

ANNUAL PROGRAM REVIEW

CHEMICAL RECOVERY

Volume I

March 6-7, 2000

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DUES-FUNDED PROJECT SUMMARY

Project Title: Black Liquor Gasification Development
Project Code:
Project Number: F028-01,-02
PAC: Chemical Recovery

Project Staff

Principal Investigator: J. Frederick
Co-Investigators: K. lisa, S. Sinuefield,
Research Support Staff: Q. Jing, V. Sricharoenchaikul

PAC Subcommittee

FY 00 Budget: \$144,000
Allocated as Matching Funds: \$25,000 (17.4%)

Time Allocation:

Principal Investigator: 4.0%
Co-Investigators: lisa: 10%; Sinuefield: 20%
Research Support Staff: Jing: 8%; Sricharoenchaikul: 12%

Supporting Research:

Special Students: M. Elam (M.S.)
External (Where Matching Is Used): Project 4260 (DOE/Agenda 2020)

RESEARCH LINE/ROADMAP: 8. Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE: To provide important process data at elevated pressures and temperatures, corresponding to commercial black liquor gasification conditions, and the fate of sulfur, sodium, potassium, chloride, and nitrogen versus gasification pressure, temperature, of air (or O₂)/fuel ratio, and water vapor content of the gasifier environment

PROJECT BACKGROUND: Efficient recovery of chemicals and energy from black liquor is a critical factor in the economics of kraft pulp manufacture. For over 60 years, this has been accomplished by burning black liquor in Tomlinson recovery boilers. Recovery boilers have been a major factor in the kraft pulping process becoming the dominant process for making papermaking fiber. However, these boilers have two important limitations. They are very expensive, costing in excess of \$100 million dollars. They are also relatively inefficient in converting the energy in black liquor to electrical power.

Gasification of black liquor is emerging as an alternative recovery technology. Gasification differs from combustion in that the organic matter in black liquor is converted to a fuel gas rather than burned to CO₂ and water vapor. The fuel gas consists mainly of CO and hydrogen as combustibles, with some CO₂ and water vapor present as well. One important advantage of gasification is that the fuel gas produced can be burned in a gas turbine to produce electrical

energy. The hot gases exiting the turbine are used to generate steam at high pressure to power non-condensing steam turbines to generate additional electricity. These integrated gasification – combined cycle (IGCC) power plants are capable of producing twice the electrical energy that the most efficient Tomlinson recovery boiler/steam power cycles can deliver, and about four times the U.S. industry's average, while still meeting the mills' steam demand. Production of more electrical energy from black liquor reduces the need for electricity generated from fossil fuel. This reduces the amount of CO₂ released to the environment.

Gasification technology is new to black liquor, but it has been used for many years in other applications. Municipal gas works used gasification to produce a fuel gas for lighting homes before electricity took over this function. In Germany, small wood-consuming gasifiers were developed to power trucks and automobiles during World War II. The chemical industry uses gasification to produce syngas for production of organic chemicals. More recently, coal-based IGCC power plants have been installed as both industrial and commercial power plants.

While gasification is an established technology, there are a number of black liquor-specific technical issues that need to be resolved before it will replace conventional recovery boilers. Some of these issues relate to the recovery and regeneration of pulping chemicals. Others concern gas cleanup – removal of particles and sulfur gases that can damage gas turbines. Materials of construction that can tolerate the hot, corrosive conditions within a black liquor gasifier need to be identified and evaluated.

In 1998, IPST had the opportunity to acquire a unique pilot facility to support the development of black liquor gasification. The Danish National Research Laboratory, Risoe, was offering to sell a pressurized entrained-flow reactor that they had built in 1993 for biomass gasification research. This gasifier is one of only four such reactors available world-wide. IPST purchased this gasifier at a small fraction of its \$2 million initial cost. It arrived in Atlanta in June, 1998 and was installed in the high bay area of the Institute's Engineering Center. It became operational approximately one year later.

The IPST pressurized gasifier can operate at pressures to 1200 psi and temperatures to 1500°C. The gas environment within the reactor can be a mixture of oxidizing and reducing gases, including water vapor. Fine particles of black liquor solids are entrained in a small fraction of the entering gas mixture, and are fed into the reactor via a water-cooled injection tube. The majority of the gas enters the reactor coaxially with the gas/particle suspension.

In the reactor, the solid particles are heated rapidly (within 0.1 second) to the reactor temperature. Carbon is gasified as it reacts with O₂, CO₂, and water vapor. Sulfur, sodium, potassium, chloride, and nitrogen within the particles are volatilized. After reacting for up to 10 seconds, the particles and gases are rapidly cooled to stop the reactions. The particles are separated from the sample gas and collected for chemical analysis. The product gas is analyzed with on-line instruments. An important advantage with this type of reactor is that the fate of all of the chemical species of interest in black liquor can be investigated simultaneously in each experimental run.

Table 1 shows the range of operating conditions for the pressurized gasifier.

Two research projects that will utilize the pressurized gasifier are under way. Both are aimed at providing basic data for the development of pressurized black liquor gasification technology. One is this member dues consortium sponsored project to investigate the impact of pressure on

the fate of sodium, sulfur, chloride, potassium, and nitrogen during gasification. The other is a DOE/Agenda 2020 sponsored project to investigate high temperature, O₂-blown, pressurized gasification of black liquor.

Table 1. Operating parameters for IPST's pressurized gasifier.

Reactor	Pressurized Entrained-Flow Reactor (PEFR)
Temperature	600-1500°C
Pressure	1.5 – 1200 psi
Black liquor solids flow rate	0.1 - 70 g/min
Primary gas flow rate	5 – 100 l/min
Secondary gas flow rate	25 – 500 l/min
Reaction gases	N ₂ , O ₂ , H ₂ O _(v) , CO ₂ , H ₂ , CO, CH ₄ , SO ₂ , H ₂ S,...
Water vapor flow rate	8 - 170 g/min

MILESTONES:

- PEFR operational: 8/30/99
- Fate of sulfur during gasification with water vapor at atmospheric pressure: 9/30/99
- sulfur compounds (split of S between gas and solids, form of S in gas phase and solids) at elevated pressures: 6/30/00
- fume formation and K and Cl enrichment: : 6/30/00
- tars formation and destruction within the gasifier at elevated pressures: 6/30/00
- nitrogen release and NO and NH₃ formation at elevated pressures: 6/30/00

DELIVERABLES: Data and kinetic models on the impact of gasifier conditions on:

- sulfur compounds (split of S between gas and solids, form of S in gas phase and solids) at both atmospheric and elevated pressures
- fume formation and K and Cl enrichment at elevated pressures
- tars formation and destruction within the gasifier at elevated pressures
- nitrogen release and NO and NH₃ formation at elevated pressures

STATUS OF GOALS FOR FY 99-00:

- See Milestones (above).
- The study of the fate of sulfur during gasification with water vapor was completed in mid-September
- The PEFR is operational. It is currently being modified so that samples for the NREL Molecular Beam Mass Spectrometer (MBMS) can be drawn directly from the reaction zone.
- 42 pressurized gasification runs have been made to date. The data is being analyzed, and will be presented at the Spring CR PAC meeting.

SCHEDULE:

See Milestones (above).

Task Descriptions (example)	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. PEFR is operational	-----x			
2. Fate of sulfur during gasification with water vapor at atmospheric pressure	-----x			
3. Preliminary pressurized gasification runs	-----	-----x		
4. Modify PEFR for runs with MBMS analysis			-----x	
5. Pressurized gasification runs with MBMS	-----	-----x	---	----x
6. Additional pressurized gasification runs w/o MBMS	-----	-----x		-----→

SUMMARY OF RESULTS:

Seventy atmospheric experiments of the fate of sulfur during H₂O gasification were made in the atmospheric laminar entrained-flow reactor at 700-1000°C. 20-50% of the sulfur was in the gas phase at temperatures of high temperature gasification (900-1000°C). At lower temperatures, the gas phase fraction was as high as 100% at some conditions but decreased to 40% as residence time was further increased. H₂S was the main gaseous sulfur compound at all temperatures but 20-50 % of the gas phase sulfur was as compounds other than H₂S, mainly as organic sulfur compounds. Methyl mercaptan and dimethyl sulfide were formed at low temperatures but they disappeared as the residence time was increased. In contrast, the formation of n-propyl mercaptan increased as temperature and residence time increased.

The PEFR became operational in late July, 1999. It has been certified for operation up to 80 bar. All components are operational. The first run with black liquor was made on July 28, 1999.

A set of preliminary pressurized gasification runs were made to explore the impact of temperature and pressure on black liquor gasification. One objective with these runs was to better define the range of operating conditions to explore when the NREL MBMS is on-site. The experimental matrix included runs at 3 temperatures, (900°C, 975°C, 1050°C), 3 pressures (5, 10, 20 bar), and 3 particle residence times (1.3, 2.6, and 3.9 seconds) was developed to evaluate the impact of these variables on black liquor gasification runs. To date, a total of 24 of the runs have been made as part of this experimental matrix. The data from these runs is still being analyzed.

SUMMARY OF KEY CONCLUSIONS:

- In low temperature fluidized bed gasifiers it is possible to obtain all of sulfur in the gas phase if the gas residence time is kept low. It may be difficult to convert all of the sulfur into gas phase in high temperature gasification. Considerable amounts of sulfur gas compounds other than H₂S (10-30% of the gas phase sulfur) are formed at all temperatures. In particular, n-propyl mercaptan may be a problem since its formation increased as

temperature and residence time increased. Methyl mercaptan and dimethyl sulfide are not expected to be problems.

- The PEFR functions well as a gasifier. It is possible to run over the range of gasification conditions (T, P, gas and particle residence times, gas composition) of interest for commercial, entrained-flow gasifiers. It is also possible to run over the range of conditions (T, P, gas residence times, gas composition) of interest for commercial, fluidized-bed gasifiers, but particle residence times are far shorter (seconds) than those of fluidized bed gasifiers (hours).
- It is not possible to analyze quantitatively and on-line for tar generated during gasification. A molecular beam sampling device and a mass spectrometer is needed for this part of the project.

DISCUSSION:

Release of Sulfur Gases During Gasification in Water Vapor

The release of sulfur during water vapor gasification was studied in the IPST atmospheric laminar entrained-flow reactor. The experimental conditions included temperatures of 700-1100°C, residence times of 0.7-1.6 s, and H₂O contents of 5-15%. At 900-1000°C, both conditions at which gasification was complete and incomplete were evaluated but at 700-800°C gasification was incomplete in all the experiments. The gas phase sulfur compounds were analyzed by gas chromatography.

Overall, the fraction of feed sulfur that was recovered in the gas phase ranged from 20% to 100% (Figure 1). At 700°C, almost all of the sulfur was in the gas phase at 1.0 s but only 40% at 1.6 s. This clearly implies that sulfur is initially released and later recaptured by the solids. At higher temperatures, the fraction of sulfur in the gas phase was always below 60%, and no clear maximum was detected at 900-1000°C. An earlier study in inert atmospheres (Sricharoenchaikul, et al., 1997) has shown that all sulfur except Na₂SO₄ was released during devolatilization at short residence times (<0.5 s) at 1000°C as well. The short residence times were not investigated in this study, and it is likely that the same maximum would have been detected in H₂O atmospheres as well.

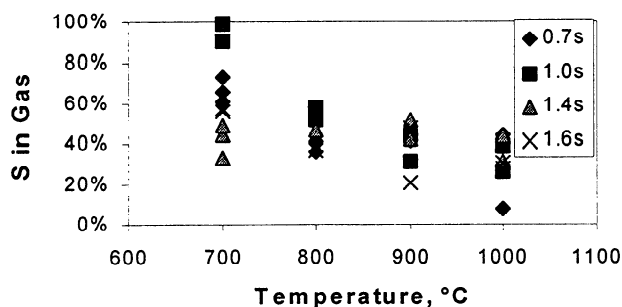


Figure 1. Fraction of sulfur recovered as gaseous products during gasification in 15% H₂O.

Hydrogen sulfide was the main gas phase sulfur species, and the trends were similar to those for the overall gas phase sulfur (Figure 2). At 700°C, there was a maximum in the H₂S

formation as a function of time. At 900-1000°C the fraction of H₂S remained relatively constant and no significant maximum was detected in the residence time range studied.

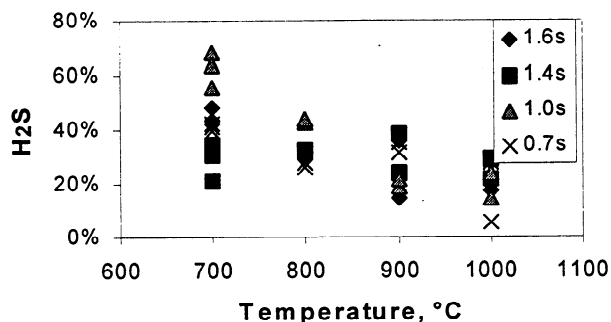


Figure 2. Conversion of sulfur to H₂S during gasification in 15% H₂O.

Other gaseous sulfur compounds were present as well, and H₂S constituted only 50-80% of the gas phase sulfur (Figure 3.) Organic sulfur compounds were the main other gaseous sulfur compounds. At low temperatures and short residence times, methyl mercaptan and dimethyl sulfide were prevalent, and up to 30% of the feed sulfur was present as these compounds (Figure 4). However, they decomposed as residence time was increased, and they were not detected at higher temperatures at all. Therefore, they are not expected to be problems during high temperature gasification, and their amount may be kept low during low temperature gasification as well if the gas residence time is sufficiently long.

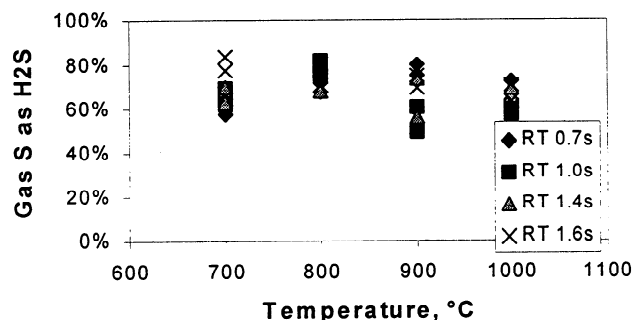


Figure 3. Fraction of gas phase as H₂S during gasification in 15% H₂O.

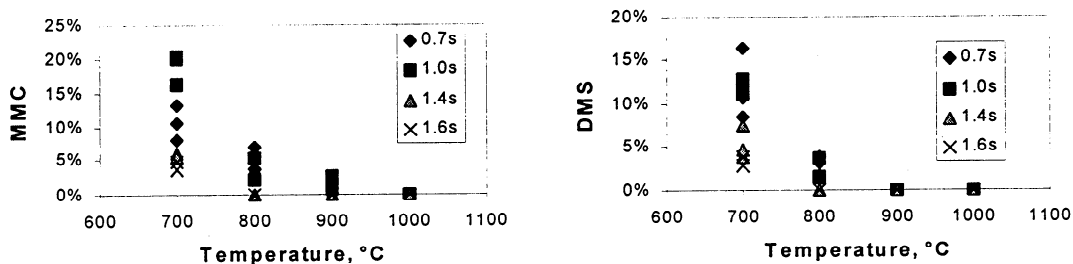


Figure 4. Conversion of sulfur to methyl mercaptan (MMC) and dimethyl sulfide (DMS) during gasification in 15% H₂O.

Another mercaptan - n-propyl mercaptan - on the other hand, was more prevalent at high temperatures and long residence times. Approximately 10% of the feed sulfur was n-propyl mercaptan at 1000°C. The formation of this mercaptan may be a problem in gasifiers.

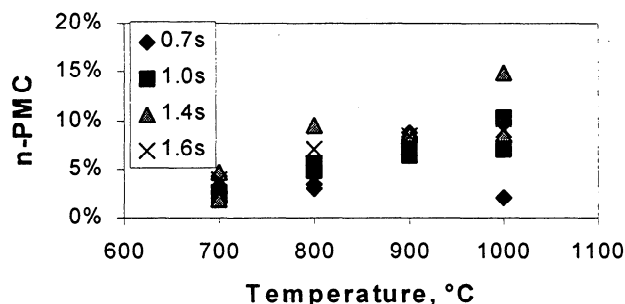


Figure 5. Conversion of sulfur to n-propyl mercaptan in 15% H₂O.

Pressurized Gasification Results

A set of preliminary pressurized gasification runs were made to explore the impact of temperature and pressure on black liquor gasification. One objective with these runs was to better define the range of operating conditions to explore when the NREL MBMS is on-site. The experimental matrix included runs at 3 temperatures, (900°C, 975°C, 1050°C), 3 pressures (5, 10, 20 bar), and 3 particle residence times (1.3, 2.6, and 3.9 seconds) was developed to evaluate the impact of these variables on black liquor gasification runs. To date, a total of 24 of the runs have been made as part of this experimental matrix. The data from these runs is still being analyzed. Some of the results are shown here. A more complete analysis will be presented at the Spring CR PAC meeting.

Figure 6 shows how the carbon, sodium, and chloride content of the char residue varied with increasing pressure. An increase in reactor pressure from 5 bar to 10 bar resulted in about 10% less carbon being gasified. There was no change in sodium content of the char residue with pressure. The chloride content of the char residue was about 25% less at the higher pressure.

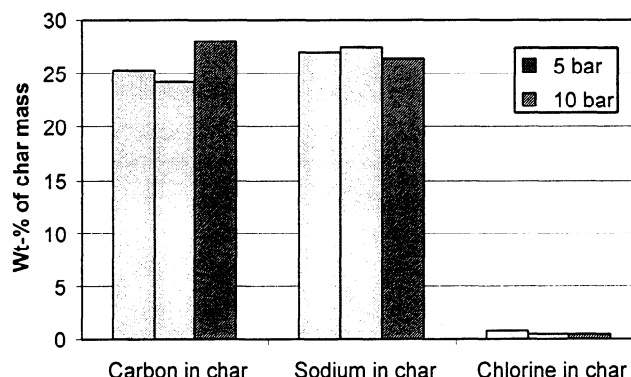


Figure 6. Impact of gasifier pressure on carbon, sodium, and chloride content of char residue for black liquor solids gasified at 900°C in 5% CO₂/95% N₂.

