introduced into this same smelt 20% mass was lost after a 1.5-3 hr exposure. The system was so reactive that the 100 g smelt charge "boiled" out of the containing alumina crucible. The encouraging note is that the portion of the coupon exposed only to the gas phase did not show significant signs of corrosion. This test confirmed that an alumina liner for the bed pan will be needed. It also showed that significant burning must not take place on the furnace walls.

The bed burning furnace will be delivered in early February 1987. The system should be operationally stable by late spring 1987.

11.4 High Temperature Borescope

The ability to observe and photographically document the combustion processes at various stages is essential. A high temperature borescope has been designed for

use with the process flow reactor. It will be supplied by Instrumentation Technology, Inc., Westfield, MA. A schematic is shown in Figure 11-3. The unit will be liquid cooled and contained in a 304 SS housing. The 90° lens will enable observations parallel to the flow of particles and gas. Its main function will be to continually observe char bed burning. This should be possible during periods of continuous feeding. The unit can also be inserted through the top SOS to inspect the in-flight section. This can only be done without liquor feeding. A gas purge port near the lens will help keep it free of fume. The observation end of the borescope can be fitted with an eye piece or C-mount for connection to photographic and video equipment.

11.5 In-situ Bed Temperature Measurements

Temperature sensing will be done primarily with sheathed thermocouples. Type-K thermocouples with an Inconel sheath will be encased in fused alumina thermowells.

The alumina protection is necessary to prevent rapid thermocouple corrosion. The thermocouples will be inserted through the instrumentation ports in the front panel of the bed burning furnace.

Optical temperature sensing will also be attempted. For these measurements sapphire rods will be embedded into the char bed. The emissions will be transmitted through the rods to optical temperature sensing equipment similar to that used in Section 3.8.1. Sapphire was chosen since it is pure alumina. Fused alumina has been quite resistant to smelt corrosive attack.

Small sapphire fiber samples were tested for corrosive attack in smelt. The fibers were tested at 1740°F (950°C) in a molten smelt (96.2 Na₂CO₃ - 3.8 Na₂S molar percentage). Two tests of 1 and 3 hour duration were conducted. Examination of the fibers with a scanning electron microscope showed no noticeable material loss. Figures 11-4a, 11-4b, and 11-4c show the SEM photographs. The 1 hour sample after water washing looked identical to the initial sample. The 3 hour sample had a build up of crystal like material on the surface. This may have been due to inefficient washing. The sapphire rods appear to be relatively stable in molten smelt. Optical transmission tests and a comparison with quartz will be conducted as a final check on this technique.

Figure 11-3. High temperature borescope to be used with the IPC PFRS.

There is an additional incentive for developing a method to transmit emissions to a detector outside of the furnace. Local characteristics such as gas species, particle concentrations, and velocities may be measurable.

a. Original rod

b. After 1 hour exposure

c. After 3 hours exposure

Figure 11-4. Scanning electron micrographs of sapphire rods after exposure to smelt.

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APPENDIX 1

VELOCITY PROFILES AND CALCULATION METHOD

A hot wire anemometer was used to determine the radial velocity profile in the IPC process flow reactor. The upward gas velocity was measured in the middle SOS, located between the lower and middle encasement heaters. The test was performed with the reactor and the air at a temperature of approximately 70°F (21°C). The velocity was measured at six radial points in the SOS ($R=0$, 0.5, 1.0, 1.25, 1.5, and 1.75 inches) and at seven flow rates (0, 2, 4, 8, 12, 16, and 20 SCFM).

The anemometer used maintains the hot wire probe at a constant temperature 943°F (506°C) (and a constant resistance) by adjusting the current through the probe. The measured value is a voltage which is proportional to the current through the probe. Using the measured voltage the heat loss from the wire is calculated as I^2R . The square root of the local gas velocity is a linear function of $I^2R/\Delta T$. The relationship between $\sqrt{V}$ and $I^2R/\Delta T$ is not known but can be calculated by an iterative procedure. The calculations were performed using the Multistat™ Spreadsheet (Appendix 7).

An initial value of the velocity at the center of the reactor $V(R=0)$ is calculated by assuming a flat velocity profile for each flowrate. Using the linear regression analysis in the Multistat program an equation was derived which gave velocity as a function of $I^2R/\Delta T$ at $R=0$. With this equation the velocity was calculated for each measured voltage in the data set.

By integrating the velocity over the area of the reactor a volumetric flowrate was obtained. The maximum velocity $V(R=0)$ was corrected based on the error between the measured flowrate and the integrated value. A new equation for velocity as a function of $I^2R/\Delta T$ was derived and the rest of the procedure was repeated two more times. At this point the last two sets of integrated flowrates were very close so the final values were used.

The velocity profiles obtained by this method are plotted on a single graph for each of the seven flowrates (pages Appen-1-4 through 1-9).

Theoretical velocity profiles were also calculated for both laminar and turbulent flows. The Reynolds number goes from 1600 at 4 SCFM to 3200 at 8 SCFM so the transition from laminar to turbulent flow should occur between these flowrates. In figures on pages 1-5 through 1-9 the measured velocity is plotted along with

theoretical velocity for laminar and turbulent flows at 20, 16, 12, and 8 SCFM. These figures show good agreement between the turbulent and measured velocity profiles.

At 4 and 2 SCFM the flow is theoretically laminar but the measured velocity does not agree with the calculated laminar profile in figures on pages Appen-1-8 and 1-9. At 4 SCFM the measured profile is very flat and at 2 SCFM the measured velocity was actually higher near the wall than at the center of the tube. The use of the hot wire probe is not recommended below velocities of 0.5 ft/sec due to convection effects, so there may be a large error in the 2 SCFM measurements.

The velocity was measured from the reactor center to the wall in only one direction. Additional tests are needed to determine if the velocity profile is symmetrical. Additional testing will also be performed to determine the velocity profile at a gas temperature of approximately 1292°F (700°C), which is the maximum temperature that this probe can tolerate.

VELOCITY PROFILES

IPC Flow Reactor

(MID SOS 70°F)

VELOCITY PROFILE (MID SOS, 20 SCFM, 70°F)

VELOCITY PROFILE (MID SOS, 12 SCFM, 70°F)

VELOCITY PROFILE (MID SOS, 8 SCFM, 70°F)

VELOCITY PROFILE (MID SOS, 4 SCFM, 70°F)

VELOCITY PROFILE (MID SOS, 2 SCFM, 70°F)

APPENDIX 2
TEMPERATURE PROFILE CALCULATIONS
IPC Process Flow Reactor

OBJECTIVE

The objective of these calculations is to determine the temperature of the ceramic reactor walls and the temperature of the gas as it flows through the reactor. These values are needed to calculate the heat transfer to the black liquor and its resultant drying rates. Temperature measurements during black liquor tests are not possible, since extreme fouling and even failure of thermocouples occur.