Figure 7 shows how the char residue changed with particle residence time for black liquor solids gasified at 5 bar total pressure, 900°C, in 5% CO₂/95 % N₂. The decrease is linear with residence time.

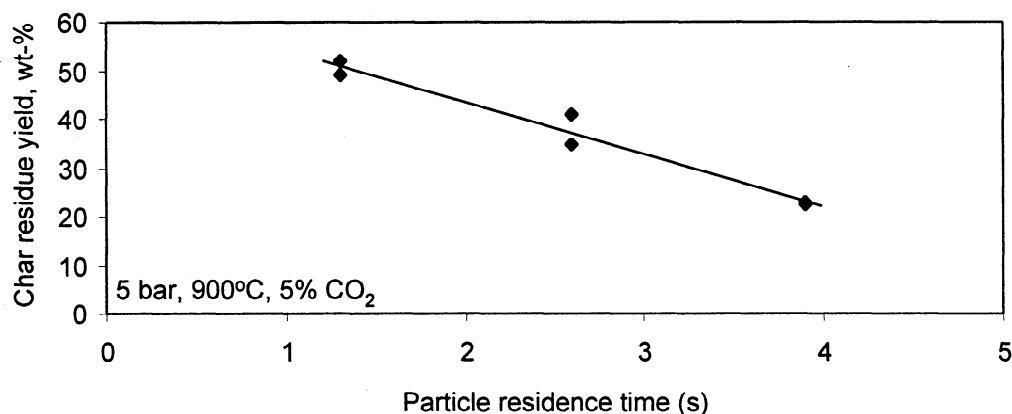


Figure 7. Char residue versus particle residence time for black liquor solids gasified at 5 bar total pressure, 900°C, in 5% CO₂/95 % N₂.

Figure 8 shows the weight fractions of carbon, sodium, and chloride in the black liquor solids that were retained in the char residue as a function of residence time. The data are for gasification at 5 bar total pressure, 900°C, and 5% CO₂. All three decrease with increasing residence time.

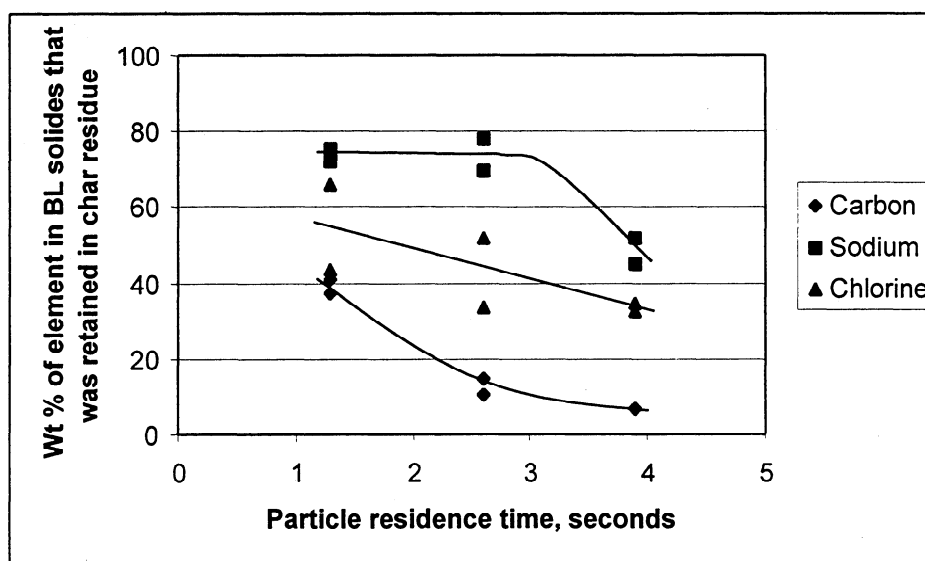


Figure 8. Weight fractions of carbon, sodium, and chloride in the black liquor solids that were retained in the char residue as a function of residence time. The data are for gasification at 5 bar total pressure, 900°C, and 5% CO₂.

In Figure 9, the measured char yields are compared with char yields calculated from the data in Figure 8. The char yield calculations were made assuming that (a) the char contained only the elements C, Na, Cl, and O, all chloride was NaCl, all remaining Na was Na₂CO₃, and all remaining C was fixed carbon. The agreement between the calculated and measured char yields is quite good, given these assumptions. Accounting for the presence of any K, Na₂SO₄, H, or inerts would increase the calculated char yield.

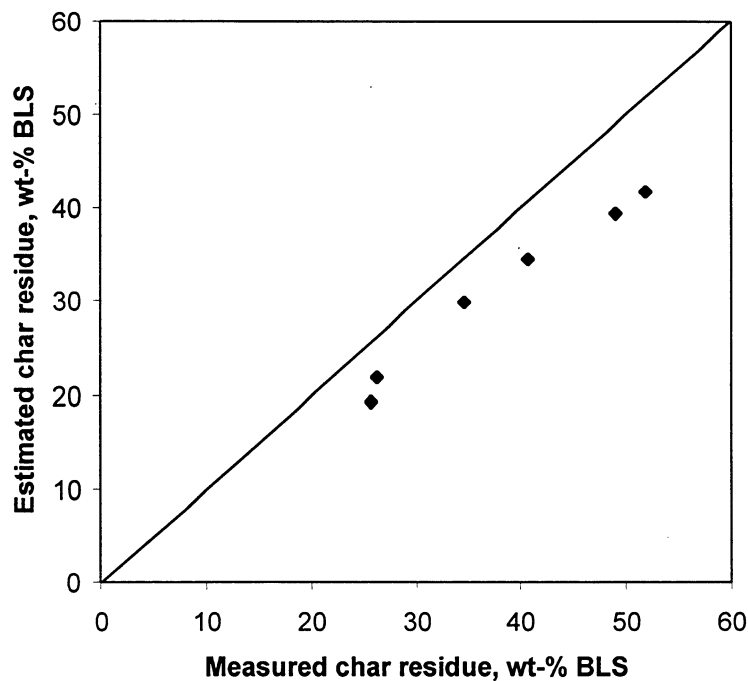


Figure 9. Measured char yields versus char yields calculated from the data in Figure 8.

References

Sricharoenchaikul, V.; Frederick, W.J.; Grace, T.M., Sulfur Species Transformations During Pyrolysis of Kraft Black Liquor." *J. Pulp Paper Sci.* 23, 8: J394-400 (1997).

DUES-FUNDED PROJECT SUMMARY

Project Title:	CATALYTIC DESTRUCTION OF TARS
Project Code:	
Project Number:	F028-03
PAC:	CHEMICAL RECOVERY
Project Staff	
Principal Investigator:	Kristiina lisa
Co-Investigators:	
Research Support Staff:	Viboon Sricharoenchaikul
PAC Subcommittee	-
FY 99-00 Budget:	\$57,895
Allocated as Matching Funds:	11% (\$6,250)
Time Allocation:	
Principal Investigator:	8%
Co-Investigators:	
Research Support Staff:	24%
Supporting Research:	
Special Students:	None
External (Where Matching Is Used):	Project 4XYZ (DOE-25,000)

RESEARCH LINE/ROADMAP: Line #8 - Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE: The objectives are (1) to develop processes for the destruction of tars from black liquor gasification that have a prolonged catalyst life, and (2) to develop economical pathways for the regeneration of aged/deactivated catalysts.

PROJECT BACKGROUND: One of the major challenges facing the commercialization of black liquor gasification is the formation of tars. With tars, a portion of the combustible material in the gasifier is lost. The build-up of tars may lead to shutdown of the gasifier or processes downstream and they are an unacceptable contaminant in green liquor with a potential safety hazard. In black liquor processing, up to 30% of the fixed carbon in black liquor potentially forms tars. Major tar compounds from black liquor gasification are benzene, phenol, toluene and naphthalene with smaller amounts of heavier compounds such as naphthalene, acenaphthalene, phenanthrene, chrysene and perylene.

Catalytic destruction is the most promising alternative for the elimination of tars. Commercial catalysts such as platinum, cobalt and nickel based catalysts have been

found to be active in destroying the main black liquor tar compounds in the absence of potential poisoning impurities. The rapid deactivation of catalysts in the fuel gas by among others sulfur compounds and alkali metals presents the largest obstacle to successful application of catalysts for tar destruction.

MILESTONES:

Preliminary screening of catalysts – November 1999
 Impact of hydrogen sulfide on catalyst activity – June 2000
 Impact of alkali metals on catalyst activity – November 2000
 Impact of other impurities on catalyst activity - March 2001
 Selection of catalyst and experimental conditions for on-site reactor – March 2001
 On-site reactor finished – April 2001
 Testing of catalyst activity in on-site reactor – October 2001
 Testing of regeneration methods in bench scale reactor finished – October 2001
 On-site experiments of catalyst regeneration finished – December 2001
 Final report and recommendations for catalyst and regeneration method – January 2002

DELIVERABLES:

- Kinetic data on catalyst activity in the presence of sulfur compounds and alkali metals
- Long-term data of catalyst performance in gases from
- Recommendation for a catalyst with a prolonged catalyst life
- Recommendation for a cost-effective regeneration method

STATUS OF GOALS FOR FY 99-00:

- 1) Selection of catalysts for poisoning studies based on preliminary screening experiments: completed
- 2) Impact of hydrogen sulfide on catalyst activity: 60% completed

SCHEDULE:

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Preliminary catalyst screening	-----	-----	-----X		
2. Effect of sulfur compounds			-----	-----	-----X
3. Effect of alkali metal penetration					-----

SUMMARY OF RESULTS:

The goal of this project is to find a commercially available catalyst that is efficient for tar destruction. Therefore no work on catalyst development has been undertaken. Fourteen catalysts were tested for tar destruction activity at 500-700°C in the presence of water vapor. Benzene was used as the model tar compound because the bonds in an aromatic ring are deemed to be the most difficult to break. Each experiment was

continued for four hours. Unsupported catalysts had low activity and deactivated rapidly but several supported catalysts that contained group X or VIII elements completely decomposed the benzene.

Four catalysts (64% Ni/Al₂O₃-SiO₂, 5% Pt/Al₂O₃, 5% Pd/Al₂O₃, and 5% Ru/Al₂O₃) have so far been tested for resistance towards poisoning by hydrogen sulfide. All catalysts were poisoned by the H₂S though the rates varied. The times for the loss of 80% of the activity were 20-85 minutes. The sulfur-induced deactivation experiments will be continued with a wider range of catalysts.

SUMMARY OF KEY CONCLUSIONS:

- Nickel, palladium, and platinum (Group X), and ruthenium (Group VIII) supported catalysts have high tar cracking capability, and their catalytic activity can be retained for hours in the absence of impurities such as H₂S.
- The optimal temperature for tar cracking was 600-700°C. The model tar compound was completely converted at this temperature in the presence of water vapor.
- All of the tested catalysts exhibited sulfur poisoning, but at variable rates. Group VIII metals have better resistance to sulfur poisoning than Group X metals
- For nickel-based catalyst, 700 °C was the optimal reactor temperature for resistance to sulfur-induced deactivation.

DISCUSSION:

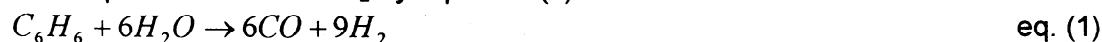
1. Screening Test of Catalysts with Model Compound

A. Significance

Screening tests have been conducted for all of the selected catalysts in order to single out the most promising catalysts for use in further thorough studies. These tests also serve as a baseline for the catalytic activity of each catalyst.

B. Approach

In the screening experiments, the catalytic reactor temperatures were 500, 600 and 700 °C. The catalyst weight was 0.2 g with 2 g of additional inert material (purified sand), except for 64% Ni on SiO₂-Al₂O₃ which was also tested at 0.02 g due to its high metal content. The model compound (benzene) input was set to 2400 ppm, while the water vapor concentration was adjusted to one and two times the stoichiometric ratio of feed compound (1.44 and 2.88% respectively) based on assuming total conversion of the model compound to CO and H₂ by equation (1) below.



The primary scope of this work was to select and test commercially available catalysts - hence no attempt has been made to create new catalysts. The catalyst selection was based on their potential ability to break aromatic compounds as reported in literature. The catalysts that were used in this study are summarized in Table 1.

A simplified diagram of catalytic reactor system is shown in Figure 1. The lines are heated to avoid the condensation of higher melting point model tars within the system.

The gas flow rates are controlled by electronic mass flow controllers to ensure the proper flow rates of helium, water vapor, and model tar feed. The desired total flow rate is controlled by a separate helium line. The product gas concentrations are measured by an FTIR analyzer every 15 minutes for a total of 240 minutes.

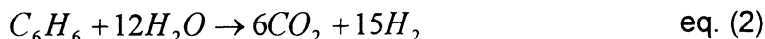
In the beginning of each experiment, a homogenous mixture of the desired catalyst and inert ingredient (purified sand) are placed on a porous disk at the center of the reactor. Once the furnace temperature has reached steady state, hydrogen is introduced into the system for an hour to reduce the catalyst, after which the tar model compounds and water vapor are introduced into the reactor. After the completion of an experiment, the catalyst bed is weighed to determine if carbon or other char has accumulated within the catalyst bed.

C. Results

Plugging of catalyst bed was a problem when no water vapor was fed to the reactor, due to excess carbon produced from tar cracking reaction. Most of the runs were terminated early to prevent breaking the reactor from pressure buildup. As a result, extensive screening experiments were performed only in a partial oxidation environment where water vapor is present in the system. By using benzene as a model compound, the product gases are CO, CO₂, CH₄, and H₂¹. Figure 2 shows typical output gas profiles from an experiment using Pt/Al₂O₃ catalyst.

Final conversion data after 4 hrs of the experiment are summarized in Table 2. Experiments with unsupported catalysts result in relatively low conversion and rapid deactivation of catalysts. In some case, decomposition of catalysts was observed. Hence only the results from unsupported CO (HDFP) and NiO are shown in Table 2. Some of supported catalyst show relatively high conversion, mainly the Group X metal (nickel, palladium, and platinum). Ruthenium, which is a Group VIII metal, also shows high conversion capability. As a result, these catalysts are to be used for further study of the effect of sulfur and alkali to their cracking properties.

Based on the typical product gas formation of CO, CO₂, CH₄, and H₂, benzene was assumed to react mainly with water vapor producing CO and H₂ as already shown by equation 1. The same reaction with water vapor can also produce CO₂ by equation 2. The water-gas shift reaction can occur concurrently (equation 3). Formation of CH₄ may result from the side reaction of CO and H₂ (equation 4) and reaction of benzene with H₂ (equation 5). The assumed overall reaction pathway can be summarized as shown in Figure 3.



D. Conclusions

- Nickel, palladium, and platinum (Group X), and ruthenium (Group VIII) supported catalysts have relatively high tar cracking capability.

¹ Can not be detected by FTIR

- Low activity and rapid deactivation occurred with unsupported catalysts.
- 600-700 °C and the presence of water vapor are optimal conditions for the cracking reaction.
- With active catalysts (Ni, Pt, Pd, and Ru), catalyst activity can be retained throughout the duration of the test (4 hrs) without significant deactivation at optimal condition.
- At the optimal condition, all of model tar compound can be converted. Approximately 70-74% the carbon input as model compound ends up in gas products (CO, CO₂, CH₄). The rest may be accumulated within the catalyst bed.

2. Effect of Sulfur on Catalyst Activity

A. Significance

In order to be able to actually use the cracking catalysts in black liquor gasification process, the catalysts must be able to resist sulfur poisoning to some degree. Due to the anticipated high concentration of sulfur gases from the gasification process, a catalyst with a high capacity for cracking would be useless if it were too sensitive to sulfur poisoning. The purpose of this study is to examine the effects of sulfur on catalysts selected from previous work.

B. Approach

The experimental approach is basically the same as the previous study, except that H₂S is added to the gas. Also, the FTIR sampling rate has been increased from every 15 minutes to 5 minutes to allow faster response to change in catalyst activity during the poisoning phase of the experiment. An ultra-small, long-path FTIR gas-sampling cell was installed to reduce the hold time of product gases that pass through the sampling cell. Hence, more accurate gas analysis was achieved.

The startup procedure was the same as in the previous study until the catalyst activity reached some steady state. Then H₂S line was switched to the system to initiate the poisoning phase. The H₂S flow rate was adjusted so that the concentration was 250 ppmv. Once the catalyst was fully deactivated, the H₂S feed was then switched off, and the system flow was adjusted to its original setting. The motivation behind this is to investigate whether any activity can be regained after the termination of the sulfur stream.

C. Results

The catalysts used in this study were those with high cracking capability as reported in the previous section. They were 64% Ni/Al₂O₃-SiO₂, 5% Pt/Al₂O₃, 5% Pd/Al₂O₃, and 5% Ru/Al₂O₃. Currently, only the nickel-based catalyst had been tested at reactor temperatures of 500-800 °C. Platinum and ruthenium-based catalysts had been tested only at 600 °C. The product gas composition profiles for these experiments are shown in Figure 4-8. In order to compare the effect of temperature on catalyst deactivation, a calculation of the change in catalytic activity from its stable, unpoisoned state was performed. The time needed for catalyst activity to reduce to 20% of its original value was determined, and the results are shown in Table 3. The nickel-based catalyst had the highest resistance to sulfur poisoning at the reactor temperature of 700 °C. In this case, 85 minutes were needed to reduce its activity to 20% of its original value. Lower

temperatures of 500 °C and 600 °C, however, resulted in a deactivation time between 20 to 30 minutes. Similarly, higher temperatures also resulted in quicker deactivation. For example, at 800 °C deactivation proceeded at approximately twice the rate of deactivation at 700 °C.