Temperature Measurements

A vertically traveling thermocouple was mounted on the top of the process flow reactor. The 1/16-inch type-K thermocouple was sheathed with an exposed bead at the tip. Surrounding the thermocouple was a 5/32-inch tube used as the radiation shield. There were four 1/16-inch holes in the tube near the exposed bead. A vacuum pump aspirated the hot gases through these holes, past the shielded bead, and out the annular space between the thermocouple and the tube. The bead rapidly approached the gas temperature.

The temperature of the metal and ceramic walls is assumed to be uniform in each section. The temperature of the metal is known for four different cases. These are listed in Table A2-1.

Table A2-1. Measured temperature data.

Section	Case 1		Case 2		Case 3		Case 4	
	C	F	C	F	C	F	C	F
Inlet gas	837	1538	900	1650	960	1760	1000	1831
Low SOS metal	524	974	600	1110	641	1185	649	1200
Low heater metal	800	1471	860	1580	940	1723	980	1795
Mid SOS metal	615	1140	590	1097	600	1111	602	1115
Mid heater metal	800	1471	860	1580	940	1723	980	1795
Top SOS metal	600	1140	589	1097	600	1111	602	1115
Top heater metal	800	1470	860	1580	940	1723	980	1795

Systems

For energy balance studies the flow reactor is divided into six sections which correspond to encasement heater and observation sections. These are shown in Figure A2-1. Each heater includes a ceramic tube which encloses the reactor gas stream. Each tube is then surrounded by an air space and a metal pipe. Although the observation sections are somewhat different, they were assumed to be the same configuration, only a shorter length, in order to simplify the heat transfer calculations.

Energy Balance

For each section of the reactor

$$Q_{mc} = Q_{cg} = Q_{g-out} - Q_{g-in}$$

These equations are used in a spreadsheet (Multistat™) procedure described in the next section. The heat transfer equations and nomenclature are also listed in Table A2-2.

Table A2-2. From metal retort to ceramic tube.

$$\begin{aligned} Q_{mc} &= Q_{NC} + Q_{Rad} \\ Q_{NC} &= h_{NC} A_m \Delta T_{m-c} \\ \frac{1}{Ah_{NC}} &= \frac{1}{hmA_m} + \frac{1}{hcA_c} \\ hm &= \frac{Nu}{L} = 0.59 \frac{k}{L} (Gr \cdot Pr)^{1/4} \Big|_{at \ T=T_m} \\ hc &= \frac{Nu}{L} = 0.59 \frac{k}{L} (Gr \cdot Pr)^{1/4} \Big|_{at \ T=T_c} \\ Q_{Rad} &= A_m f_{mc} \sigma (T_m^4 - T_c^4) \\ \frac{1}{A_m f_{mc}} &= \frac{1}{A_m F_{mc}} + \frac{1}{A_m} \left(\frac{1}{\epsilon_m} - 1 \right) + \frac{1}{A_c} \left(\frac{1}{\epsilon_c} - 1 \right) \end{aligned}$$

Assume: $F_{mc} = 0.82$

$\epsilon_c = 0.75$

$\epsilon_m = 0.60$

From Ceramic to Gas

$$Q_{cg} = Q_{con} + Q_{rad}$$

$$Q_{con} = A_c h_g \Delta T_{c-g}$$

$$h_g = 1.86 \frac{k}{D} \left(Re \cdot Pr \cdot \frac{D}{L} \right)^{1/3} \left(\frac{\mu_b}{\mu_c} \right)^{0.14}$$

$$\text{Assume } \mu_b = \mu_c$$

$$Q_{Rad} = \left(\frac{1 + \epsilon}{2} \right) A \sigma (T_c^4 \alpha_w - T_g^4 \epsilon_w) \text{ (gray body)}$$

$$\text{assume } \alpha_w = 0.0083$$

$$\epsilon_w = 0.008$$

$$\epsilon = 0.75$$

where:

A = area of surface

F_i = view factor

Gr = Grashof number

h_i = heat transfer coefficient

k = gas thermal conductivity

L = length of tube for a specific section

Pr = Prandtl number

Q_{cg} = heat transfer from the ceramic tube to the reactor gas

Q_{con} = convective heat flow

Q_{g-out} = heat energy of the gas out of the section

Q_{g-in} = heat energy of the gas into the section

Q_{mc} = heat transfer from the metal retort to the ceramic tube

Q_{NC} = natural convective heat flow

Q_{Rad} = radiant heat flow

Re = Reynolds number

f_i = gray body view factor

σ = Stefan-Boltzmann constant

α_i = absorptivity

ε_i = emissivity

μ_i = gas viscosity

Subscripts

b = bulk gas

m = at metal surface

c = at ceramic surface

NC = natural convective

g = gas

w = water

Figure A2-1. IPC process flow reactor sectioned for temperature profile calculations. Listed dimensioned sections are approximately the same in temperature. These are not the correct physical dimensions. See Table A2-2 for nomenclature definition.

Multistat™ Procedures

Spreadsheet

TEMP3 FILE. The temperature of the gas into the first section was measured at the outlet of the second-stage air heater. A ceramic wall temperature was assumed and then adjusted until $Q_{mc} = Q_{cg}$. Since the gas temperature in and Q_{g-in} are known, Q_{g-out} and the temperature out can be calculated. This temperature is then used as the inlet temperature to the next section. The procedure is repeated throughout the reactor.

TEMP4 FILE. The data calculated in TEMP3 was tabulated in a form that allows the temperature profiles to be graphed.

TEMP1 FILE. These calculations are similar to those performed in TEMP3, but a log-mean temperature difference was used to calculate the heat transfer to the reactor gas. This also required that the calculations be performed in a slightly different order. It was necessary to calculate an outlet gas temperature before the heat transfer rate to the gas could be established.

TEMP2 FILE. The data calculated in TEMP1 were listed in this file in a form that made it possible to produce graphs of the temperature profile. These data were also converted to metric form.

Results

The measured temperature of the metal retort and the calculated temperatures of the ceramic tube and the reactor gas are plotted against the reactor height at a heater setpoint of 1472°F (800 C) in Figure A2-2. These data are also plotted for [1580, 1724, and 1796°F] (860, 940, and 980 C) (Figures A2-3 thru A2-5). Figures A2-3 through A2-5 correspond to Cases 1 through 4 in Table A2-1. The gas flow rate for these cases is 6 scfm (170 std. Lpm). These graphs show that although there is a large temperature difference between the wall of the heater and the SOS (up to 630°F, 350 C) the gas temperature only varies 35-90°F (20-50°C). The largest change in the gas temperature occurs when the hot gas from the second-stage air heater passes through the lower SOS and support section.

Figure A2-2. Calculated temperature profiles of the metal housing, the ceramic inner liner, and the flowing gas compared with measured temperature values (t), Case 1. Encasement heater setpoint 1472°F (800°C).

Figure A2-3. Calculated temperature profiles of the metal housing, the ceramic inner liner, and the flowing gas compared with measured temperature values (t), Case 2. Encasement heater setpoint 1580°F (860°C).

Figure A2-4. Calculated temperature profiles of the metal housing, the ceramic inner liner, and the flowing gas compared with measured temperature values (t), Case 3. Encasement heater setpoint 1724°F (940°C).

Figure A2-5. Calculated temperature profiles of the metal housing, the ceramic inner liner, and the flowing gas compared with measured temperature values (t), Case 4. Encasement heater setpoint 1796°F (980°C).

Table A2-3. Average reactor gas temperature, calculated vs. measured.

Heater Setpoint	Calculated Gas Temp.	Measured Gas Temp.
800	783	746
860	834	805
940	901	872
980	937	913

The average gas temperature for a given test is taken as a length weighted average of the calculated gas temperature. The lengths used for this weighting are shown in Fig. A2 1.

The reactor has a strong tendency to eliminate the effect of varying inlet gas temperatures (Figure A2-6). If the inlet temperature is reduced by 180°F (100 C), the gas reaching the outlet of the lower heater is only about 72°F (40 C) lower. Further up the reactor the difference becomes even less.

The temperature of the ceramic liner is very close to the temperature of the metal retort. For future work it is probably adequate to use the metal temperature to calculate the heat transfer to the gas.

Figure A2-6. Calculated gas temperature profiles in the reactor as a function of varying inlet gas temperatures. The gas flow used was 6 scfm. Encasement heater setpoint 1580°F (860°C).

APPENDIX 3
COMPUTER DATA ACQUISITION PROGRAMS
IPC Process Flow Reactor

GENERAL DESCRIPTION

The IPC process flow reactor data acquisition system consists of several parts. Data acquisition programs reside in the IBM PC XT computer, which is interfaced with an ISAAC 2000 computer. ISAAC 2000 is connected to the sensors in the process flow reactor pilot installation via different boards in ISAAC 2000.

IPC developed programs provide communication between the IBM XT and the ISAAC 2000 and use the ISAAC 2000 data acquisition system to continuously acquire, convert, and store digital counts of the data from sensors installed in the reactor system. The counts are stored together with the time for subsequent Multistat™ statistical analysis.

Programs also allow for manual entry of values describing the test conditions, list some of the data on the printer, and draw temperature curves for one channel at a time.

The black liquor flow reactor data acquisition system configuration is shown in Figure 4-11. First the main programs are described. Second, the flow charts for the main programs are displayed in Figures A3-1A through A3-13.

PROGRAM DESCRIPTIONS

BLSTART

The purpose of this program is to store the starting values for the process flow reactor - test and start data acquisition on the ISAAC. The program is run once at the beginning.

How to start the program: Type BLSTART on the DOS command level.

Batch file name : BLSTART.BAT (basica bstart /f:4)

Program name : BSTART.BAS

Datafiles used by the program: BLSTART.DATA, TESTNUM.DATA TIME.DAT, COM1
(communication file)

Program description:

The program asks you if you have copied the previous test files on the diskette. If you answer "n" (or "N" = no), the program ends. After copying the files you start the program again by typing BLSTART.

If you answer "y" (or "Y" = yes), to the copy question, the program deletes the previous datafiles. After that the program asks you to give the starting values for the new test. The test number is checked against the test number file and if it is found, a new test number is requested. The other starting values are checked by the program, so that they are within the allowed limits, these are:

- black liquor number	0-50 (integer)
- solids content (%)	60-85 (decimal)
- injector tip size (mm)	0.5-5 (decimal)
- target average gas temperature (Celsius)	200-1000 (integer)
- target gas flowrate (scfm)	0-25 (integer)

The program returns the entered starting values to the screen and asks if the data were entered correctly. If you answer "n" (or "N" = no) the program continues to request new starting values until the data are correct. After the starting values are stored the program stores the starting time for the test which also serves as the time for the first collected data record in BLVIEW, opens the communication line (com1), checks the communication line, clears the task and data buffers, defines the string containing instructions to read the desired channels on different devices as a task, turns the continuous mode on, and sends the task to ISAAC. I-160 channels are read twice because of the long settling time. ISAAC checks the syntax of the task and, if it is correct, starts the data acquisition.

The message

DATA ACQUISITION STARTING RIGHT NOW!

appears on the bottom of the screen. Finally, the program gives the program menu and returns control to DOS. In case there is a communication failure between IBM and ISAAC and the program is not capable of starting the data acquisition on ISAAC, the error message

***** get help: communication failure *****

appears on the bottom of the screen. After that the program ends, by giving the program menu and returning control back to DOS.

If communication failure or another condition, which prohibits continuing the program exists, the person responsible for the data acquisition programs should be contacted.

BLVIEW

BLVIEW consists of two programs, BPOINTS.BAS and APUVIEW.BAS. The purposes of the programs are to interrupt data acquisition in the ISAAC, transfer and store collected data in the IBM, and request the next action. Options exist to view the data on the monitor and continue data acquisition in the ISAAC or to end the data acquisition. BLVIEW is programmed to run for six hours without interrupting data acquisition. Data acquisition can continue as long as wanted by running BLVIEW every six hours.

How to start the programs: Type BLVIEW at the DOS command level

Batch file name : BLVIEW.BAT
(basica bpoints /c:26624
basica apuview /c:20480 /f:4)
Program names : BPOINTS.BAS, APUVIEW.BAS
Datafiles used by BPOINTS.BAS: TIME.DAT, COM1, DATAP.DAT
Program description (BPOINTS.BAS) :

The program opens the communication line (file), and sends interruption code [CHR\$(3)] to the ISAAC to break data acquisition, the command to stop continuous mode, and the command to empty the buffer to the IBM-side. The program reads the

number of the datapoints collected during the data acquisition, and writes the data to the file.

The BLVIEW program reads the data for six hours, because the program which handles the data (APUVIEW.BAS) ran out of memory.