In addition to reactor temperature, deactivation from sulfur poisoning was also shown to vary with the catalyst composition. The catalysts derived from the Group X metals platinum and nickel were found to yield similar deactivation times of 20 minutes at a constant temperature of 600 °C. The catalyst derived from the Group VIII metal ruthenium was shown to have a deactivation time of approximately 40 minutes at 600 °C. More work is currently being conducted to determine whether these observations will hold over the whole experimental range of reactor temperature and all promising catalysts identified from earlier work. Finally, the effects of variable water vapor and H₂S concentration on catalyst deactivation rate.

D. Conclusions

- All of the tested catalysts were shown to exhibit sulfur poisoning, but at variable rates.
- For the nickel-based catalyst, 700 °C was determined to be the optimal reactor temperature for resistance to sulfur-induced deactivation.
- At both lower and higher temperatures than 700 °C, the rate of deactivation was greater.
- Group VIII metals may have better resistance to sulfur poisoning than Group X metals
- More work is necessary to establish trends with greater confidence.

Tables

Table 1. Catalysts used in this study

Catalyst	Manufacturer
Supported Catalysts	
64%Ni on SiO ₂ /Al ₂ O ₃	Acros
24.4%Ni on SiO ₂	In house
43%CuO+39%Cr ₂ O ₃ on Al ₂ O ₃	Alfa Aesar
3.5%CoO+14%MoO ₃ on Al ₂ O ₃	Alfa Aesar
3%FeCl ₃ on SiO ₂	Alfa Aesar
10%MoO ₃ on Al ₂ O ₃	Alfa Aesar
5%Pd on Al ₂ O ₃	Alfa Aesar
5%Pt on Al ₂ O ₃	Aldrich
5%Rh on Al ₂ O ₃	Alfa Aesar
5%Ru on Al ₂ O ₃	Alfa Aesar
Unsupported Catalysts	
CoO	OMG Americas
CoOH	OMG Americas
Co (HDFP)	OMG Americas
NiO	OMG Americas

Table 2 Catalyst screening experiments - Conversion data after 4 hrs

Catalyst : 64%Ni on SiO₂/Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	2.88	Yes	0.0205	32.15	9.95	1.31	20.89
600	2.88	Yes	0.0197	72.60	52.85	0.88	18.88
500	2.88	Yes	0.2038	48.07	19.05	3.79	25.22
600	2.88	Yes	0.2037	62.91	45.88	0.69	16.35
500	1.44	Yes	0.2	49.72	25.63	4.22	19.86
500	1.44	Yes	0.1961	50.67	27.81	3.87	18.98
600	1.44	Yes	0.202	39.12	19.90	0.00	19.22
600	1.44	Yes	0.204	55.14	50.16	1.01	3.97

Catalyst : 3.5%CoO+14%MoO₃ on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	1.44	Yes	0.2061	0.82	0.37	0.00	0.46
500	1.44	No	0.2058	0.79	0.30	0.00	0.49
600	1.44	Yes	0.2057	1.01	0.48	0.00	0.53
600	1.44	No	0.2007	1.07	0.53	0.00	0.54
700	1.44	Yes	0.2022	2.07	0.56	0.31	1.19

Catalyst : 24.4%Ni on SiO₂

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	1.44	No	0.2	0.54	0.00	0	0.54
600	1.44	No	0.2	49.97	39.78	0.12	10.07

Catalyst : 43%CuO+39%Cr₂O₃ on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	1.44	Yes	0.2033	1.17	0.05	0.00	1.12

Catalyst : 5%Pd on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	2.88	Yes	0.202	26.00	6.36	0.18	19.46
600	2.88	Yes	0.2056	72.09	50.59	0.82	20.69
700	2.88	Yes	0.2005	66.95	54.65	0.00	12.30
500	1.44	Yes	0.2019	19.12	5.35	0.00	13.77
600	1.44	Yes	0.2036	49.97	43.79	0.99	5.19
700	1.44	Yes	0.2082	64.00	61.56	0.32	2.12

Catalyst : 5%Rh on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	1.44	Yes	0.2018	3.09	1.00	0.00	2.09

Catalyst : 5%Pt on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	2.88	Yes	0.209	14.34	4.85	0.73	8.76
600	2.88	Yes	0.2039	54.33	40.13	2.20	12.00
700	2.88	Yes	0.2013	71.38	64.83	0.42	6.12
500	1.44	No	0.2025	16.30	1.90	0.58	13.82
500	1.44	Yes	0.2041	18.08	4.85	0.54	12.69
600	1.44	No	0.2013	50.94	33.78	1.27	15.88
700	1.44	Yes	0.2128	42.61	36.01	0.24	6.36

Catalyst : 5%Ru on Al₂O₃

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Catalyst wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
500	1.44	Yes	0.1986	22.17	9.17	0.00	13.01
600	1.44	Yes	0.2102	61.25	57.03	0.66	3.57
700	1.44	Yes	0.212	70.76	69.49	0.11	1.16

Catalyst : Unsupported Co (HDFP) and NiO

Temp. (°C)	Water vapor content (%)	H ₂ reduced	Cataly st wt. (g)	Final conversion after 4 hrs (%C in Benzene)			
				Total	CO	CH ₄	CO ₂
CO (HDFP)							
500	1.44	No	0.2	4.93	2.66	0.00	2.26
600	1.44	No	0.2	23.15	19.16	0.00	3.99
NiO							
500	1.44	No	0.222	3.45	0.88	0.00	2.57
600	1.44	No	0.2	1.50	0.62	0.00	0.88

Table 3. Poisoning by sulfur compounds.

Catalyst	Reactor Temperature, °C	Time to 20% activity, min
64%Ni/Al ₂ O ₃ -SiO ₂	500	30
64%Ni/Al ₂ O ₃ -SiO ₂	600	20
64%Ni/Al ₂ O ₃ -SiO ₂	700	85
64%Ni/Al ₂ O ₃ -SiO ₂	800	45
5%Pt/Al ₂ O ₃	600	20
5%Ru/Al ₂ O ₃	600	40

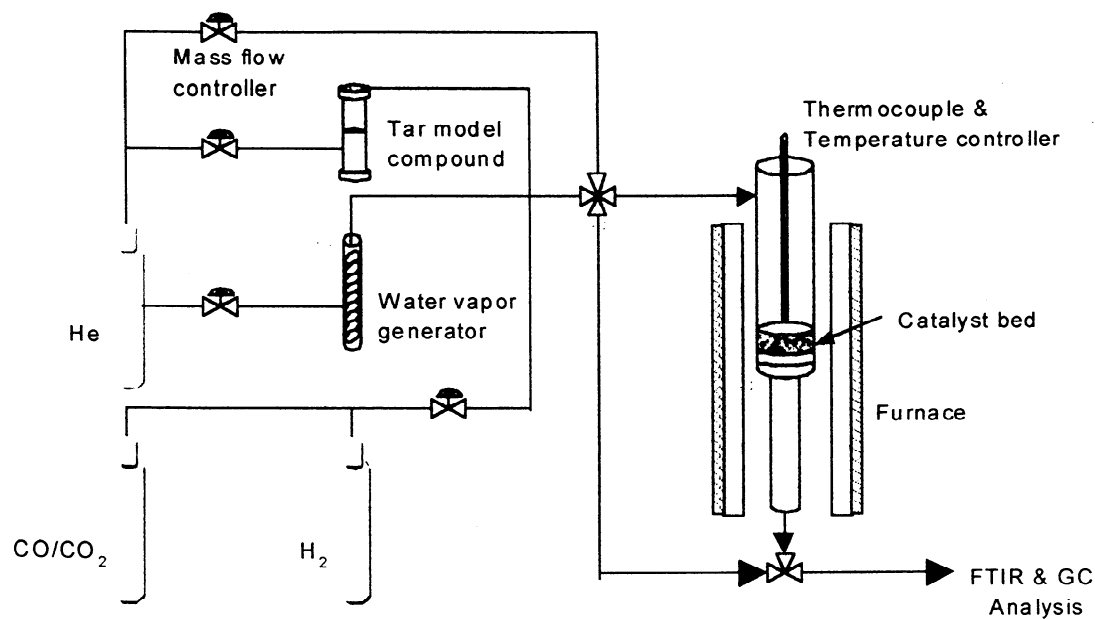
Figures

Figure 1 Simplified diagram of a bench scale catalytic reactor system

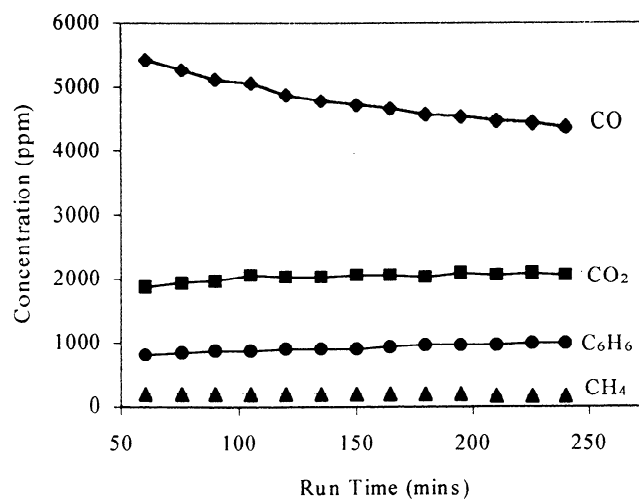


Figure 2 Typical product gas profiles from catalyst screening test

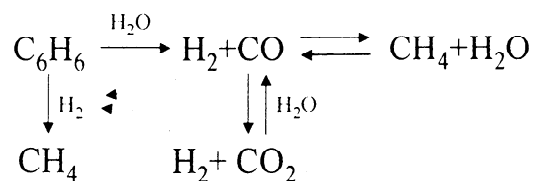


Figure 3 Reaction pathway of catalytic cracking of benzene

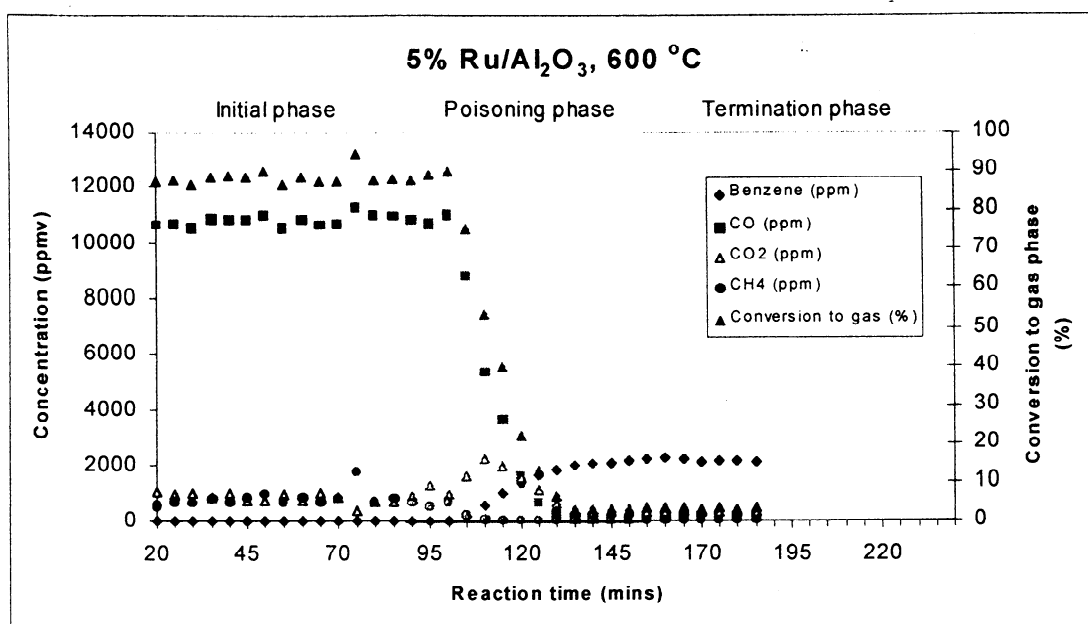


Figure 4. Product gas composition profiles from the experiment with 5% Ru/Al₂O₃ at 600 °C

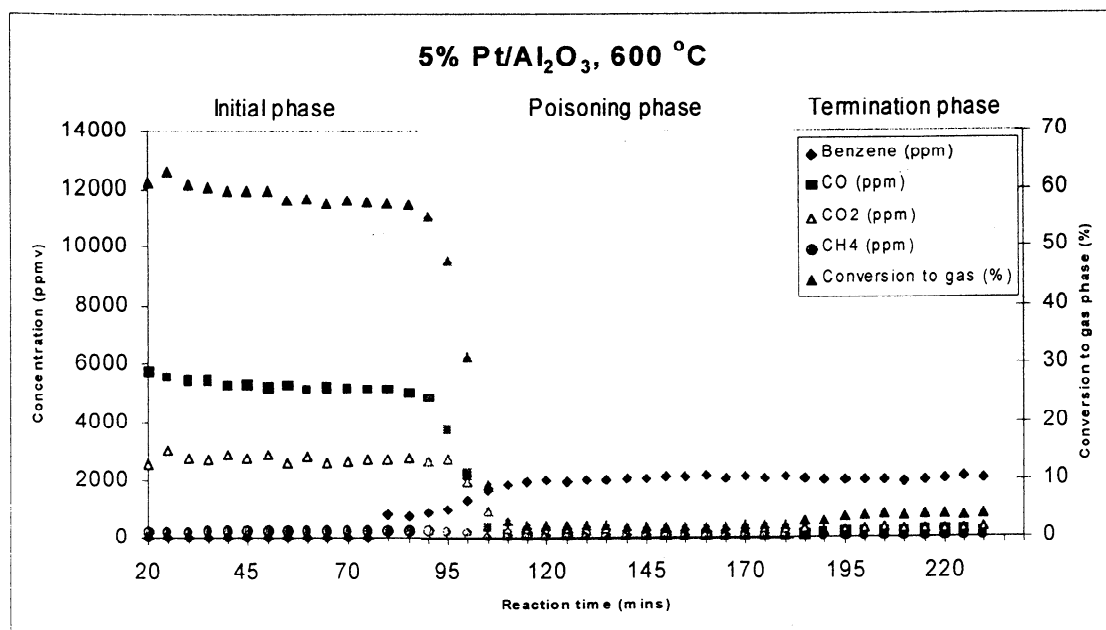


Figure 5. Product gas composition profiles from the experiment with 5% Pt/Al₂O₃ at 600 °C

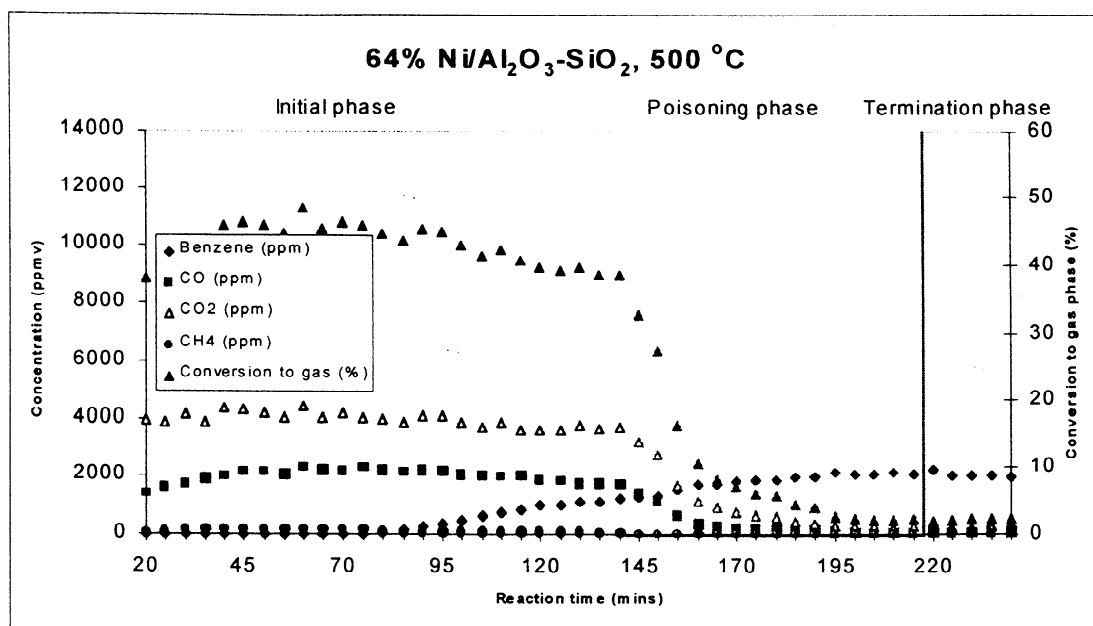


Figure 6. Product gas composition profiles from the experiment with 64% Ni/Al₂O₃-SiO₂ at 500 °C

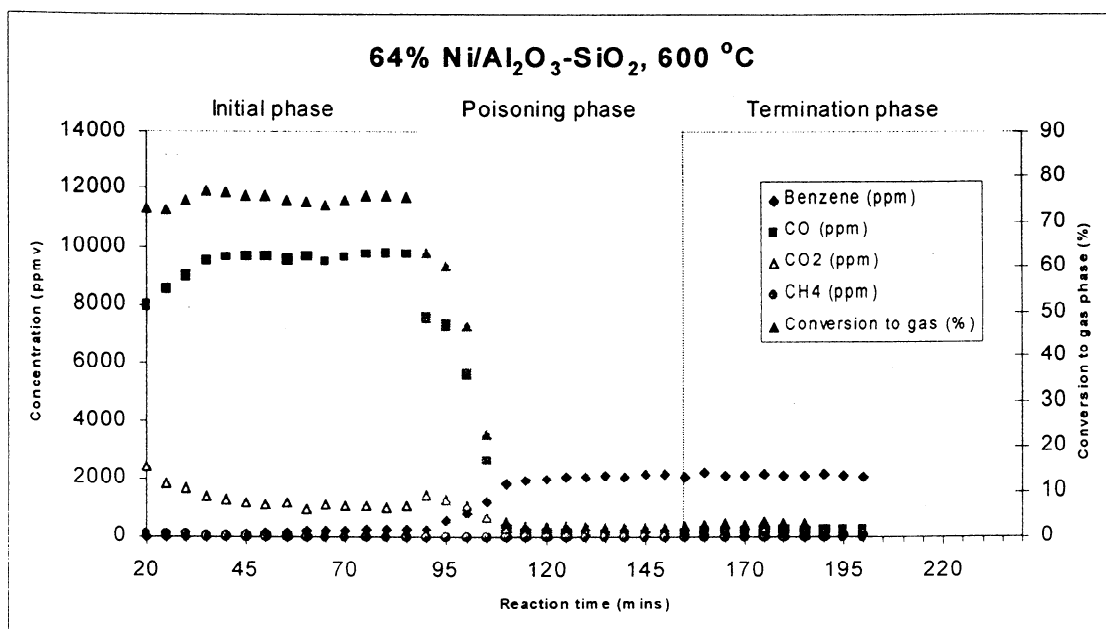


Figure 7. Product gas composition profiles from the experiment with 64% Ni/Al₂O₃-SiO₂ at 600 °C