Datafiles used by APUVIEW.BAS : BLVIEW.DAT, TIME.DAT, COM1, DATAP.DAT

Program description (APUVIEW.BAS) :

The program gives two options; either view and store the collected data and continue data acquisition on the ISAAC (option v) or end the data acquisition on the ISAAC (option e). In both cases the program reads the time for the first record to be stored, and the number of data collected and stored by BPOINTS.BAS. It then opens the communication file, transfers the data from the ISAAC buffer to the IBM in two hour shifts, and finally stores them on the hard disk. Time variables are increased by one minute for each record to be stored. When using option v the time for continuing data acquisition again is stored and the data collected for the last minute is displayed on the screen following its conversion into the desired units. After that the program checks the communication line and clears the data buffer on ISAAC, turns on the continuous mode and sends the task to the ISAAC to continue data acquisition.

When using the option e the last minute values are not displayed on the screen. When all the data are stored on the disk the message

END OF TEST

appears on the bottom of the screen.

The program reverts to the program menu when any key is hit. In both cases when a second key is hit the computer returns the control back to DOS.

Channel codes and names are in Fig. 4-11.

BLMULTI

The purpose of the program is to change the BLVIEW.DAT - file (where the collected data is) into the MULTISTAT™ form which the statistical package, accepts.

How to start the program : Type BLMULTI at the DOS command level.
Batch file name : BLMULTI.BAT (basica bmulti)
Program name : BLMULTI.BAS
Datafiles used by the program : BLVIEW.DAT, BLMUTLI.DAT
Program description:

The program reads the input file, BLVIEW.DAT, and changes the minutes so that the first one is 0 and the increment is 1. The output file is a sequential file with the comma being the delimiter. The program gives messages when all the records have been written. Finally, the program gives the menu.

CALIBR

The purpose of CALIB is to facilitate instrument calibration. It gives the temperature or count for the given channel code about every 5 seconds.

How to start the programs: Type CALIBR at the DOS command level
Batch file name : CALIBR.BAT (basica clibr)
Program names : CLIBER.BAS
Datafiles used by the program: COM1 (communication file)
Program description:

The program requests the channel code to be sampled, opens the communication line to the ISAAC and sends the instruction to read the desired channel. The program empties the ISAAC buffer to the IBM-side, and if it is a thermocouple reading converts the reading into temperatures, and prints the channel code, temperature (if thermocouple) and counts on the screen. Press any key to stop program execution.

Figure A3-1A. Computer program flowsheet for BLSTART.

Figure A3-1B (Continued). Computer program flowsheet for BLSTART.

Figure A3-1C (Continued). Computer program flowsheet for BLSTART.

Figure A3-2A. Computer program flowsheet for BLVIEW.

Figure A3-2B (Continued). Computer program flowsheet for BLVIEW.

Figure A3-2C (Continued). Computer program flowsheet for BLVIEW.

Figure A3-3. Computer program flowsheet for BLMULTI.

Figure A3-4. Computer program flowsheet for CALIBR.

APPENDIX 4

PROGRAM FOR CALCULATION OF DROPLET TERMINAL VELOCITIES

The program calculates the dynamics of a spherical droplet falling in a vertically moving stream of gases. The time at injection of the droplet into the gas stream is defined as $t=0$. The equations of motion contain three parameters: time after injection, position, and velocity. If one of these is specified, the program calculates the other two. For example, if time is an input, the particle velocity and its position are calculated. Since the velocity approaches terminal velocity at long times, it was convenient to express it in terms of percent of terminal velocity.

Several initial conditions can be used. The particle can be at rest and then fall into a stagnant or an upward moving gas. For another initial condition, the particle could have an initial velocity and be falling in a stagnant or an upward moving gas.

Calculations of particle velocities are done at 0.001 second intervals. If the particle is initially at rest and then falls into a stagnant gas, the free-fall equations of motion are used to calculate the velocity and displacement in the first time interval. For subsequent successive calculations, and for all other calculations that have initial gas or particle velocity, drag forces are included. For calculating the drag coefficient, the particle Reynolds Number is calculated first and then the drag coefficient. The different correlations for drag coefficient and the range of Reynolds Numbers for which they apply are given in Table A4-1. Table A4-1 also includes the associated terminal velocities. The drag force, $F_D = C_D U_S^2 \rho_g S/2g$, where S is the projected area of the particle normal to the flow, is applied to the equation of motion to calculate the particle velocity and position. The net particle displacement and terminal velocity is calculated and updated for each incremental time.

A second version of this program calculates the particle velocity and displacement for slightly more complicated initial conditions, with a particle initially at rest falling into a gas moving in the same direction. The particle is first accelerated by drag forces and then passes through a point where it has the same velocity as the gas with no net drag forces. Beyond that point, the drag has a

retarding effect, so the particle has a lower velocity than in free fall. All other aspects of this program are the same.

Table A4-1. Formulas used for particle velocity calculations.

Flow Regime	Re	C_D	U_t
Stokes'	< 0.5	$24/Re$	$\frac{(\rho_p - \rho_g) g dp^2}{18 \rho_g \nu}$
Intermediate I	0.5 to 30	$28/(Re)^{3/4}$	$\left[\frac{(\rho_p - \rho_g) g (dp)^{7/4}}{21 \rho_g \nu^{3/4}} \right]^{4/5}$
Intermediate II	30 to 730	$12/(Re)^{1/2}$	$\left[\frac{(\rho_p - \rho_g) g (dp)^{3/2}}{9 \rho_g \nu^{1/2}} \right]^{2/3}$
Newton's	> 730	0.445	$\left[\frac{3(\rho_p - \rho_g) g dp}{\rho_g} \right]^{1/2}$

g - acceleration due to gravity

ν - kinematic viscosity of gas

ρ - density

Subscripts: g - gas

p - particle

APPENDIX 5

APPARATUS FOR MEASUREMENT OF PARTICLE TRAVEL TIMES

Despite provisions for optical access, neither the NBS dilute-phase flow reactor nor the IPC process flow reactor allow continuous observation of a falling particle over the entire reactor length. The residence time of a falling particle between two points in the reactor separated by opaque segments must be obtained by timing between the points. The NBS effort, therefore, contained a brief task to demonstrate the feasibility of producing timing signals by the scattering of laser radiation from a falling black liquor droplet. Detection of scattered light was chosen because the commonly used light-interruption techniques are not applicable when the exact trajectory of the falling particle is not known. While it has been shown in both flow reactors that droplet trajectories before ignition are nearly vertical, they can certainly not be predicted to the required accuracy of about a millimeter, which is the order of magnitude of both the laser beam and the droplet diameters.