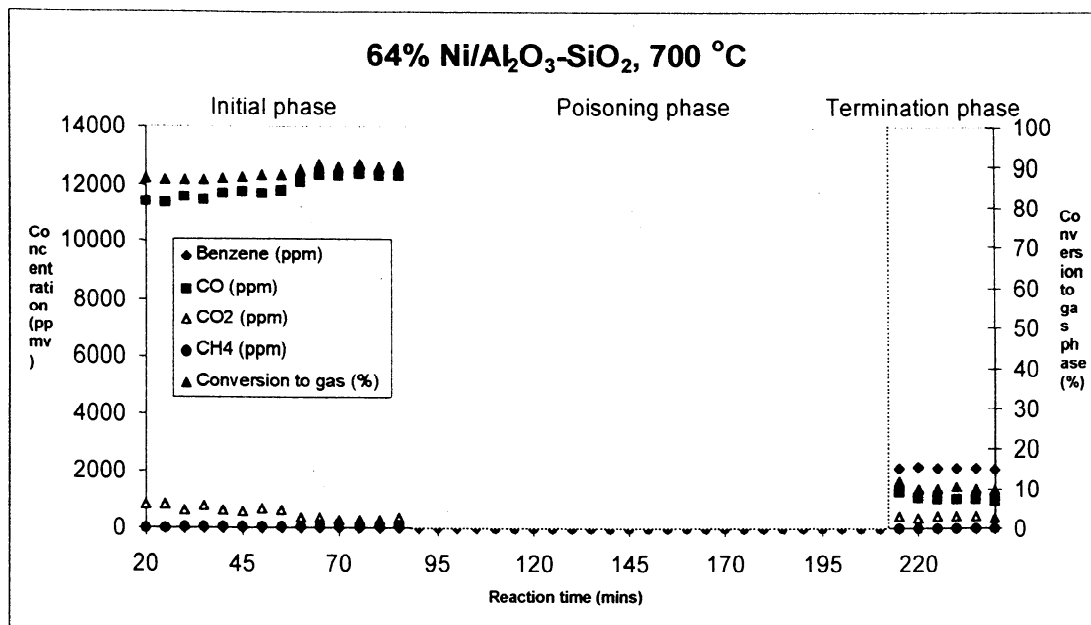


Figure 8. Product gas composition profiles from the experiment with 64% Ni/Al₂O₃-SiO₂ at 700 °C

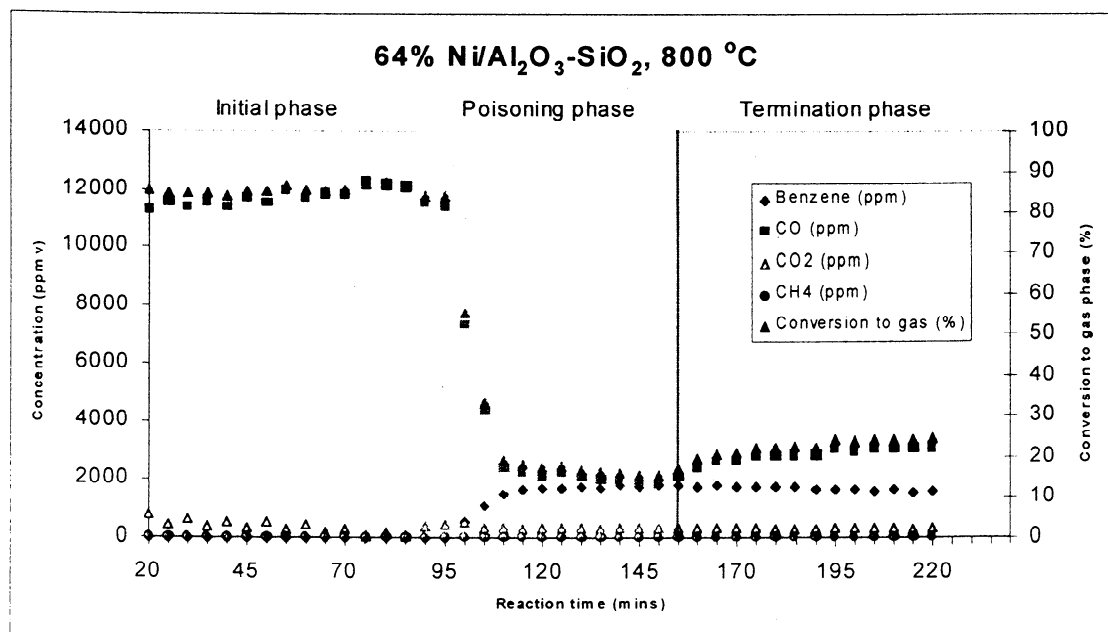


Figure 9. Product gas composition profiles from the experiment with 64% Ni/Al₂O₃-SiO₂ at 800 °C

DUES-FUNDED PROJECT SUMMARY

Project Title:	CONTROL OF EVAPORATOR FOULING
Project Code:	
Project Number:	F032
PAC:	CHEMICAL RECOVERY
Project Staff	
Principal Investigator:	Wolfgang Schmidl
Research Support Staff:	Maribeth Amundsen
PAC Subcommittee	
FY 99-00 Budget:	\$67,000
Allocated as Matching Funds:	100%
Time Allocation:	
Wolfgang Schmidl:	20%
Maribeth Amundsen:	20%
Supporting Research:	
Special Students:	Dan Euhus, Jason Smith (both Ph.D students at Georgia Tech)
External (Where Matching Is Used):	Project 4258 (DOE-\$268,000)

RESEARCH LINE/ROADMAP:

Improved Capital Effectiveness. 8. Develop technologies (compatible with present pulp-mill assets) to allow cost-effective expansion of kraft-pulp-equivalent fiber capacity (hardwood and softwood) by 30% without adding Tomlinson recovery boilers.

PROJECT OBJECTIVE:

1. Obtain basic data on the solubility behavior of Na_2CO_3 and Na_2SO_4 in kraft black liquor at dry solids concentrations to 80 wt-%.
2. Obtain fundamental data on the kinetics of crystallization of Na_2CO_3 and Na_2SO_4 from kraft black liquor at dry solids concentrations to 80 wt-%.
3. Obtain experimental data on the rate of soluble scale fouling of falling film high solids concentrators.
4. Develop a model for the rate of soluble scale fouling of falling film high solids concentrators based on the basic solubility (from 1) and crystallization kinetics data (from 2), and the fouling rate data (from 3).
5. Prepare a monograph on the causes and control of soluble scale in high solids, falling film concentrators.

PROJECT BACKGROUND:

At the time of the Spring 1999 PAC Meeting, this project was proceeding on schedule. Work was in progress on all four major objectives:

1. Preliminary solubility experiments with black liquor had identified numerous problems with the equipment and experimental procedures.
2. An experimental crystallizer had been constructed and preliminary experiments had been completed.
3. Construction of the falling film evaporator pilot plant was underway.
4. A survey of falling film flow models, and an extensive literature review of black liquor evaporation technology and physical properties, had been completed, and a preliminary flow dynamics model was under development.

MILESTONES:

Project milestones correspond to those for DOE project 4258.

Milestone	Date
1. Solubility experiments with one kraft black liquor completed.	6/99
2. Crystallization experiments with inorganic model solutions completed.	9/99
3. Solubility data obtained with other liquors.	9/99
4. Pressurized pilot falling film evaporator constructed and operational.	9/99
5. Detailed computational flow model for falling film evaporator completed.	9/99
6. All solubility data analyzed.	1/00
7. Crystallization experiments with one kraft black liquor complete.	9/00
8. Pressurized pilot falling film evap. data for fouling rate model completed.	9/00
9. Heat transfer effects incorporated into detailed computational flow model.	9/00
10. Crystallization experiments with other kraft black liquors complete.	3/01
11. Crystallization data analyzed and modeled.	5/01
12. Fouling rate model complete.	5/01
13. Pressurized pilot falling film evap. data obtained to eval. fouling rate model.	5/01
14. Detailed model for falling film evaporator fouling completed and evaluated.	9/01
15. Monograph completed.	9/01

DELIVERABLES:

As a result of this project, the pulp and paper industry and its suppliers will receive (a) basic data on the solubility and crystallization characteristics of Na_2CO_3 and Na_2SO_4 in high solids kraft black liquor, (b) a monograph to guide improvements in design and operation of high solids falling film evaporators for kraft black liquor, and a model with which to evaluate design improvements or operating changes. This information will provide the basis for improving the design of new high solids concentrators, for modifying the design of existing high solid concentrators, and for better operating strategies to minimize Na_2CO_3 and Na_2SO_4 fouling in them.

At or before the conclusion of this work, pilot- or full-scale trials will be proposed to evaluate the results at a mill site where soluble scale has been a major problem in the high solids concentrators.

STATUS OF GOALS FOR FY 99-00:

Goal	Date	Status
1. Complete solub. exp'ts. with one kraft black liquor.	6/99	10% complete
2. Complete cryst. exp'ts. with inorg. model solutions.	9/99	Complete
3. Obtain solubility data with other liquors.	9/99	Not started
4. Complete construction of pressurized pilot falling film evaporator and startup.	9/99	90% complete

- | | | |
|--|------|--------------|
| 5. Complete detailed computational flow model for falling film evaporator. | 9/99 | 70% complete |
| 6. Complete analysis of all solubility data. | 1/00 | Not started |

Notes and Comments:

- The date is the originally scheduled completion date.
- Goal #4: Installation and preliminary testing of the Annular Test Cell (ATC) apparatus has been completed. Assembly of the larger Plate Evaporator unit is also nearing completion.

SCHEDULE:

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
A.1. Solub. Exp'ts.-one kraft black liquor	-----x				
A.2. Solubility experiments-other liquors		-----x			
A.3. All solubility data analyzed			-----	---x	
B.1. Cryst. Exp'ts.-inorg. model sol'ns.	-----	-----x			
B.2. Cryst. Exp'ts.-one kraft black liquor			-----	-----	-----→
C.1. Pilot falling film evap. operational	-----	-----x			
C.2. Pilot evap. data for fouling rate model			-----	-----	-----→
D.2. CFD flow dynamics model for falling film evaporator	-----	-----x			
D.3. Heat transfer effects incorporated into CFD flow model			-----	-----	-----→

SUMMARY OF RESULTS:

The scope of work on this project covers four primary objectives:

1. Solubility experiments with black liquor.
2. Crystallization experiments with inorganic solutions and black liquor.
3. Construction and operation of a falling film evaporator pilot to obtain soluble scale fouling rate data.
4. Development of a soluble scale fouling rate model for falling film high solids concentrators.

Progress in each of these areas since the Spring 1999 PAC meeting is summarized below.

Preliminary solubility experiments with black liquor had identified several experimental problems that required modifications to the apparatus and the procedures. A removable three-stage filter assembly was added to the liquor sampling line in order to minimize the amount of suspended precipitates that will be counted as dissolved solids. The condensate collection system was improved to provide an easier and more accurate

measurement of the amount of condensate that is being collected, and a heated and insulated flash tank was installed in the condensate line so that liquor is not carried over into the condensate during occasional "burping" which is the most vexing operational problem that occurs during concentration. The entire sample line has been heat traced and insulated in order to minimize the chance of high solids liquor solidifying in the line and filters, and its skin temperature is monitored via a thermocouple. The objective is to control the sample line temperature to approximately the same value as the reactor operating temperature throughout the sampling process. Shakedown runs to establish appropriate operating parameters are still ongoing.

An experimental crystallizer has been constructed to study the secondary nucleation kinetics of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ model solutions and black liquor. For aqueous solutions of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$, the evaporation process can be divided into four stages: (1) nucleation of sodium carbonate or sodium sulfate that occurs on liquid-air interfaces due to surface evaporation, and subsequent growth of the crystals, (2) nucleation of Burkeite crystals in the bulk solution due to supersaturation build-up, (3) predominantly secondary nucleation and crystal growth of Burkeite crystals, and (4) nucleation and crystal growth of sodium carbonate and Burkeite.

The evaporator pilot plant currently consists of an Annular Test Cell (ATC) which is now operational, and a plate falling film evaporator that is approximately 90% complete. The ATC unit has been tested using water and the entire system appeared to work as designed. The data acquisition system was also tested and found to work properly and all of the measured values were consistent. The measured overall heat transfer coefficient (U_o) in the annular heated zone ranged from 2,500 to 4,700 Watts/m²/°C (440 to 825 BTU/hr/ft²/°F). These numbers compare reasonably well to values measured in previous work with this type of system. An operating procedure has also been developed for this equipment.

The main mechanical parts of the Plate Evaporator unit have now been assembled. This includes the piping for the black liquor feed system and the recycle loop, a hot water flush system, the steam feed control system, and condensate collection systems for both the steam and the black liquor vapor condensate streams. An electrical heat tracing system and insulation have been added to maintain the liquor temperature throughout the loop.

Instrumentation has also been installed to record the system operating conditions, including temperature, pressure and flow-rates. Remaining work includes connecting the instrumentation to the data acquisition system, installing a black liquor outlet, and a sampling assembly. Preliminary testing with water only was performed and evaporation rates of 4-5 lb H₂O/hr/ft² were measured. After the data acquisition system has been installed, preliminary testing with water, and with $\text{Na}_2\text{CO}_3/\text{Na}_2\text{SO}_4$ solutions, will be performed, prior to testing with black liquor.

A simplified fouling rate model was developed for a falling film of water flowing under isothermal conditions on the surface of an evaporator plate, and solutions for the three-dimensional flow fields produced explainable effects on the velocity magnitude contours. To refine this basic model, methods to account for non-idealized flow effects, such as waves, non-uniform distributions, and laminar/turbulent transitions, were taken from the literature and compared. Expressions were developed to estimate relations between

film Reynolds number and film velocity for approximated black liquor evaporator conditions. Thin film experimental results, taken from the literature for a range of conventional fluids, were compared to predictions using these selected methods, and extrapolations were attempted to approximate black liquor evaporator conditions.

SUMMARY OF KEY CONCLUSIONS:

Key results and conclusions since the Spring 2000 PAC meeting are:

- Preliminary solubility experiments with black liquor identified numerous modifications in the equipment and operating procedures. Unfortunately, no meaningful experiments have been completed yet.
- Crystallization kinetics for the formation of Burkeite from $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ model solutions have been determined.
- The ATC is now fully operational, and the falling film plate evaporator is nearly complete and operational.
- A simplified three-dimensional falling film fluid flow model (isothermal, water only) has been developed that produced graphical flow field results with explainable three-dimensional effects on the velocity magnitude contours.

DISCUSSION:

A. Solubility Experiments

Background

High solids concentrators are increasingly operating in a region above the second critical solids point, where Na_2CO_3 co-precipitates with Burkeite, leading to increased rates of soluble scale fouling. Experimental solubility measurements for Na_2CO_3 and Na_2SO_4 salts in kraft black liquors, as a function of temperature (~ 100 - 140°C) and total solids (to ~ 80 wt. %), will be incorporated into a comprehensive model for predicting the rate of soluble scale fouling in falling film high solids concentrators. In addition, this data will be used to verify the predictive capabilities of thermodynamic equilibrium modeling software such as NAEELS.

The solubility work is carried out in a heated stirred tank reactor starting with black liquor of ~ 48 wt. % total solids, which is below the first critical solids point. The liquor is slowly concentrated by evaporating off water in a step-wise manner, and allowed to equilibrate at specific total solids levels. Liquor samples are then withdrawn and analyzed for soluble Na_2CO_3 and Na_2SO_4 .

Results

Preliminary solubility experiments with black liquor had identified several experimental problems that required modifications to the apparatus and the procedures. A removable three stage filter assembly, consisting of $140 + 60 + 2 \mu\text{m}$ filters, was added to the liquor sampling line. This filter assembly is an improvement over the $15 \mu\text{m}$ filter that was used in the initial experiments, and is designed to minimize the amount of suspended precipitates that will be counted as dissolved solids. It was satisfactorily tested with a 50 wt. % total solids liquor at ambient temperature--the liquor was forced through the filters with only a 15-20 psi pressure drop.

The condensate collection system was improved to provide an easier and more accurate measurement of the amount of condensate that is being collected, and hence

the approximate total solids content of the black liquor inside the reactor. A heated and insulated flash tank was installed in the condensate line so that liquor is not carried over into the condensate during occasional "burps" that occur during concentration. The entire sample line has been heat traced and insulated in order to minimize the chance of high solids liquor solidifying in the line and filters, and its skin temperature is monitored via a thermocouple. The objective is to control the sample line temperature to approximately the same value as the reactor operating temperature throughout the sampling process.

Several shakedown runs have been carried out to establish appropriate operating parameters to minimize liquor "burping" which is currently the most vexing operational problem. Unfortunately, these are still ongoing, and the optimum operating conditions have not yet been determined.

Conclusions

The modifications to the apparatus and the procedures that are described above should address the primary operational problems that have been already encountered and are foreseen for future experiments. When the shakedown runs have been completed, actual solubility experiments will finally start.

B. Crystallization Experiments

Background

The solubility experiments in part A only address thermodynamic aspects of the scaling process. It is also necessary to investigate two kinetic phenomena: crystal nucleation and growth, and properties of the interface formed between crystalline solids and the heating surfaces. A key parameter here is the metastable zone width, which is the temperature difference between the metastable limit and the solubility limit for Burkeite (in this case) at a specific concentration.

Initial experiments established the metastable zone width for crystallization in the Na_2CO_3 - Na_2SO_4 - H_2O system as a function of total solute concentration and the ratio of Na_2CO_3 to Na_2SO_4 . Supersaturation conditions were generated by heating the system at a constant rate, and the metastable zone was constructed. The width of the metastable zone depended on the rate at which supersaturation was generated.

An experimental crystallizer was constructed to study the secondary nucleation kinetics of Na_2CO_3 + Na_2SO_4 model solutions. Crystal size is monitored by a Lasentec® FBRM 600L system which is a laser based high speed particle scanning and size measurement instrument. For later experiments with black liquor, the crystallizer apparatus was upgraded because black liquor is more viscous than aqueous solutions and leads to mixing and sampling problems. Some specific modifications to the crystallizer included the addition of a metering valve, PID temperature-control, cooling, and a data acquisition system.

Crystallization experiments on Na_2CO_3 + Na_2SO_4 model solutions have included studies on the effects of sodium hydroxide, and black liquor (1%) addition, on the metastable zone width of Na_2CO_3 + Na_2SO_4 solutions. These have been completed, but only some preliminary experiments with black liquors have been performed.

Results

In separate experiments, the addition of sodium hydroxide, and black liquor (1 %) to the $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ system decreased the metastable zone width for Burkeite. Crystals have been identified as Burkeite by x-ray powder diffraction, and experiments showed that Burkeite formed a solid solution with Na_2CO_3 or Na_2SO_4 , and the ratio of the two could vary when kept in contact with the solution.

As the inorganic solutions have been evaporated at constant rates, two critical points have been observed for solutions with high sodium carbonate to sodium sulfate ratios. The distances between the first and the second critical points decrease as the carbonate to sulfate ratios increase. Nucleation rates at the first critical point are greater than those at the second critical point.

Based on the crystallization experiments on $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ model solutions, the evaporation process for these aqueous solutions can be divided into four stages: (1) nucleation of sodium carbonate or sodium sulfate that occurs on liquid-air interfaces due to surface evaporation, and subsequent growth of the crystals, (2) nucleation of Burkeite crystals in the bulk solution due to supersaturation build-up, (3) predominantly secondary nucleation and crystal growth of Burkeite crystals, and (4) nucleation and crystal growth of sodium carbonate and Burkeite. However, the identity of the crystals formed has yet to be confirmed by x-ray powder diffraction.

Preliminary experiments with black liquor have been limited to developing methods to convert cord length distribution, which is measured by the FBRM probe, to crystal size distribution, which is required for the kinetic modeling. This preliminary work has been successful--for simple geometry crystals, the two parameters can be converted. The relationship between the number of particles per unit volume and the number of chords per unit time is still under investigation.

Conclusions

An experimental crystallizer has been constructed to study the secondary nucleation kinetics of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$ model solutions and black liquor. For aqueous solutions of $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$, the evaporation process can be divided into four stages: (1) nucleation of sodium carbonate or sodium sulfate that occurs on liquid-air interfaces due to surface evaporation, and subsequent growth of the crystals, (2) nucleation of Burkeite crystals in the bulk solution due to supersaturation build-up, (3) predominantly secondary nucleation and crystal growth of Burkeite crystals, and (4) nucleation and crystal growth of sodium carbonate and Burkeite.

C. Soluble Scale Fouling Rate Data from Pilot Falling Film Evaporator

C.1. Evaporator Pilot Plant

Pilot Plant Construction Schedule

Task Descriptions	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
<u>Annular Test Cell</u>					
ATC --Piping	-----	---x			
ATC --Electrical	-----x				

ATC –Instrumentation	-----	-----	-X		
ATC –Insulation		-----X			
ATC –Preliminary Tests		-----	-----X		
<u>Plate Evaporator</u>					
Design	-----	-----	-----	-----X	
Installation					
– Piping	-----	-----	-----	-----X	
– Electrical	-----	-----	-----	---X	
–Other		-----	-----	-----X	
Instrumentation		-----	-----	-----X	
Preliminary Tests			-----	-----X	
Run Experiments					-----

Annular Test Cell

Description

The Annular Test Cell (ATC) apparatus is designed to measure the reduction in the overall heat transfer coefficient caused by the formation of scale. The central component of the apparatus is a rod heater encased in a stainless steel tube with a diameter of 0.495 inches. The liquor flows over the tube surface in an annular region between the stainless tube and a glass tube with an inside diameter of 1.00 inches. The overall length of the annular section is 14 inches of which 4.0 inches is heated.

By controlling the power to the heater and monitoring the temperature of the liquor flowing through the annulus and the temperature of the inner surface of the stainless steel tubing it is possible to calculate the heat transfer rate and an overall heat transfer coefficient.

ATC Calculations

The overall heat transfer coefficient U can be determined from the following basic equation. Maintaining a constant power to the heater controls the heat flux rate. At steady state the heat flux is equal to the power to the heater.

$$q = U \cdot A \cdot \Delta T$$

where :

$$q = \text{heat flux (BTU / hr)}$$

$$U = \text{overall heat transfer coefficient (BTU / hr / ft}^2 \text{ / } ^\circ\text{F)}$$

$$A = \text{active surface area (ft}^2\text{)}$$

$$\Delta T = \text{driving force}$$

The region of interest for heat transfer from the inside tube surface to the bulk temperature of the black liquor is shown below in Figure 1. The overall heat transfer coefficient U is then calculated as:

$$U = q / (A \cdot (T_S - T_B))$$

where :

q = Power to heater

$$\Delta T = T_S - T_B$$

T_S = inside tube surface temperature ($^{\circ}\text{F}$)

T_B = bulk liquor temperature ($^{\circ}\text{F}$)

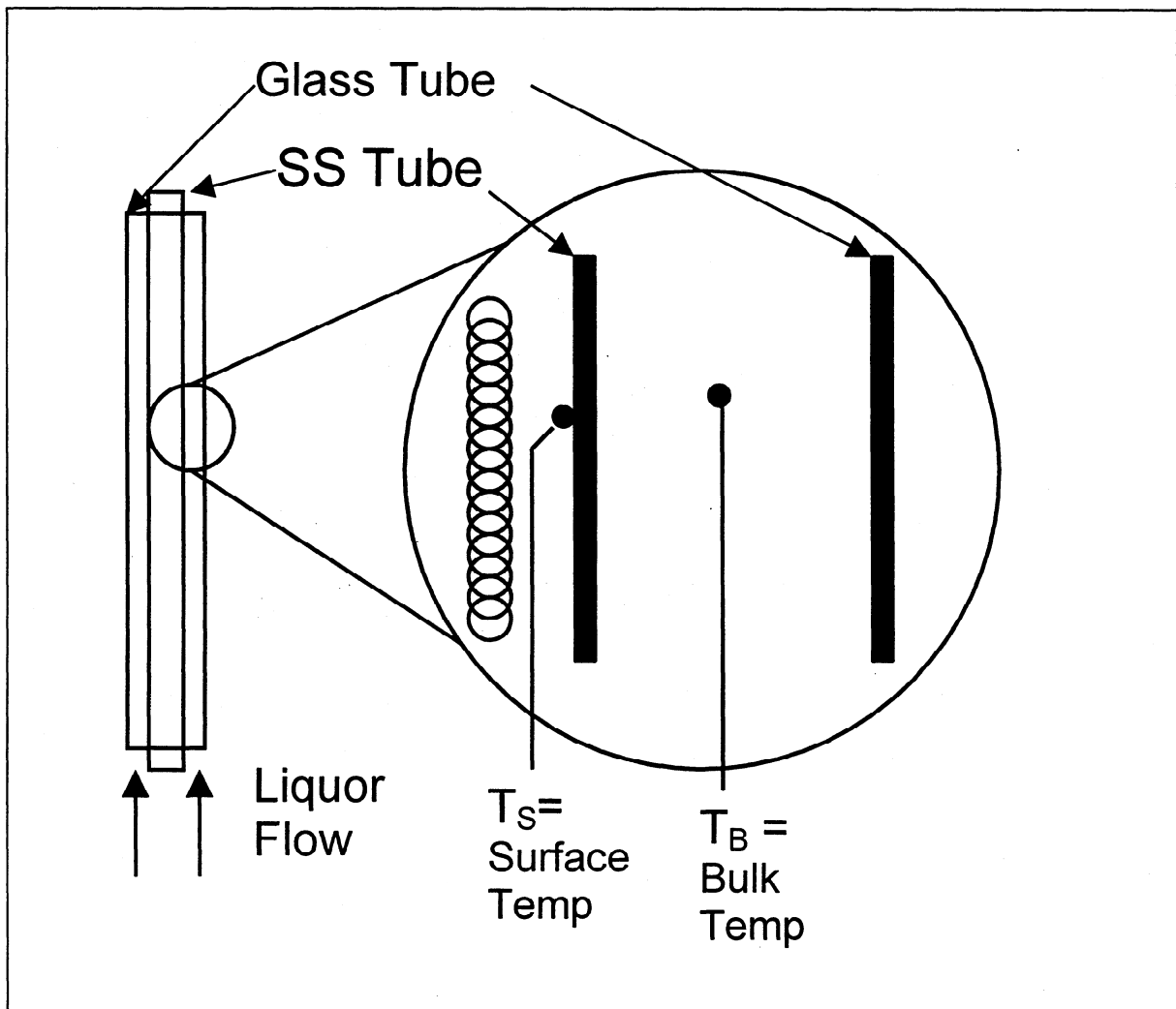


Figure 1. Annular Test Region.

Overall Equipment Design

In addition to the primary test cell region, the system is supported by a large amount of auxiliary equipment in order to maintain accurate control and steady-state conditions in the test section. This ensures that even a small amount of fouling can be detected as a change in the heat transfer coefficient. A schematic of the overall arrangement is shown below in Figure 2. The entire system is insulated to reduce heat losses, maintain good control, and provide a safe working environment.

The test liquor is stored in a large stainless steel tank with a capacity of about 100 gallons. Typically no more than 60 gallons of liquor will be contained in the tank in order to provide adequate volume for the separation of the liquid and vapor phases. It is estimated that at least 20 gallons of liquor will be needed to fill the main piping loop and allow the system to operate properly. The lower section of the tank is heated with electrical heaters to preheat the liquor supply. A centrifugal pump is used to mix and recirculate the liquor supply, maintaining a uniform feed supply.

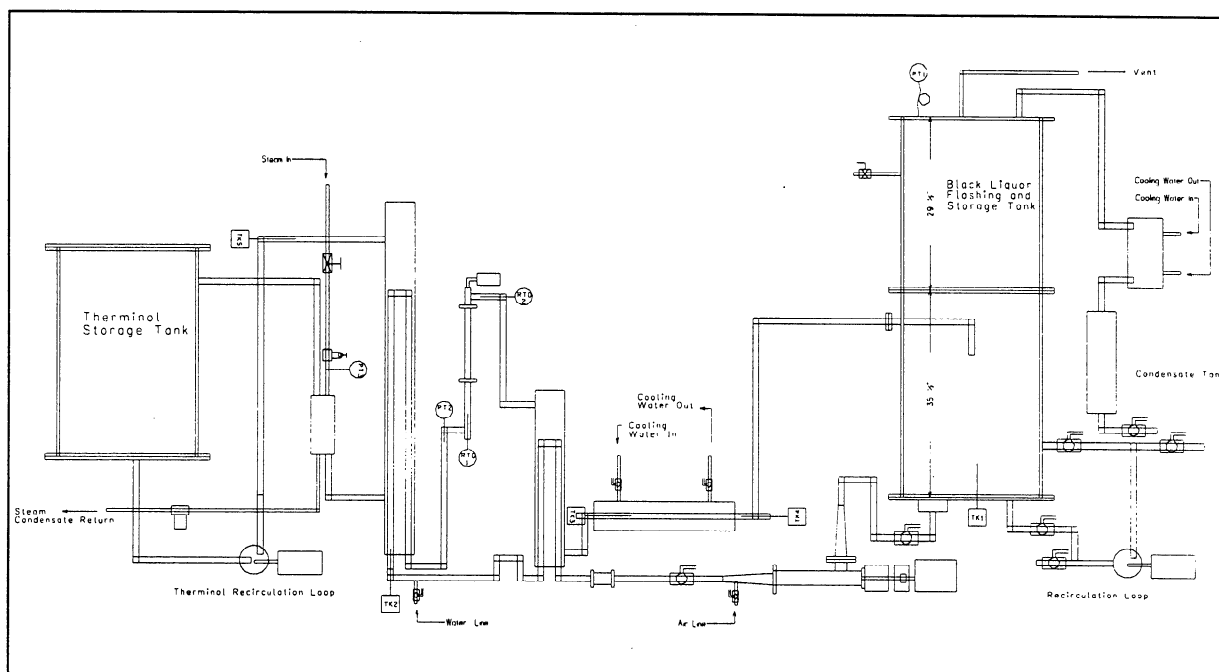


Figure 2. Overall Annular Test Cell System.

From the tank, the liquor leaves and circulates through a series of heat exchangers in order to insure that the liquor is at the desired temperature for operation of the test section. The heat exchangers are all oversized so that the heat flux and the delta-T is very low and little or no scaling will occur outside of the annular test section.

The liquor is pumped using a Moyno progressive cavity type pump. The pump is equipped with a variable speed controller to accurately control the liquor feed rate. After leaving the pump and going through a magnetic flow meter the liquor enters heat exchanger #1, where heat from the liquor leaving the test section is withdrawn to preheat the liquor. The next larger unit (heat exchanger #2) uses a heat transfer fluid to heat the liquor to the desired test condition. Following this, in the annular test cell, the liquor is heated under the controlled conditions described above.

After leaving the test section, the liquor is cooled in heat exchanger #1. Further cooling can then be obtained in heat exchanger #3 using chilled water, before returning to the storage tank. In addition the system can be used to concentrate the liquor by flash vaporizing the liquor as it enters the storage tank. The water vapor produced is then condensed using a final heat exchanger (#5).

The heat transfer fluid (Therminol XP) used to heat the liquor to the test conditions is heated in yet another heat exchange unit (#4) using steam. A large (40 gallon) storage tank is used to dampen variations in the temperature of the Therminol XP and ensure that operating conditions are steady.

The system is provided with instrumentation throughout to measure and control the operating system. Thermocouples are used to measure the liquor temperature, except at the inlet and outlet of the annular test section, where RTDs are used to provide more accurate temperature data. The system pressure is monitored with pressure transducers at the storage tank and at the inlet to the annular test section.

The power consumption of the electric rod heater is monitored with a wattmeter and the flow rate is measured with a magnetic flow meter. All of the signals are connected to a PC based data acquisition system that records the test conditions throughout the runs, as well as displaying critical operating parameters. The PC is also used to control the power to the heater in the annular test section via an SCR.

Plate Falling Film Evaporator

Description

The plate evaporator is a falling film unit, which consists of a 12 ft² plate enclosed in a vessel (20 inch ID and 10 ft tall) that allows for the collection and recirculation of the black liquor (Figure 3). Ahlstrom donated this piece of equipment to the Institute of Paper Science and Technology and it has been retrofitted to meet the specific operating needs of the project. This type of unit will allow operation over a wide range of conditions and at solids levels up to 80%.

Equipment

The primary heat transfer unit is a dimple-plate, which has overall dimensions of 6 ft high and 1 ft wide providing a surface area of 12 ft². With this type of plate unit, the black liquor flows downward over the plate surfaces. The dimples create a turbulent flow pattern and provide mixing of the liquor.

The plate is contained within a vessel that can be used at pressures up to 15 psig. The bottom of the vessel has the capacity for collection and storage of approximately 25 gallons of liquor. The liquor is pumped out of the bottom and back to the top of the plate, using a Moyno pump. This recirculation allows for enhanced heat transfer rates. The Moyno pump is equipped with a variable speed motor control system, providing accurate control of the flow-rate from 2 to 17 gpm. All of the equipment is mounted on a foundation skid with a support frame.

A gear pump is used to feed a small stream of fresh liquor (typically at low solids levels – 40%) to the system. After the recycled liquor has reached the desired solids level a controlled outlet stream will be removed from the unit.

Overall heat transfer rates will be measured by collecting the condensate from both sides of the unit. The condensed steam will be collected in one tank and measured. The black liquor vapor will also be condensed and collected in a second vessel. In both cases, the accumulation of condensate will be measured using a differential pressure transmitter.

of 15 psig. On the steam side a pressure relief valve will prevent steam pressure from exceeding 50 psig.

Instrumentation

A data acquisition system is provided to monitor and control the operation of this system. Temperatures are monitored throughout the system using both RTDs and type K thermocouples. In addition to measuring the liquor temperature, weld type RTDs have been attached directly to the dimple plate to provide wall temperature profiles within the unit. This information will be used to monitor the overall heat transfer rates in the unit.

The flowrate of the liquor is measured at the feed stream into the system and in the recirculation loop. On the recirculation loop, the flowmeter is a Yokagawa magnetic meter, which was also donated to IPST.

Pressure measurements are made using gauges and transducers to monitor the pressure of the black liquor recirculation loop, inside the vessel, and the steam pressure inside the dimple plate. Temperature and pressure are also measured in the condensate collection vessels, one for the steam condensate and one for the condensed water vapor driven out of the black liquor.