The simple demonstration at NBS was made, without any special instrumentation purchases for this task, with optical components which were on hand. These included a 4-mw helium-neon laser, a cylindrical lens and a photodetection system. The lens was positioned so as to expand the laser beam into a horizontal sheet having a cross-section of about 6 cm (2.5 inches). Alumina spheres, water droplets, and black-liquor droplets, with 1 to 2 mm diameters were dropped from a height of about 30 cm through the sheet. Scattered light could be seen briefly from all directions as each droplet passed through the beam.

To record the scattered light, a flexible fiber was pointed toward the area where the falling droplet was expected to cross the sheet beam. At the exit end of the fiber the optical signal was focused, by means of a lens, onto a silicon photodiode with an amplifier and displayed on a CRO. The angle of the entrance end of the fiber relative to the sheet beam was varied empirically to maximize the scattered signal. Although the arrangement clearly was not optimized, signal-to-noise ratios up to about 4 were observed.

A detailed list of recommended optical components was assembled and sent to IPC for construction of a more elaborate light-scattering apparatus to be used in

the IPC process flow reactor. In particular, it was recommended to include a narrow band-pass filter for the 633 nm laser line in order to reject the background luminosity in high-temperature experiments.

APPENDIX 6
ANALYTICAL METHODS

Process measures

- a. High heating value - essentially TAPPI Test Method T 684 pm-84.
- b. Sulfated ash - TAPPI Test Method T 625 ts-64.
- c. Residual active alkali - TAPPI Test Method T 625 ts-64.

Fixed carbon determination in char

- a. Use dry ground sample.
- b. Weigh sample in duplicate.
- c. Using a 250 mL beaker with 3 boiling balls, bring to a boil in 100 mL distilled water.
- d. Filter through a tared 11 cm Whatman GF/A glass microfibre filter.
- e. Wash with approximately 100 mL 1 N NaOH.
- f. Wash with approximately 100 mL 1 N HCl.
- g. Wash with approximately 100 mL distilled water.
- h. Dry under N₂ in a vacuum oven @ 105°C for 2 hours, weigh, redry for 1 hour and reweigh.
- i. Percent fixed carbon = $\frac{\text{weight (h)}}{\text{weight (b)}} \times 100 = \% \text{ fixed carbon.}$

Soluble organic carbon (SOC) and total inorganic carbon (TIC) in filtrate from char washing

Procedure specified for use with the Beckman Instruments TOCAMASTER Model 915B. The char sample is boiled in water. The filtrate is separated into two parts. The first part is analyzed as is. The evolved CO₂ from the instrument is a measure of the total carbon (TC). The second part is acidified to precipitate the Na₂CO₃. The precipitate is removed. The sample, containing only the organic carbon, is analyzed. The SOC is measured directly from the last analysis. The TIC is the difference between the TC and the SOC.

Lost carbon

The C/Na ratio in the original black liquor solids is compared to the C/Na ratio in the char. The difference is the lost carbon. It is expressed as a percentage of the original C/Na ratio.

Composition measures

- a. NaOH - calculated difference between residual active alkali and Na₂S.

- b. Na_2S - NCASI Technical Bulletin No. 68.
- c. Na_2CO_3 - Ion chromatography exclusion.
- d. Na_2SO_4 - TAPPI Test Method T 699 pm-83.
- e. Na_2SO_3 and $\text{Na}_2\text{S}_2\text{O}_3$ - ion chromatography.
- f. Solids - surface area extended via ignited sand. Dried at 105°C (221°F) in a forced air convection oven for at least 6 hours, preferably overnight. TAPPI T-650 pm-84.

Elemental analyses

- a. Na - perchloric acid digestion followed by flame emission.
- b. K - same as Na.
- c. S - Schoniger flask oxidation followed by TAPPI Test Method T 699 pm-83.
- d. Cl - TAPPI Test Method T 699 pm-83.
- e. C - measured by Huffmann Laboratories, Wheatridge, Colorado.
- f. H - same as C.
- g. O - same as C. Merz modification.

COMBUSTION TESTS

Pyrolysis Swollen Volume

A black liquor droplet at room temperature and nominally 40 mg (3.8 mm) in total mass is suspended on a wire within a wire spiral. The solids have been measured. The sample is hung from the Cahn microbalance in the convective SPR (Fig. 6-1). The reactor is sealed, then 932°F (500°C) N_2 flows over the droplet. Photographs are taken as the droplet swells. The particle maximum volume is determined from the largest area measurement of the photographs. The calculated swollen volume is that of a sphere with the same measured frontal area. Dividing this volume by the original mass of the droplet solids yields the specific swollen volume.

Combustion Swollen Volume

A nominal 9 mg (2.3 mm) droplet is burned in air in the convective SPR (Fig. 6-1). The air temperature is 800°C (1472°F). High speed movies (to be described later) are taken and the frame where the largest volume occurs is blown up. Measurements are then made analogous to the pyrolysis volume measurement.

Time to Ignition

During the combustion tests described above medium speed films were taken of the droplet burns. Both color and black/white were used. Speeds were either 32 fps or 64 fps. When the damper opens in the SPR the hot air impinges on the particle. This is time zero. Ignition is the time when the first glow of burning volatiles is seen on the particle. Time to ignition is the difference between these times.

Reaction Time from Ignition to Maximum Volume

The time from ignition to the maximum volume of the swollen char particle was obtained by measuring film length. The volume of the flame front is not included unless the particle outline cannot be distinguished. This was converted to time.

Reaction Time from Ignition to Smelt Bead

This is the time from the maximum volume until the char mass collapses into a tight smelt bead. The first appearance of the smelt bead is the measurement point. This continues to glow for some time until the inorganics are fully oxidized. The difference between this time and the time to maximum volume is the char burning time.

Pyrolysis Normalized Rate

During the pyrolysis described above the microbalance records the droplet mass loss. The mass loss is approximately linear. The slope of the mass loss vs. time plot divided by the mass of the initial solids is the pyrolysis normalized rate. The wire spiral around the droplet maintains a relatively constant drag despite a changing particle size.

Combustion Normalized Rate

The same procedure described for the pyrolysis normalized rate is done, except in air, with nominally a 9 mg (2.3 mm) droplet and at 1472°F (800°C) to obtain the combustion normalized rate. The slope of the mass loss vs. time curve on the approximate linear region is linearized. This is during the volatile burning stage. The slope divided by the mass of the initial solids is the combustion normalized rate.