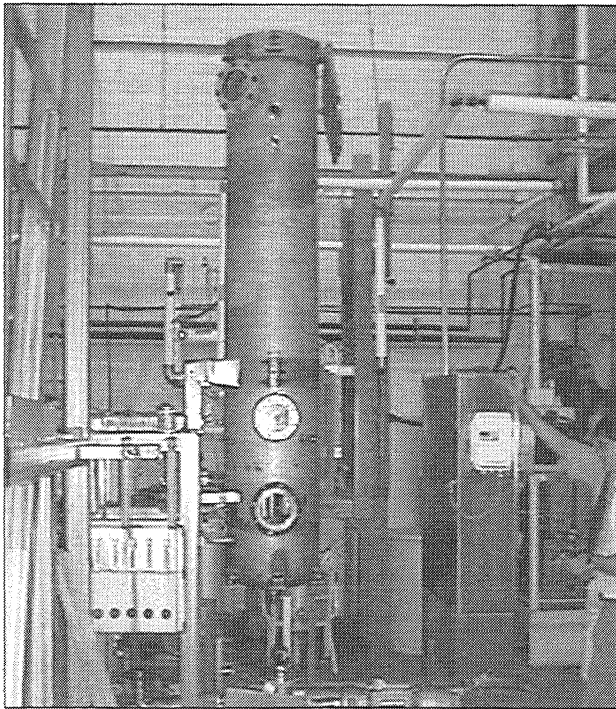


Figure 3. Plate Evaporator Unit.

C.2. Preliminary Fouling Rate Data

Background

Preliminary fouling experiments with model solutions and black liquor have been carried out on two bench-top evaporators that have been obtained for scouting experiments.

C.2. Preliminary Fouling Rate Data

Background

Preliminary fouling experiments with model solutions and black liquor have been carried out on two bench-top evaporators that have been obtained for scouting experiments. This preliminary fouling rate data will be used to establish some operating parameters for the pilot falling film evaporator which should become operational in February 2000.

Results

Fouling rates were measured for both black liquor and model solutions at circulation rate to feed rate ratios of 5, 10, and 15 to 1. The results indicate that increasing this ratio significantly reduces the fouling rate in falling film evaporators. In addition, preliminary data also indicate that lower heat fluxes will reduce fouling. A batch experimental technique has been developed to quantify the appearance and potentially the magnitude of black liquor fouling at higher solids. This technique involves slowly concentrating black liquor past the critical solids level and measuring the resultant dramatic increase in the fouling rate within the evaporator.

Conclusions

Preliminary experimental results indicate that higher circulation rate to feed rate ratios, and lower heat fluxes, will reduce the rate of fouling.

D. Soluble Scale Fouling Rate Model for Falling Film High Solids Concentrator

Background

Oak Ridge National Labs (ORNL) is developing a computational fluid dynamics (CFD) flow model for the rate of soluble scale fouling in falling film high solids concentrators. This model will mesh the thermodynamic solubility data and fouling rate data generated in the pilot falling film evaporator at IPST, and the crystallization kinetics data for Na_2CO_3 and Na_2SO_4 generated at Georgia Tech, into a dynamic fluid flow model that incorporates both heat and mass transfer.

Results

A simplified case for a falling film of water flowing under isothermal conditions on the surface of an evaporator plate was simulated as a three dimensional grid of a vertical rectangular channel. For the boundary conditions, the four side faces were specified as solid walls, the top face as part solid wall and part uniform velocity inlet (a "slot" for fluid to enter as from a distribution box) and the bottom face as an open outflow. The three-dimensional version of FLUENT 5.0 computational fluid dynamics code was used to solve for the resulting graphical flow fields, which produced explainable three-dimensional effects on the velocity magnitude contours.

To refine this basic model, methods to account for non-idealized flow effects, such as waves, non-uniform distributions, and laminar/turbulent transitions, were taken from the available literature and compared. Expressions were developed to estimate relations between film Reynolds number and film velocity for approximated black liquor evaporator conditions. Thin film experimental results, taken from the literature for a range of conventional fluids, were compared to predictions using these selected

methods, and extrapolations were attempted to approximate black liquor evaporator conditions.

Conclusions

A simplified three-dimensional falling film fluid flow model has been developed that produced graphical flow field results with explainable three-dimensional effects on the velocity magnitude contours.

DUES-FUNDED PROJECT SUMMARY

Project Title: Control of Non Process Elements
Project Code:
Project Number: F03302
PAC: Recovery

Project Staff

Principal Investigator: P. Pfromm, W. Schmidl
Co-Investigators: J. Frederick (advising)
Research Support Staff: -

PAC Subcommittee

-

FY 99-00 Budget: \$77,730
Allocated as Matching Funds: -

Time Allocation:

Principal Investigator: Pfromm 20% Schmidl 70%
Co-Investigators: -
Research Support Staff: -

Supporting Research:

Special Students: -
External (Where Matching Is Used): -

RESEARCH LINE/ROADMAP:**Environmental Performance:**

4. Reduce water usage in Bleached Kraft Pulp production to 2500 gallons per ton. (primary)
5. Reduce emissions of the entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule criteria while maintaining global competitiveness. (secondary)

PROJECT OBJECTIVE:**Overall objective including predecessor projects:**

The objective is to provide the pulp and paper industry with an equilibrium calculator capable of accurately handling dissolved inorganic ions, their complexation behavior with organic matter, their interaction with wood pulp fibers, and inorganic precipitates. The simulator should be compatible and interfaceable with the major process simulators used by the pulp and paper industry.

At the time of this report there is no commercial process simulator available that allows a link to an equilibrium simulator for NPE behavior.

Objective of the project for FY00

Obtain an overview of NPE projects at IPST and elsewhere and map a path to a useful enduser product that will give an advantage to IPST's Members. Resolve remaining inconsistencies between mill data and OLI simulations in regard to Mg, Mn in white and green liquor.

PROJECT BACKGROUND:*Scientific Background*

Non-process elements are becoming a major problem in both kraft pulp mills and bleach plants as water use is reduced. A limiting factor for these mills is that there is currently no way to predict accurately the level to which critical elements such as Al, Cl, Fe, K, Mg, Mn, Si, and other metals will accumulate as chemical cycles are closed more tightly. The process simulation tools available lack the capability for predicting the equilibrium distribution of these elements between inorganic ions, dissolved organometal complexes, ions adsorbed on wood pulp fibers, and inorganic precipitates.

Project administrative background

The project PI was initially Jim Frederick. In fall 1999 Peter Pfromm was assigned as PI, with Wolfgang Schmidl also spending a significant effort. Technician time was to be used as needed in case further sampling/experimentation was needed.

MILESTONES:

1. Summarize what data on NPE behavior is available at IPST
2. Include additional solid phases in the Mg and Mn simulation for the recovery cycle.

DELIVERABLES:

1. Integrate IPST's data (as collected/organized during FY00) in the OLI database as custom data, and set up simulations using IDEAS. Resolve remaining problems with Mg, Mn simulation. The suspicion is that previously not included finely divided solid phases are present. Use mill sampling data collected by P. Bryant, and other available IPST data sets for validation. (Schmidl)
2. Perform mill sampling for selected unit operations (Schmidl, staff technician) if needed.
3. Collect available information on this and related NPE behavior projects and chart a path to a useful product, that is proprietary to IPST's members (Pfromm)

STATUS OF GOALS FOR FY 00:

1. Integrate IPST's data (as collected/organized during FY00) in the OLI database as custom data, and set up simulations using IDEAS. Resolve remaining problems with Mg, Mn simulation. The suspicion is that previously not included finely divided solid phases are present. Use mill sampling data collected by P. Bryant, and other available IPST data sets for validation. (Schmidl)

Status: Simulations and validations against IPST's mill sampling data sets are ongoing.

2. Perform mill sampling for selected unit operations (Schmidl, staff technician) if needed.

Status: hold

3. Collect available information on this and related NPE behavior projects and chart a path to a useful product, that is proprietary to IPST's members (Pfromm)

Status: Collection of information is under way.

SCHEDULE:

Task Descriptions	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
1. Run Mg, Mn simulations	-----	-----	-----	-----X
2. Validate against existing mill data		-----	-----	-----X
3. Gather information on previous projects		-----	-----	
4. Recommend future work				-----X
5. Write yearly report				-----X

SUMMARY OF RESULTS:

1. Simulations of green and white liquor including increased amounts of silicon as chloride did not improve the accuracy of the Mg and Mn predictions
2. A project overview of NPE work at IPST is in progress.

SUMMARY OF KEY CONCLUSIONS:

1. Simulations with new solid phases are needed.
2. The NPE work is fragmented due to the number of sponsors and projects. A useful path forward would be a proprietary custom database assembled by IPST and available only to IPST Members as an OLI add-on.
3. Proposal for continuation of project F03302 "Control of Non Process Elements" for consideration by PAC:

Continue funding of the project at the current level from DFRC only (~\$100,000 per year, not to be used as matching funds). IPST Researchers will continue to update and develop a private databank that can be added at no cost by any IPST Member user of commercial IDEAS with the integrated OLI capability. This private databank will be held in confidence by IPST and any of IPST's Members using it.

The databank will include fiber/solute and organic/solute interactions. The funding level will allow additional experiments for recovery area issues. The project will coordinate with A. Rudie (Project F017) to also integrate bleach plant and papermachine data as it becomes available.

If data appears in the public domain it will be integrated after some form of validation.

DISCUSSION:

The discussion is in two sections:

1. Information gathering on status of NPE work at IPST (Pfromm)
2. Simulation of NPE Behavior (Schmidl)

1. Information gathering on status of NPE work at IPST

A. Significance

Non-Process Element (NPE) work at IPST has been fragmented by

- process area (recovery, bleach plant and paper machine),
- sponsor (DOE, State of Georgia, Dues funded Research Consortium(DFRC), Dues funding prior to DFRC)
- principal investigator (P. Bryant (now Eka Chemicals), A. Rudie, C. Woitkovich, J. Frederick, W. Schmidl, P. Pfromm)
- project Advisory Committee (Recovery, Pulping&Bleaching)

This task endeavors to gather what was done, identify what could be proprietary, and present a picture of the status of NPE work at IPST to find future pathways to a product that could be directly useful and proprietary to members.

B. Approach

Interviews with IPST researchers and collection of reports etc. will be used to develop an overview of available work. Outside interviews are also conducted. Literature search and compilation will also be done.

C. Current Vision for this project

It appears virtually impossible to determine exactly which data in regard to NPE behavior in the pulping cycle, at the bleach plant, and around the papermachine could be currently owned by IPST. Therefore, the following vision is developed here as a path forward to a proprietary product for IPST Members only.

The Simons/IDEAS and OLI cooperation (see below) allows any company to obtain a process simulator with limited NPE capability for their use. However, most of the NPE problems will likely not be well simulated since there is very little data that can be simply integrated by OLI into their database. Pulp and paper expertise, good judgement, and potentially laboratory experiments must often be used.

OLI allows the use of a "OLI Private Databank". IPST has already created such a databank and IPST researchers could continue to add data to this as the data becomes available and is validated. This must be done with caution and validation. IPST does own several complete mill sampling datasets for NPE's for validation. Laboratory experiments may be needed in the recovery area. In the bleach plant area laboratory work is under way under DFRC funding (A. Rudie). This must be integrated.

Proposal for continuation of F03302 "Control of Non Process Elements"

Continue funding of the project at the current level from DFRC only (~\$100,000 per year, not to be used as matching funds). IPST Researchers will continue to update and develop a private databank that can be added at no cost by any IPST Member user of commercial IDEAS with the integrated OLI capability. This private databank will be held in confidence by IPST and any of IPST's Members using it.

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If data appears in the public domain it will be integrated after some form of validation.

D. Results

Current Status of available commercial software

OLI Inc. and Simons (IDEAS) will announce the availability of IDEAS with integrated OLI capability. This could be first commercially available process simulation package that is already widely used in the paper industry that will add a powerful equilibrium simulator (OLI) that can treat some non-process element issues. The NPE capability is strictly limited by the database underlying the OLI system. OLI generally only culls data from public sources to add to it's database. Many issues in NPE behavior in pulping and bleaching, however (organic/inorganic interaction, inorganic/fiber interactions, behavior at high ionic strengths of certain ions specific to pulp and paper etc.) will not be treated well since no public and sometimes even generally no data is available.

Previous and ongoing work at IPST

The project history of NPE work at IPST is complex due to changes in personnel and overlap of projects funded from multiple sources, sometimes simultaneously (cost share). Issues such as use of funds as costshare for publicly funded work, change of IPST's funding structure (installation of the Dues Funded Research Consortium),

The following projects at IPST can be seen as contributing to non-process element behavior prediction (This does not include projects geared towards solving NPE problems such as chloride purges etc.).

Project name	Time frame	Sponsor	PI	Result	Proprietary
F017 Closed Mill Operation	95-current \$50k FY95-98 \$100k FY99+00	IPST (initially Dues funding, now DFRC)	Bryant (94-96) then Rudie, continuation proposal pending for FY01	Mill sampling around 3 mills, data sets available, wingems for 1 complete, 1 80% 1 50% complete Bleach plant, papermachine: Set of coefficients to describe dilute pulp/metal interactions	Some data has been published, A. Rudie is requesting from Pulping&Bleaching PAC to publish more.
Reducing Fresh Water Use in Papermaking	97-99 \$100K/year (Woitkovich), \$50-75k (Rudie)	TIP3, State of Georgia	Rudie, Pfromm, Woitkovich	Mill sampling, metals and solids around two papermachines, simple simulation for one machine	Public
F01704, later F03302 Control of NPE's	\$80,000 FY 99	IPST (initially Dues funding, now DFRC)	Frederic, Pfromm since Fall 1999	Al and Si exp. data/simulation in green and white liquor. Some fiber/inorg. data (see also F017 and DOE). BL organics interaction wth inorg.	Some data has been published, some funding was used as matching for public projects.
Control of the Accum. of NPE's and Org. Compounds in Pulp Mills with Bleach Filtrate Reuse	97-99? (with some IPST matching)	DOE (DE-FC07- 96ID13441	Frederic, Rorrer (Oregon State U., IPST)		Public

E. Publications

A list of publications where IPST researchers were involved was compiled. Please note that some publications originated with current IPST researchers that were at the time working for other organizations. Some of the researchers are no longer with IPST.

Bryant, P. S., "Metals Management in the Fiber Line", 1996 Tappi Minimum Effluent Mills Symposium Proceedings, pg. 95-100.

Bryant, P. S., "Practical Implications of Closing Up Fiber Lines", IPST Technical Paper Series 613. (see also Jordan and Bryant)

Bryant, P. S., Malcolm, E. W., Woitkovich, C. P., "Pulp- and Paper-Mill Water Use in North America", 1996 International Environmental Conference Proceedings, pg. 423-432.

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2. Simulation of NPE Behavior

Summary of Results

Preliminary simulations for NPE's in clear green and white liquors were unsuccessful. The predicted saturated solution concentrations for Ca, Mg, and to a lesser extent Mn, were still wildly unrealistic when compared to measured concentrations in mill sampled liquors. The addition of Al and Si to the model liquor compositions, as chloride salts, did not appreciably affect the predicted Ca and Mg concentrations. However, this is only an initial set of simulations. Additional modeling work should focus on including specific aluminosilicate compounds that are known to be present in green and/or white liquors and are in the OLI databases, and other anions, such as sulfite, thiosulfate, and oxalate, in the model.

Background

Previous simulations of NPE concentrations in clarified green and white liquors have produced some wildly unrealistic predictions as compared to analytical data from mill samples. For the four specific metals that were modeled: Ba, Ca, Mg, and Mn; Ca and Mg were grossly underpredicted in both green and white liquors, and Mn was grossly overpredicted in white liquor. The model liquors do not include numerous other NPE's, such as Al and Si in the form of aluminosilicates, and anions such as sulfite, thiosulfate, and oxalate that are present in mill liquors. The suspicion is that these absent cations and anions could complex with Ca and Mg resulting in higher predicted concentrations for soluble Ca and Mg.

Model Development

A new set of simulations were run using the OLI ESP software for model green and white liquors containing Ba, Ca, Mg, and Mn. Each liquor simulation was run with, and without, Al and Si added into the model composition to investigate if these metals could form complexes that would tie up the NPE metals in solution. In this initial set of simulations, the Al and Si were added as AlCl_3 , and SiCl_4 , respectively; specific aluminosilicate compounds have not yet been identified. All of the simulations were run at 95°C.

The model green liquor and white liquor base compositions are described in Table I.

Table I. Model Green Liquor and White Liquor Compositions.

Species	Green Liquor, g/L as Na_2O	White Liquor, g/L as Na_2O
NaOH	10	90
Na_2CO_3	100	20
Na_2S	40	40
Na_2SO_4	3	3

Potassium and chloride have also been included in the model at 4,000 and 2,000 mg/kg of solution, respectively. These concentrations correspond approximately to those measured in "hot filtered" clear green and white liquors sampled at a mill in Georgia.

Results

The predicted and measured NPE metal concentrations for the model green liquor and model white liquor are summarized in Table II, and Table III, respectively. The comparative mill data is for suspended solids free liquor.

Table II. Predicted NPE Concentrations in Model Green Liquor at 95°C.

Metal	Mill Data, mg/kg sol'n.		Predicted Concentration, mg/kg sol'n.	
	Bryant	Schmidl	without Al, Si	with Al, Si
Ba	2	1.7	1.1	1.2
Ca	18	10	0.07	0.07
Mg	4.4	1.7	1.2×10^{-4}	1.7×10^{-4}
Mn	2.4	1.6	0.50	0.23

Table III. Predicted NPE Concentrations in Model White Liquor at 95°C.

Metal	Mill Data, mg/kg sol'n.		Predicted Concentration, mg/kg sol'n.	
	Bryant	Schmidl	without Al, Si	with Al, Si
Ba	0.53	0.62	3.6	3.5
Ca	39	18	0.52	0.53
Mg	2.2	3.4	9.3×10^{-6}	1.0×10^{-5}
Mn	2.3	0.51	33	31

The simulations predicted the following precipitated solid phases for Ba, Ca, Mg, and Mn: BaCO₃, CaCO₃, and Mg(OH)₂ in both green and white liquors, MnS in green liquor, and Mn(OH)₂ in white liquor. Aluminum and silicon species remained completely soluble, and no aluminosilicate species were predicted to form.