APPENDIX 7

STATISTICAL METHODS

Analysis of the test data from the IPC process flow reactor was performed mainly through the use of the DCS Multistat™ spreadsheet program on the IBM XT PC. Multistat™ is a product of Davell Custom Software, Cleveland, TN. The data collected during the tests by the data acquisition system are stored in a Multistat™ spreadsheet. These data are then reduced to a single value for each variable which is the average value during steady-state operating conditions. These average values for each test are then transferred to another file which contains data from all of the tests in a group. Other measured data such as chemical and physical analysis of the char sample and drop size calculations are manually added to this spreadsheet.

The multiple regression program of Multistat™ is then used to determine which of the variables have significant relationships. For a given dependent variable, a linear equation is derived which estimates the dependent variables as a function of one or more independent variables. This equation is the best fit of the data to a linear equation based on the least-squares method. Other statistical values are provided to help in determining how well the linear equation predicts the dependent variable. R Square is an indication of how well the equation explains the variation in the dependent variable with 1 being a perfect fit and 0 being no fit at all.

The most important statistical value for this analysis is the t-value, based on Student's t-distribution (Hogg, 1969). This can be used to determine the probability that the correlation is statistically significant compared to the null hypothesis, i.e., the variables coefficient is zero. For example, with 10 data points and one independent variable (8 degrees of freedom) there is a 95% probability that the correlation is significant if the absolute value of the t-value is greater than 2.31, the critical value. Standard statistical texts present critical t-value tables as a function of the degree of freedom.

This procedure was used for each dependent variable as a function of a single independent variable to determine first order correlations. It is also possible to derive correlations which contain two or more independent variables

which are significant at the 95% confidence level based on the t-test. A correlation with two or more variables may be statistically significant even though neither of the variables had a significant influence on the dependent variable by themselves. The null hypothesis is tested for each variable coefficient, i.e., a t-value is calculated for each variable. The following procedure was used to determine the most important multiple correlations.

For each of the independent variables a linear regression equation was derived with the most significant (highest r^2 value) dependent variable. The residuals, i.e., the difference between the actual and predicted value, were then listed in an empty column. Then the statistics were recalculated using the residuals as the dependent variable. From the statistics spreadsheet the column with the best correlation to the residuals was determined and added to the original regression equation. The same procedure can be repeated to add a third and subsequent variables to the multiple regression equation. This procedure is continued until the absolute value of the t-value of the most recently added dependent variable is less than that corresponding to the critical t-value at 95% confidence level.

APPENDIX 8a
IPC TABULAR DATA
Residence Time Tests

Test Number	Residence Time (second)	Exp. Dia, (mm)	Spec. Vol. cc/gm s	Lost Total Sulfur, % cc/gm s	Fixed & Lost Carbon, % cc/gm s
4	1.8	4.6	5.6	9.07	13.95
5	1.6	4.3	4.6	18.33	19.66
6	1.6	5.3	3.4	5.07	7.73
7	1.4	4.9	2.9	-3.21	-13.40
8	1.8	6.1	15.4	7.78	5.69
9	1.6	5.2	8.1	-3.24	9.40
10	1.5	5.1	3.2	9.26	-13.34
11	1.4	4.6	2.3	21.90	14.19
13	1.6	4.6	6.9	12.77	-19.44
14	1.6	4.6	8.1	19.13	-9.61
15	1.7	4.3	11.0	28.63	-8.83
16	1.6	5.2	10.0	20.48	-9.12
17	2.0	5.8	27.0	26.04	13.66
18	1.6	4.4	6.3	19.29	56.14
19	1.9	5.6	25.0	34.89	37.21
20	1.6	6.1	11.0	11.18	8.30
21	1.3	5.1	3.2	5.51	6.00
22	1.3	4.3	3.6	-2.46	14.55
23	1.2	4.7	2.3	2.41	6.87
24	1.6	6.3	12.0	4.05	11.65
25	1.3	4.9	2.8	5.78	4.23
26	1.2	4.3	3.7	1.82	19.60
27	1.3	4.8	2.4	2.53	13.03
28	1.6	5.6	9.9	10.39	-4.19
29	1.3	4.9	2.7	3.26	-10.41
30	1.4	3.4	1.7	2.86	-0.12
31	1.6	3.1	3.8	1.91	24.24
33	1.6	5.2	18.8	3.10	7.96
34	1.7	4.0	21.8	41.23	59.88

APPENDIX 8b
TRAJECTORY OBSERVATIONS

Test	Gas Temp. (Deg. C)	Gas Flow (scfm)	Observations
40	Ambient	0, air	Preformed char particle. Hit wall if large. Small ones sometimes did not.
		4, air	Large - always hit wall Small - seldom hit wall but stayed away from furnace.
		8, air	All samples hit near top SOS
		12, air	Light samples would be entrained Dense samples fell and hit walls. Quadjet would hold up samples and disturb flow pattern.
	830	0, air	Ignition - lower furnace. Wall impact but came down. Smelt and char on mirror.
		4, air	Same
		8, air	Ignition - upper half of reactor More smelt than char on mirror. Many hit walls in lower furnace; they stuck and burned up.
		12, air	Ignition is in top furnace. 95% char hits walls in lower furnace. Very little smelt on mirror.

APPENDIX 8b

TRAJECTORY OBSERVATIONS

Test	Gas Temp. (Deg. C)	Gas Flow (scfm)	Observations
41	750	0, air	Ignition - mid SOS/lower furnace 80% reach mirror 30% burn at mirror Some wet. No smelt.
		4, air	Ignition - mid SOS. Some stick 60% reach mirror Very little smelt
		8, air	Ignition - top SOS 30% hit wall but release Glowing char at mirror
		8, air + quadjet @ 14 Lpm	40% char samples hit walls at quadjet. Those that clear do reach mirror.
		12, air	Ignition - top SOS 80% hit wall and burn. Glowing char at mirror
		12, air + quadjet @ 14 Lpm	Samples stuck to mid SOS and lower furnace. Disturbance at quadjet. 10% make it down.
		12, N ₂	Large char particles. 80% hit wall and stuck below mid-SOS.
		12, air + quadjet @ 7 Lpm	No real effect over test with no quadjet.

APPENDIX 8b
TRAJECTORY OBSERVATIONS

Test	Gas Temp. (Deg. C)	Gas Flow (scfm)	Observations
42	650	0, air	Ignition - lower furnace to 2nd stage air heater. 30% make it to bottom.
		4, air	Ignition - same. 50% hit wall and burn in lower furnace. Slight red color in char.
		8, air	Ignition - mid SOS and furnace. 60% reach mirror. All still burning.
		12, air	Ignition - same.
		12, N ₂	Hit wall in mid-furnace. No apparent size increase but are mostly dry.
		4, N ₂	Moist samples. Wall impact.
43	950	8, air	Smelt hit mirror with air flow. Char hit mirror with N ₂ flow.
44	830	4, N ₂	Char at mirror
		8, N ₂	No product at mirror

APPENDIX 8c
IPC TABULAR DATA
In-Flight Tests
(Blank implies no available data)

Black Liquor Feed									Gas Conditions		
Test	Flowrate (g/min)	Solids (%)	Temp. (Deg C)	Density (g/mL)	Viscosity @ TE50 (cp)	TE50 (Deg C)	Injector Tube ID (mm)	Droplet Dia (mm)	Flowrate (std. Lpm)	Avg. Temp. (Deg C)	Inlet O ₂ (%)
TG1											
47	16.0	67.4	93				0.84		113	870	0.0
50	16.0	64.8	97				0.84		113	870	0.0
51	16.0	64.8	94				0.84		113	870	21.0
52	16.0	64.0	102				0.84		113	716	0.0
53	16.0	64.0	103				0.84		113	731	21.0
54	16.0	64.0	103				0.84		113	870	21.0
56	16.0	64.0	105				0.84		113	866	10.0
57	16.0	64.0	115				0.84		113	867	10.0
58	16.2	64.0	95				0.84		113	866	10.0
59	16.0	64.0	104				0.84		113	876	21.0
60	16.0	63.6	116				0.84		113	876	21.0
TG2											
64	17.0	63.7	113				0.84		57	807	0.0
65	15.9	63.7	101				0.84		28	808	0.0
66	16.5	63.8	108				0.84		120	909	0.0
67	15.6	63.8	105				0.84		57	909	0.0
68	16.5	63.8	108				0.84		28	909	0.0
69	16.2	63.8	108				0.84		85	808	0.0
70	16.9	63.8	101				0.84		28	710	0.0
TG3A											
73	23.4	66.8	134	1.45		41	1.32	6.23	115	913	21.0
74	23.4	66.8	135	1.45		42	1.73		115	913	21.0
76	23.4	66.4	139	1.43		103	1.07	6.75	116	912	21.0
77	23.4	63.2	139	1.43		103	1.07	6.61	115	915	21.0
78	23.4	61.1	129	1.43		104	1.32	5.66	115	914	21.0
79	23.4	60.4	129	1.40		100	1.73	5.79	115	913	21.0
80	22.4	64.8	129	1.42		98	1.07	5.54	114	913	21.0
81	22.4	64.8	129	1.42		97	1.32	5.15	114	913	21.0
82	22.4	64.8	129	1.42		97	1.73		114	913	21.0
TG3B											
83	23.5	68.9	121	1.47		40	1.32	2.80	115	912	21.0
84	23.5	68.9	121	1.47		40	1.73	4.18	115	912	21.0
85	23.5	68.9	121	1.47		41	1.07	2.54	115	912	21.0
86	16.1	59.6	121	1.42	43	100	0.84	1.97	115	908	21.0
87	16.1	59.6	119	1.43	55	94	1.32	2.90	115	908	21.0
88	16.1	59.6	118	1.42	59	93	1.73	3.85	115	908	21.0
89	16.5	62.0	116	1.43	70	98	0.84	2.22	169	911	21.0
90	16.5	62.0	112	1.42	66	99	1.32	3.02	169	911	21.0
91	16.5	62.0	109	1.43	65	99	1.73	3.65	169	911	21.0
92	16.5	62.0	109	1.44	64	100	0.84	2.73	113	911	21.0

APPENDIX 8c

Product Char Characteristics

Test	Aggregate						Elemental Analysis (Mass Basis)						Elements
	Moisture (% ODS)	Fixed C (% ODS)	Char HHV (Btu/lb ODS)	Swollen Vol (cc/g ODS)	Bulk Den- sity (g/L)	Carbon (% ODS)	Hydrogen (% ODS)	Oxygen (% ODS)	Sulfur (% ODS)	Sodium (% ODS)	Potassium (% ODS)	Chloride (% ODS)	Accounted %
TG1													
47	1.70	2.78		4.17	65.4	27.45	2.21	35.97	5.22	23.00	2.90	0.67	97.42
50	1.02	5.29		10.30	65.4	31.86	2.53	35.28	4.78	22.40	2.90	0.67	100.42
51	1.60	4.19		8.76	97.6	30.72	2.50	35.26	5.20	22.60	2.90	0.67	99.85
52	0.90	10.27		15.50	27.4	29.78	1.85	34.66	3.81	24.60	3.28	0.67	98.65
53	1.22	3.87		10.10	66.4	31.53	2.56	35.48	4.20	23.20	3.08	0.67	100.72
54	0.55	4.92		9.75	75.6	31.19	2.67	34.48	4.42	22.80	3.12	0.67	99.35
56	1.83	3.05		10.40	101.0	33.02	3.10	35.92	3.90	20.20	2.75	0.67	99.56
57	2.71	3.53		10.00	107.0	32.36	2.79	35.68	4.14	20.80	2.74	0.67	99.18
58	2.14	3.35		5.40	103.0	31.48	2.70	36.17	4.80	21.80	2.78	0.67	100.40
59	0.87	4.68		9.50	91.4	30.94	2.74	35.49	4.71	22.60	2.90	0.67	100.05
60	2.26	2.65		14.50	113.0	32.07	2.86	36.35	4.43	21.10	2.84	0.67	100.32
TG2													
64	6.29	2.67		11.60	110.0	32.60	2.70	34.80	4.20	21.00	1.87	0.54	97.71
65	8.47	5.52		9.70	144.0	32.90	2.60	34.90	4.00	21.70	1.93	0.59	98.62
66	2.05	6.45		16.50	85.0	31.84	2.55	35.20	4.12	21.90	2.56	0.90	99.07
67	1.44	2.99		9.50	86.0	32.12	2.67	36.67	4.41	21.70	2.30	0.66	100.53
68	2.64	4.54		11.80	104.0	32.46	2.49	35.99	4.34	21.60	2.49	0.71	100.08
69	6.47	5.78		9.60	109.0	31.50	2.40	36.19	3.98	21.80	2.17	0.59	98.63
70	8.57	29.34		8.00	113.0	29.34	1.90	35.27	4.03	24.20	2.98	0.72	98.44
TG3A													
73	1.94	3.63	5150		75.4	32.57	2.67	34.98	4.02	21.80	2.97	1.26	100.27
74	2.28	3.34	4940		84.8	32.49	2.63	34.76	4.50	22.50	2.75	0.81	100.44
76	2.71	4.88	4950		58.0	32.33	2.42	35.13	4.69	22.80	2.86	0.49	100.72
77	3.01	5.15	4830		61.2	31.12	2.16	36.70	4.50	23.40	2.78	0.67	101.33
78	7.23	2.66	5030		95.4	32.68	2.73	34.99	4.40	21.80	2.76	0.51	99.87
79	8.33	2.54	5230		102.6	32.99	2.74	35.07	4.30	21.20	2.80	0.57	99.67
80	3.28	3.22	5340		76.0	33.30	2.70	34.72	4.60	21.10	2.95	0.54	99.91
81	4.22	1.79	5410		87.6	33.65	2.83	34.99	4.48	20.40	2.86	0.52	99.73
82	5.79	1.59	5430		92.2	33.89	2.85	34.94	4.56	20.20	2.64	0.51	99.59
TG3B													
83	4.55	1.76	5400	5.38	127.8	34.10	3.00	35.02	4.44	20.80	2.43	0.50	100.29
84	6.79	3.10	5450	21.96	128.2	33.44	2.88	35.02	4.35	21.30	2.44	0.32	99.75
85	2.31	3.44	5350	5.30	108.0	33.71	2.95	34.85	4.41	21.20	2.49	0.51	100.12
86	3.29	4.92	4770	10.15	109.4	31.43	2.40	35.18	4.96	21.90	2.91	0.85	99.63
87	6.26	4.67	5150	2.27	113.2	32.62	2.50	35.00	4.64	20.70	2.65	0.60	98.71
88	8.30	2.33	5110	1.25	115.2	32.71	2.82	35.52	5.40	20.90	2.59	0.47	100.41
89	3.63	3.85	5240	8.02	115.2	32.98	2.68	34.75	4.39	21.50	2.68	0.55	99.53
90	4.20	9.16	5160	3.52	84.4	29.64	1.83	35.34	4.59	26.10	3.14	0.55	101.19
91	8.16	1.49	4650	2.31	175.0	33.45	2.88	35.36	4.29	20.60	2.51	0.60	99.69
92	5.34	1.22	5250	4.35	136.0	32.65	2.86	35.48	4.43	22.40	2.57	0.49	100.88