Discussion

From the measured and predicted NPE concentrations in green and white liquors that are presented in Tables II and III, it is obvious that the predictions for saturated solution concentrations for Ca, Mg, and to a lesser extent Mn, are still wildly unrealistic. Apparently, adding Al and Si to the model as chloride salts had an insignificant effect on the predicted NPE concentrations. Aluminosilicate compounds, which can have complex structures that can include Ca and Mg, were not predicted to form under these simulation conditions, but these compounds are likely to be present in green and white liquors. The simulation temperature (95°C) may also have been too high; probably 80-90°C is a more realistic temperature. Finally, additional anions such as sulfite, thiosulfate, and oxalate were not included in the model, as were other cations such as iron, phosphorous, and vanadium. These are all details of the modeling approach that should be addressed as this problem is investigated further.

Conclusions

This initial modeling approach has been unsuccessful. The addition of Al and Si to the model green and white liquors in the form of chloride salts did not appreciably affect the

predicted Ca and Mg concentrations. This modeling effort should be continued and refined in order to more thoroughly evaluate whether it can be successful. At this point, several specific approaches that should be pursued are:

1. Include specific aluminosilicate compounds that are known to be present in green and/or white liquors, and are in the OLI databases, into the model.
2. Include additional anions, such as sulfite, thiosulfate, and oxalate, in the model.
3. Run the simulations at lower temperatures, e.g. 80-90°C.

Ideally, the model should have as few species as possible, yet maintain accurate predictive capability. In reality, however, the model may have to include many species in order to present a relatively complete picture of the liquor compositions.

DUES-FUNDED PROJECT SUMMARY

Project Title: Methanol Formation/Emission
Project Code:
Project Number: F03303
PAC: Chemical Recovery PAC

Project Staff
Principal Investigator: J.Y. Zhu
Co-Investigators: X.S. Chai
Research Support Staff: Garry Heedick

PAC Subcommittee None

FY 99-00 Budget: \$48,439
Allocated as Matching Funds: 0

Time Allocation:
Principal Investigator: 8%
Co-Investigators: 5%
Research Support Staff: 36%

Supporting Research:
Special Students: M.S. Jeremy Thomas
External (Where Matching Is Used): 415701 (DOE)

RESEARCH LINE/ROADMAP: Line – 5. Environmental Performance: Reduce emissions of the entire pulp and paper manufacturing process to meet Tier 3 Cluster Rule criteria while maintaining global competitiveness.

PROJECT OBJECTIVE:

The overall objective of this work is to assist the industry in meeting the Cluster Rule VOC requirements in a timely and cost-effective manner.

- Methanol formation model development in storage tanks and evaporator.
 - Provide mills with technological guidance through mill sampling and model prediction.
- DOE Sponsorship Part with NCASI and Univ. Idaho:
- Selecting mill sites, conducting mill sampling, and analyzing mill data to complete the database and for computer model VOC prediction. NCASI's collaboration in measuring air emissions
 - New predictive evaporator/stripper models will be added to the fiberline models already developed
 - Full-mill process simulation. Integration of all models and the data base into full-mill simulations

PROJECT BACKGROUND: Methanol emission in Kraft mills is now regulated by the Cluster Rule. Understanding and predicting methanol emission can help mills to meet the requirements.

MILESTONES:

Complete methanol Henry's constant in black liquors
Evaporator operation

DELIVERABLES:

- Fast and automated techniques and protocols for VOC and Henry's constant measurements in mill samples (Reports I, II and III Issued)
- VOC formation model in pulping (Report IV issued)
- Methanol Henry's constant in black liquors (Report V issued)
- Methanol formation in alkaline wood pulping (Report VI issued, attached)
- The Fate of HexA in alkaline pulping (Report VII issued, attached)
- Methanol formation model in black liquor evaporation (Report to be issued)
- Methanol formation model in black liquor storage tanks (Report to be issued)

STATUS OF GOALS FOR FY 99-00:

Methanol formation in storage: ongoing

Methanol formation in evaporation of black liquor: waiting for pilot scale evaporator operational

SCHEDULE:

Task Descriptions (example)	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
VLE database					→
Methanol Formation (pulping)		→			
Methanol Formation (Storage)					→
Methanol Formation Evaporation (Bench scale)	→				
Methanol Formation Evaporation (Pilot scale)					→

SUMMARY OF RESULTS:**See Member Company Reports I-VII Issued**

- Fast and automated techniques and protocols for VOC and Henry's constant measurements in mill samples (Reports I, II and III Issued)
- VOC formation model in pulping (Report IV issued)
- Methanol Henry's constant in black liquors (Report V issued)
- Methanol formation in alkaline wood pulping (Report VI issued, attached)
- The Fate of HexA in alkaline pulping (Report VII issued, attached)
- Methanol formation model in black liquor evaporation (Report to be issued)
- Methanol formation model in black liquor storage tanks (Report to be issued)

SUMMARY OF KEY CONCLUSIONS:

See Member Company Reports I-VII Issued

DISCUSSION:

See Member Company Reports I-VII Issued

1. Topic 1

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

E. References

F. Tables

G. Figures

2. Topic 2

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

E. References

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INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Henry's Law Constant of Methanol in Pulping Spent Liquors

Project F03303/ or F01708 (Previously)

Report 5

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu and X.S. Chai

November 1999

Previously Published Reports of This Project:

1. Zhu, J.Y., Liu, P.-H., Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part V. Henry's Constants of Methanol in Pulping Spent Liquors.**" (This report)
2. Zhu, J.Y., Chai, X-S, and Dhasmana, B., (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part IV. The Formation of Volatile Organic Compounds (VOCs) during Pulping.**"
3. Zhu, J.Y. and Chai, X-S, (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part III. Vapor-Liquid Phase Equilibrium Partitioning of Methanol in Black Liquors.**"
4. Zhu, J.Y. and Chai, X-S, (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part II. Protocol Development to Measure the Contents and Henry's Constants of VOCs in Kraft Mill Streams.**"
5. Zhu, J.Y., Chai, X-S, and Dhasmana, B., (1997), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part I. Method Development for Quantification of VOC contents in Liquids and Vapor-Liquid Phase Equilibrium Partitioning.**"

Upcoming Reports of This Project (In Preparation)

Zhu, J.Y. and Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VI. Methanol Formation During Alkaline Wood Pulping.**"

Zhu, J.Y. and Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VII. The Formation of Hexenuronic Acid Groups in Alkaline Wood Pulping.**"

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Part V: Henry's Law Constant of Methanol in Pulping Spent Liquors

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EXECUTIVE SUMMARY

The release of volatile organic compounds in kraft mills has been an environmental concern. The vapor-liquid equilibrium (VLE) of VOCs in mill streams is a key factor that dictates VOC air emission. Unfortunately, the VLE behavior of VOCs in most kraft mill streams is different from that in binary VOC-water solutions. A good understanding of VLE behavior of VOCs in various mill streams is of significant importance in providing a database for computer model prediction of VOC air emission and design strippers for VOC removal.

Because methanol has been identified as the main VOC species in kraft mill streams, in this study, a direct headspace gas chromatographic method was used to study the methanol Henry's constant in pulping spent liquors collected from kraft pulp mills and laboratory batch pulping processes using various wood species. The total solids content of the pulping spent liquors was less than 25%. It was found that temperature and inorganic solids, mainly sodium salts, are the two parameters that significantly affect the methanol Henry's constants. A two-parameter (temperature and liquor total solids content) empirical model was developed based on the experimental data to predict methanol Henry's constants in pulping spent liquors.

Keywords: Methanol, VOC, Henry's Constant, Black Liquor, Vapor-liquid Equilibrium, Headspace, Gas Chromatography.

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INTRODUCTION

Henry's law constant directly relates the partial vapor pressure to the infinite dilution activity coefficient of a dissolved species in a given solution. In environmental science, the partial vapor pressure of a volatile pollutant species can be used to predict the air emission of the pollutant in many industrial sites. In the chemical industry, the partial vapor pressure dictates the design of strippers and other facilities to separate the volatile species. Therefore, the study of vapor-liquid equilibrium (VLE) of volatile solutes in infinitely dilute solutions has significant practical applications in chemical engineering and environmental science.

We report on Henry's law constant of methanol in pulping spent liquors in this study. It is well known that methanol can be formed through the reaction of methoxyl groups in hemicellulose and lignin with hydroxide during alkaline pulp manufacturing processes in kraft pulp mills [1-3]. The formation of methanol in these processes has created an environmental concern because methanol is soluble in water and an important source of biodegradable organic compounds that increase the biochemical oxygen demand (BOD). Furthermore, methanol is very volatile and can be released into the atmosphere through the vents and hoods of many kraft mill process facilities, e.g., a vent on a spent pulping liquor storage tank, an open hood of a vacuum brownstock pulp washer. Methanol air emission in kraft mills is now regulated by the U.S. Environmental Protection Agency through the Cluster Rule [4]. The prediction of methanol air emission through process simulation [5, 6] can provide kraft mill engineers a tool for process optimization to reduce methanol emission. The emission prediction requires the methanol concentration in the flow of a vent or a hood that is proportional to the methanol concentration in the vapor phase inside a facility. For most kraft mill operation processes, it is a good approximation to use Henry's law to describe the methanol partitioning between the vapor and the process stream liquid phases inside process facilities. Study of the Henry's constant of methanol in various kraft mill streams, therefore, can provide a database for air emission predictions.

The infinite dilution activity coefficient of methanol in water has been reported in several studies [7-13]. However, the data reported in these studies are not consistent as discussed by

Christensen [7]. Furthermore, the extrapolation of these data to solutions that contain components in addition to methanol and water, such as those found in pulp and paper streams, is not reliable. There are many experimental methods available for the study of infinite dilution activity coefficient as reviewed by Kojima et al. [14] recently. Most of these methods can be used to determine the Henry's constants of solutes, but not without limitations in measurement accuracy and other related problems. Static headspace gas chromatography has been widely used to obtain partition coefficients (or Henry's constants) because of its accuracy, consistency, speed, and versatility. Direct [15, 16], indirect [17-19], and multiple extraction [20] headspace GC methods have been developed for this purpose. The direct headspace GC method measures the solute in the vapor and liquid phases directly and separately to determine Henry's constant. The indirect method makes two headspace measurements in two separate sample vials without measuring the liquid phase to derive the Henry's constant through material balance and VLE of the solute. The multiple extraction GC method was developed and experimentally demonstrated by Chai and Zhu [20] and is similar to dynamic gas extraction but is carried out in steps. It relies on VLE of the solute and the fact that the total solute mass can be integrated over infinite numbers of extractions to obtain a linear equation. The equation relates the n th measurements to the sum of the first $(n-1)$ measurements by the Henry's constant. Chai and Zhu [18] have compared methanol Henry's constants (or activity or partitioning coefficients) measured by several researchers using different static headspace GC methods and found that the data agree well. However, the headspace GC measured values are consistently higher than those predicted by UNIFAC and ASOG methods and much higher than those measured by differential ebulliometry [21], which is known to be inaccurate in determining activity coefficients of very small values, such as methanol infinite dilution activity coefficient in water. Detailed comparisons of methanol Henry's constants can be found in a separate research that we conducted [22].

In this study, a direct headspace gas chromatographic method described by Kolb et al. [16] was employed to directly determine the Henry's law constant of methanol in dilute solutions. Binary solution measurements were used to validate the experiments. Measurements in pulping spent liquors were used to derive an empirical correlation of Henry's law constant of methanol for air emission predictions in kraft mills.

EXPERIMENTAL

Measurement Facility and Method

All the measurements were conducted using a commercial headspace gas chromatograph. The instrument consists of a headspace sampler (HP-7694, Hewlett-Packard, Palo Alto, CA) and a capillary gas chromatograph (HP-6890, Hewlett-Packard).

The Henry's law constant H_i of a species i is defined according to the following equation:

$$H_i = \lim_{x \rightarrow 0} \frac{P_i^v}{x_i} = \lim_{x \rightarrow 0} \frac{y_i \cdot P}{x_i} \quad (1)$$

where x_i and y_i are the mole fraction of the species i in the liquid and vapor phase, respectively. For a system at equilibrium in a static headspace, the vapor phase can be assumed to follow the ideal gas law,

$$y_i \cdot P = P_i^v = C_{Gi} \cdot RT \quad (2)$$

where C_{Gi} is the solute mole concentration in the headspace (vapor phase) and R is the universal gas constant. In a system in which all solutes are at infinite dilution, we can approximate the mole fraction of solute i in the liquid phase can be approximated as

$$x_i \approx \frac{n_i}{n_j} = \frac{C_{Li}}{\rho_j / M_j} = C_{Li} \cdot v_j \quad (3)$$

where C_{Li} is the solute concentration in the liquid phase at equilibrium, and ρ_j , M_j , and v_j are the density, molecular weight, and the molar volume of the solvent, respectively. Eqn. (3) is still a good approximation even for pulping spent liquors with total solids content around 20%.

Combining Eqns. (2), (3), and (1) leads to a relationship between the Henry's constant of species i and its partition coefficient $K_i = C_{Li}/C_{Gi}$ in a static headspace:

$$H_i = \frac{RT}{v_j K_i} = \frac{\rho_j RT}{M_j \cdot K_i} \quad (4)$$

A direct headspace GC method [16] was used in the present study to determine the partition coefficient K_i . In this method, the initial methanol concentration C_0 in a sample black liquor was first measured using an indirect headspace GC method [23, 24] (a standard addition procedure). The methanol concentration C_G in the static headspace at VLE in terms of GC recorded peak area A was then measured. Therefore,

$$K_i = \frac{C_{Li}}{C_{Gi}} = \frac{C_0 - \beta C_{Gi}}{f \cdot A_i} \quad (5)$$

where f is the GC response factor and $\beta = V_G/V_L$ is the phase ratio. In the present study, the volume of the sample vial was 20 mL and the liquor sample size was 10 mL for all the experiments conducted, which gave the headspace volume of 10 mL and the phase ratio $\beta = 1$. Therefore, if K_i is much greater than 1, i.e., $K_i > 10$, $C_{Gi} \ll C_{Li} (< C_0)$ can be ignored in Eqn. (5), and, hence,

$$K_i \approx \frac{C_0}{f \cdot A_i} \quad (6)$$

We adopted an external calibration standard to obtain the GC response factor f by using a standard water-methanol solution with known methanol concentration of $C_{so} = 800$ mg/L and methanol VLE partition coefficient K_{si} , (e.g., $K_{si} = 570$ at 70°C [18]), and, hence,

$$K_i = \frac{A_{si}}{A_i} \cdot \frac{C_o}{C_{so}} \cdot K_{si} \quad (7)$$

where A_{si} is the GC peak area recorded in measuring the headspace vapor of the standard solution at the temperature corresponding to K_{si} .

Pulping Spent Liquor and Chemicals

Pulping spent liquor, also called black liquor from its color, is an aqueous solution containing dissolved organic and inorganic solids. It is a byproduct of the wood delignification process in pulp manufacturing. The dissolved organic materials are complex substances derived from cellulose, hemicellulose, lignin, and other extractives in the wood. The soluble inorganic solids are mainly sodium salts with minimal quantities of potassium salts. The total solids content of pulping spent liquor or weak (unconcentrated) black liquor is around 5-20% with the organic to inorganic ratio around 0.45. Black liquor is caustic with a pH value of about 13. It also contains many volatile organic compounds (VOCs), such as methanol, methyl ethyl ketone (MEK), and dimethylsulfide (DMS), formed during pulping. The concentrations of these VOCs are very low and can be assumed to be at infinite dilution from a thermodynamic point of view.

Weak black liquors derived from various wood species and collected from both kraft pulp mills and laboratory pulping processes were used in this study. Four softwoods of Douglas-fir, white spruce, western hemlock, and southern pine, and six hardwoods of aspen, basswood, birch, maple, oak, and sweetgum are used in laboratory pulping experiments. The total dissolved solids contents of all the liquors were less than 25%, and, the black liquors were therefore treated as aqueous solutions. Analytical grade sulfonated lignin, mixed wood kraft lignin, sodium carbonate, sodium sulfate, sodium chloride, sodium hydroxide, dimethylsulfide (DMS), dimethyldisulfide (DMDS), methyl ethyl ketone (MEK), and α -pinene were added to standard water-methanol solutions to study the effects of these minor constituents of black liquors on the Henry's constant of methanol.

Experimental Conditions

To achieve good signal to noise ratio in GC measurements, GC conditions were set as follows: HP-5 capillary column at 30°C; carrier gas helium flow: 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: gentle shaking for equilibration of the sample for 25 minutes, vial pressurization time of 0.2 min to create a pressure head in the headspace for sample transfer to the sample loop, sample loop fill time of 1.0 min, and loop equilibration time

of 0.05 min. The sample loop is heated to avoid condensation. In instrument evaluation tests, we found that the GC signal peak area did not vary with the sample loop filling time and loop equilibrium time in certain operating ranges, respectively, indicating that the sample in the loop is a good representative of the sampled vapor phase.

Equilibrium Time

It was necessary to establish that vapor-liquid equilibrium had been achieved in these experiments. Sample size, temperature, and equilibration time are the three major factors that can affect equilibrium. To accelerate the vapor-liquid equilibrium process between the liquid and vapor phase in the headspace of a sample vial, the commercial HP-7694 headspace sampler applies gentle or strong shaking to the sample vial. In the experiments, we used a liquid sample volume $V_L = 10$ mL, or a phase ratio of $\beta = 1$, and applied gentle shaking. We found that an equilibrium time of 25 minutes is sufficient to achieve methanol vapor-liquid equilibrium in the static headspace of a sample vial [24]. Similar equilibrium test was also conducted using black liquor at a temperature of 323 K in the present study and found that a 25-minute equilibrium time is sufficient.

Measurement Uncertainty

Although black liquor can be treated as an aqueous solution, the distribution of various dissolved solids in the liquor can be inhomogeneous, which makes it difficult to obtain uniform and representative samples during experiments. Therefore, liquor sampling can contribute to measurement uncertainty. Sampling of the liquid phase and the vapor phase can also contribute to measurement uncertainty. We conducted 11 replicate measurements (repeatability test) using black liquor collected from a kraft mill to estimate the actual measurement uncertainty. We found that the maximum error of the 11 individual measurements relative to the average value of the 11 measurements was 15%. However, the relative standard deviation of the 11 measurements was 8.8%. We conducted triplicate experiments and averaged the results; therefore, the actual measurement uncertainty of the data presented in this study is less than the relative standard deviation of the single measurement of 8.8%.