APPENDIX 8c

Product Char Characteristics						Product Gas Components			
Test	Inorganics					(Molar Basis)			
	Na ₂ CO ₃ (% ODS)	Na ₂ SO ₄ (% ODS)	Na ₂ SO ₃ (% ODS)	Na ₂ S ₂ O ₃ (% ODS)	Na ₂ S (% ODS)	O ₂ (%)	CO (%)	CO ₂ (%)	H ₂ O (%)
TG1									
47	35.88	11.72	2.80	4.30	0.80				
50	24.32	8.74	1.97	5.19	0.77				
51	25.04	9.80	2.30	5.56	0.64				
52	36.03	7.17	1.81	3.27	0.64				
53	26.52	9.80	2.08	3.53	1.16				
54	27.62	6.85	1.45	3.91	2.15				
56	25.83	6.89	1.01	4.90	0.14				
57	26.00	7.05	1.09	5.26	0.16				
58	27.94	7.16	1.27	5.01	0.73				
59	25.75	7.02	1.21	4.40	1.71				
60	25.36	6.71	1.31	5.71	0.45				
TG2									
64	20.66	7.25	1.03	4.25	0.25	11.70			
65	25.00	7.46	0.87	3.56	0.25	11.70			
66	24.14	7.07	1.15	4.38	0.29	14.90			
67	22.30	5.80	0.97	4.44	0.29	7.60			
68	26.74	7.76	1.38	4.23	0.26	7.70			
69	25.84	7.40	0.68	5.22	0.25	11.00			
70	35.91	7.79	0.87	2.81	0.14	10.30			
TG3A									
73	22.66	14.52	3.64	8.59	0.59	18.50	0.00	2.00	3.30
74	19.43	3.04	1.62	3.79	0.63	18.50	0.00	1.00	
76	21.51	3.56	1.81	4.62	0.52	18.10	0.00	2.00	
77	26.12	2.08	2.28	3.95	0.49	16.10	0.00	4.00	2.90
78	22.00	9.30	1.04	4.79	0.14	16.30	0.00	4.00	3.10
79	20.29	2.84	0.80	5.02	0.13	16.90	0.00	3.00	3.40
80	20.15	6.24	1.07	5.12	0.23	15.00	0.00	5.00	5.20
81	17.09	5.84	0.69	5.16	0.12	15.60	0.00	4.00	5.30
82	18.77	6.34	0.60	5.13	0.10	16.30	0.00	4.00	4.90
TG3B									
83	14.49	6.59	1.18	5.10	0.15	17.20	0.05	2.24	4.60
84	14.26	5.06	0.62	3.50	0.11	16.80	0.06	2.26	5.00
85	14.02	6.35	1.30	4.63	0.32	17.00	0.02	1.57	4.40
86	24.20	7.45	1.46	4.43	0.19	18.10	0.01	2.33	5.60
87	20.15	6.92	0.73	4.12	0.09	18.70	0.02	1.78	5.70
88	18.60	6.88	0.42	5.14	0.07	19.20	0.02	1.14	4.50
89	19.40	7.02	0.97	4.03	0.16				
90	27.80	7.29	1.24	4.42	0.19				
91	15.90	6.86	0.30	5.90	0.05				
92	17.10	6.48	0.42	5.12	0.11	18.30	0.02	1.86	5.60

APPENDIX 9
HEAT TRANSFER EQUATIONS FOR DRYING

Basic Drying Model Equations

Convection

$$Q_c = Ah \cdot (T_g - T_d)$$
$$Nu = hD/k = 2.0 + 0.6 Re^{1/2} Pr^{1/3}$$

Radiation

$$Q_r = \sigma A F_A F_\epsilon (T_g^4 - T_d^4)$$

Wall Radiation

$$Q_{rw} = \sigma A_w F_\epsilon (T_w^4 - T_d^4)$$

where Q = energy flow
 A = droplet surface area
 h = convective heat transfer coefficient h• includes mass transfer effects.
 T = temperature
 Nu = Nusselt number
 D = droplet diameter
 k = droplet thermal conductivity
 Re = Reynolds number
 Pr = Prandtl number
 F = radiation view factors
 σ = Stefan-Boltzmann constant

Subscripts: c = convection
 r = radiation
 g = gas
 d = droplet
 ε = emissivity
 A = area
 w = wall