RESULTS AND DISCUSSIONS

Effect of Temperature

Twenty two black liquor samples were collected from both kraft mills and our laboratory pulping processes of various wood species. Because the operating process temperature of weak black liquor in kraft mills varies significantly, we measured the Henry's constants of the 22 black liquors in a temperature range of 50 to 80°C. Our measurements indicate that the Henry's constant of methanol in all the black liquors follows the van't Hoff relationship with temperature. Table I lists the linear regression results along with the correlation coefficients for the liquors tested. Only the results from 4 black liquor samples are shown in Fig. 1 for clarity. The van't Hoff equation [25] is given by:

$$\ln(H) = \frac{a}{T} + b \quad (8)$$

where a is directly related to the partial molar excess enthalpy of a solute in a solvent and b is an empirical constant.

For comparison, we have also plotted Henry's constants of methanol in water in Fig. 1. The results as listed in Table I show that the slopes for the 22 black liquor samples were very close to the slope of the methanol-water mixture. The relative standard deviations of the slopes for black liquors (22 data sets) and all the samples (23 data sets including water-methanol mixture) were 6.4 and 6.9%, respectively. Also, the slopes of all the black liquor samples were slightly smaller than that of the water-methanol mixture, indicating that the partial molar excess enthalpy of methanol in black liquor (a multicomponent system) is only slightly smaller than that in water (a two-component system).

Figure 1 indicates that there are significant variations in measured methanol Henry's constants among various black liquors. The variations in the compositions of the black liquors due to inorganic and organic solids content, pH, and the presence of other species are a possible cause of these differences.

Effect of Lignin

Black liquor contains significant amounts of dissolved organic materials, such as lignin. To understand the effect of lignin on Henry's constants of methanol, we have measured methanol Henry's constants in several model solutions containing water, methanol, and sulfonated lignin. We found that the methanol Henry's constant is not affected by the presence of sulfonated lignin. Figure 2 shows the normalized Henry's constants of methanol measured in such solutions at two temperatures, 343 and 353 K, and various sulfonated lignin concentrations. Similar experiments were also conducted using mixed wood lignin (MWL) in a slightly caustic solution (MWL can only be dissolved in caustic solutions) yielded from kraft pulping of softwood to liner board grade pulps (Westvaco Corp., SC). It was found that Henry's constant of methanol is only a weak function (increases with the increase) of mixed wood lignin mass concentration ranging from 0 to 13%.

Effect of pH

We took a similar approach to study the effect of pH on the Henry's constant of methanol in black liquors. Black liquor is a caustic solution with a nominal pH value of about 13. Different amounts of sodium hydroxide were added to methanol-water solutions. Henry's constants in these solutions were measured. As shown in Fig. 3, our results indicate that the Henry's constant of methanol is proportional to the hydroxide concentration to the power of 0.2, which means that the effect of pH is not significant. It should be noted that the sodium ion concentration also contributes to the variations shown in Fig. 3. The effect of ionic strength, or more specifically, sodium salt concentration on methanol Henry's constant is discussed in the next section.

Effect of Inorganic Salt

Black liquor contains significant amounts of inorganic solids. These inorganic solids are mainly sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4) plus minimal amounts of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium chloride (NaCl), and potassium salts. To understand the effect of inorganic solids on methanol Henry's constant, we measured the Henry's constant in

water-methanol solutions containing Na_2CO_3 , Na_2SO_4 , $\text{Na}_2\text{S}_2\text{O}_3$, and NaCl , respectively. We found that the logarithm of Henry's constant of methanol increases linearly with the sodium salt mass concentration at a given temperature, but dependent on the type of salt as shown in Fig. 4. The measured Henry's constants of methanol in actual black liquors are also shown in Fig. 4. The total mass concentrations of the inorganic materials (more than 95% are sodium salts) in the 22 black liquor samples studied were obtained by subtracting the lignin (organic solids measured by UV absorption) content from the measured total solids content. We used the following equation to express this relation [26]:

$$\ln(H) = c \cdot S_{\text{salt}} + d \quad (9)$$

where S_{salt} is the total sodium salt mass concentration of the liquor.

Effects of dimethylsulfide, dimethyldisulfide, methyl ethyl ketone, α -pinene, β -pinene, fatty acids, resin acids

Many other chemical species, such as dimethylsulfide (DMS), dimethyldisulfide (DMDS), α -pinene, β -pinene, fatty acids, resin acids (MEK), present in weak black liquors can affect the methanol Henry's constant. To determine the effect of these compounds, we prepared methanol-water solutions containing one of these compounds to study their individual effects on Henry's constant of methanol. The results indicate that the effect of these compounds on methanol Henry's constant is insignificant at the concentration levels present in weak black liquor. Figures 5-8 show the effects of α -pinene, DMS, MEK, and DMDS.

Empirical Correlation

The results presented in this work show that temperature and inorganic solids (salts) content are the two main variables that affect Henry's constants of methanol in black liquors. The effects of pH, lignin concentration, and other organic compounds are not significant and can be neglected. Because the ratio of the inorganic to organic solids (wood lignin) in black liquors does not vary significantly and the total solids content can be easily determined with very good accuracy, the total solids content S can be used to account for the effect of inorganic salts on

Henry's constant of methanol. Furthermore, the slight effect of wood lignin on methanol Henry's constant can be accounted for by using the total solids content. To demonstrate the validity of this assumption, we plotted the measured methanol Henry's constants in the 22 black liquors against the total solids content. As shown in Fig. 9, we found that the logarithm of Henry's constant of methanol is linearly related to total solids content at four different temperatures tested, indicating that the minor effect of wood lignin on methanol Henry's constant is well accounted for by using the total solids content. The scatter in the data can be attributed to experimental errors, the effects of minor variables such as pH, the presence of other components, and the small variations of inorganic/organic ratio from liquor to liquor. This is demonstrated by the fact that the measured Henry's constants of methanol in a given black liquor sample at the 4 temperatures (50, 60, 70, and 80°C) are very consistent, i.e., all the measured data points are either lower or higher than the expected (regression) value.

The experimental data can be correlated using the following expression, based on the work of Stumm and Morgan [25] and Schwarzenbach et al. [26]:

$$\ln(H) = -\frac{A}{T} + B \cdot S + C \quad (10a)$$

or

$$H = m \left[\exp\left(-\frac{A}{T} + B \cdot S\right) \right]. \quad (10b)$$

with $m = 3.77 \times 10^{12}$, $A = 5620$, $B = 1.63$, and H in *Pa*. Figure 10 plots the direct comparison of the methanol Henry's constants of 22 black liquors measured at 4 temperatures with those predicted using Eqn. (10). We found that the model-predicted methanol Henry's constants agree very well with those measured experimentally.

CONCLUSIONS

We studied Henry's constants of methanol in various kraft pulping spent liquors collected from kraft mills and laboratory pulping processes by a headspace gas chromatographic technique. We found that temperature and inorganic solids content are the two major variables that affect methanol Henry's constants. The effects of other parameters, such as pH, lignin content, and the presence of other organic compounds are insignificant. We developed a two-

parameter (temperature and total solids content) empirical model for the prediction of methanol Henry's constant based on the experimental data obtained in this study.

ACKNOWLEDGEMENT

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Fig. 1

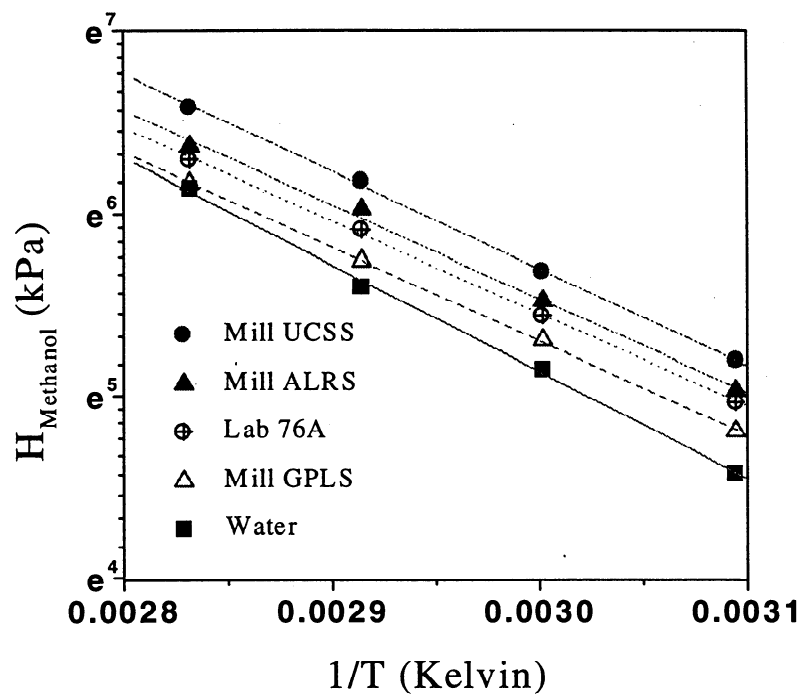


Fig. 2

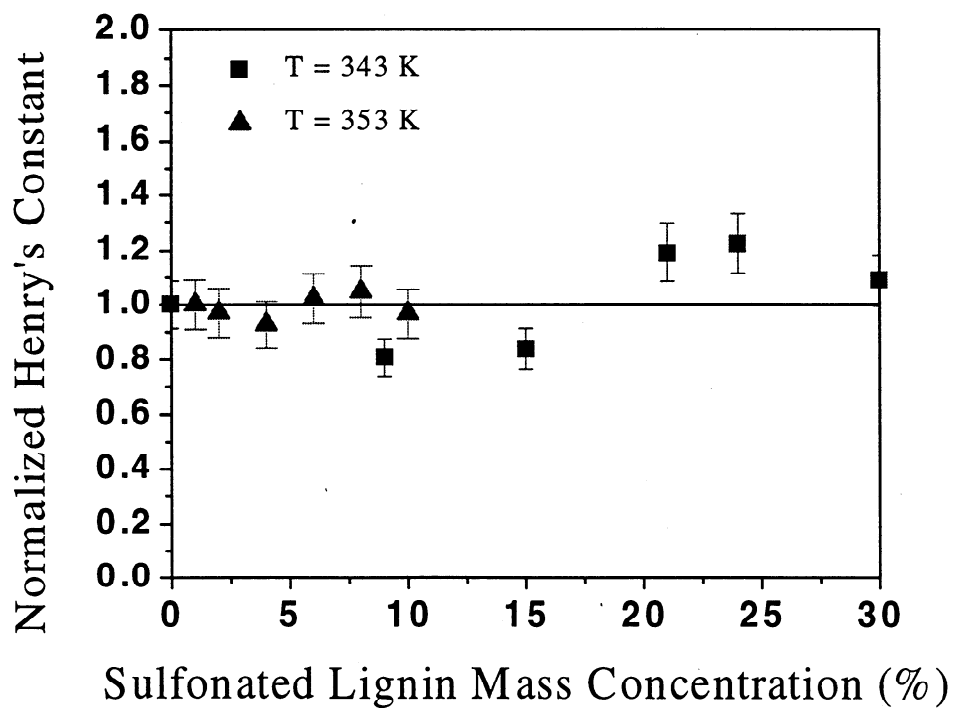


Fig. 3

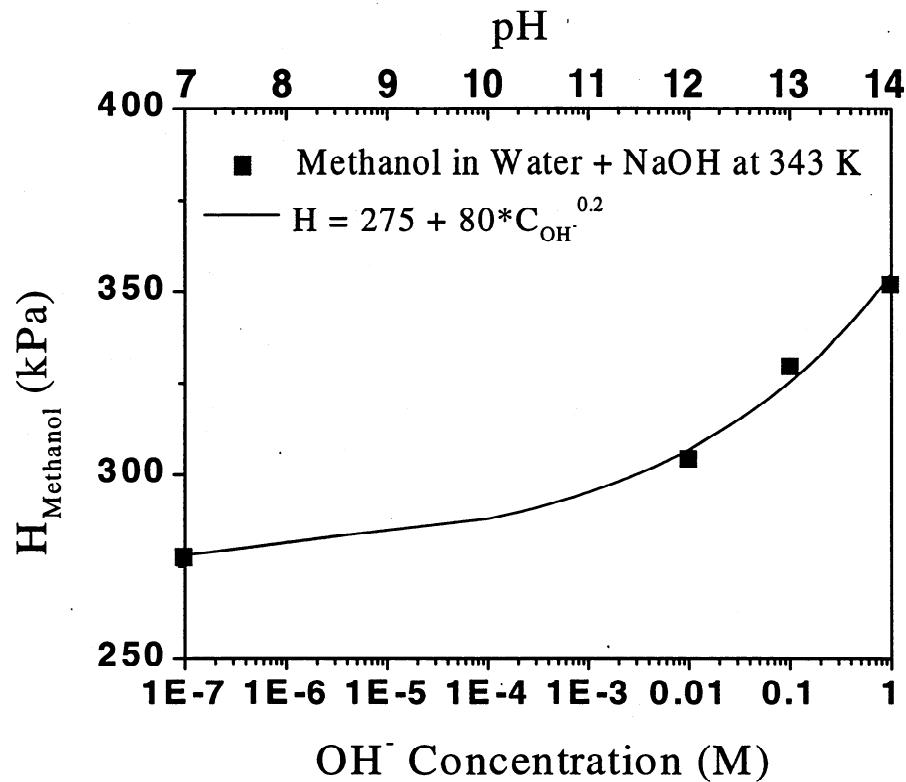


Fig. 4

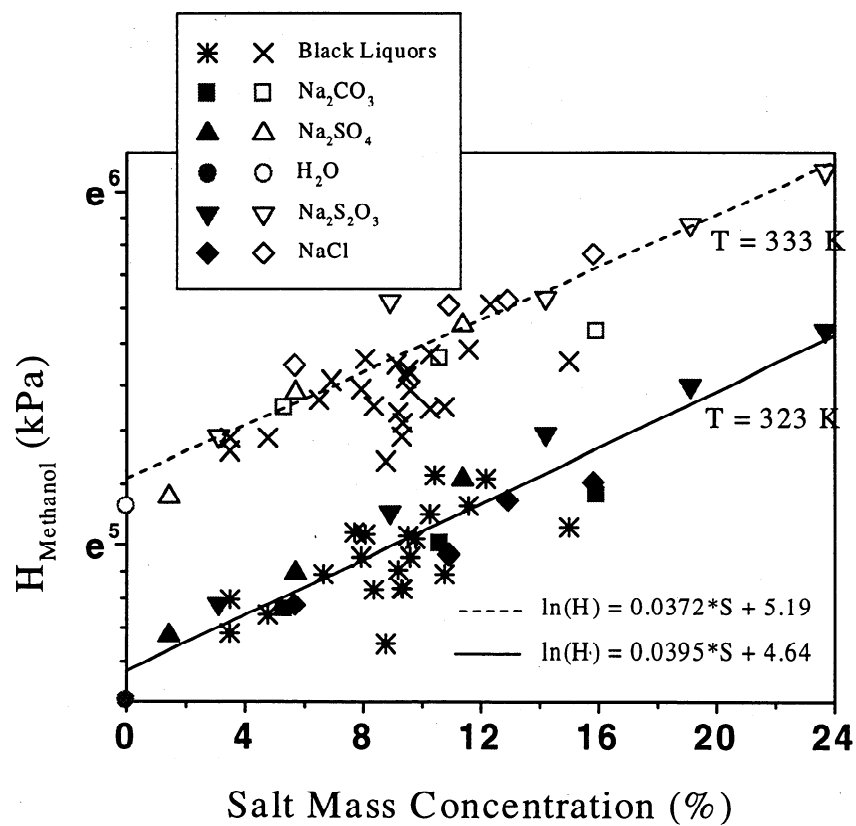


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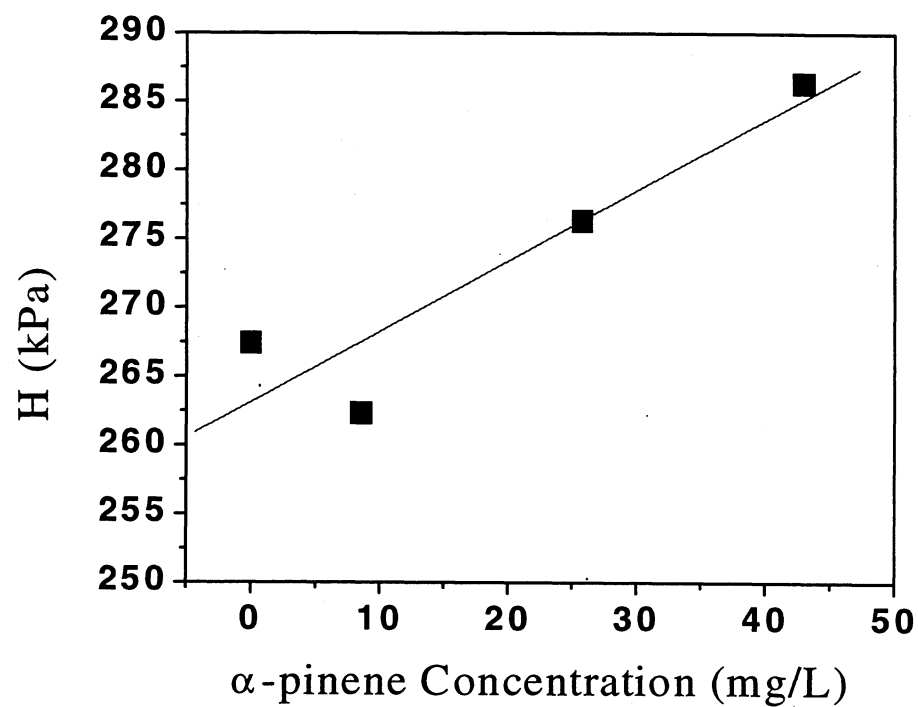


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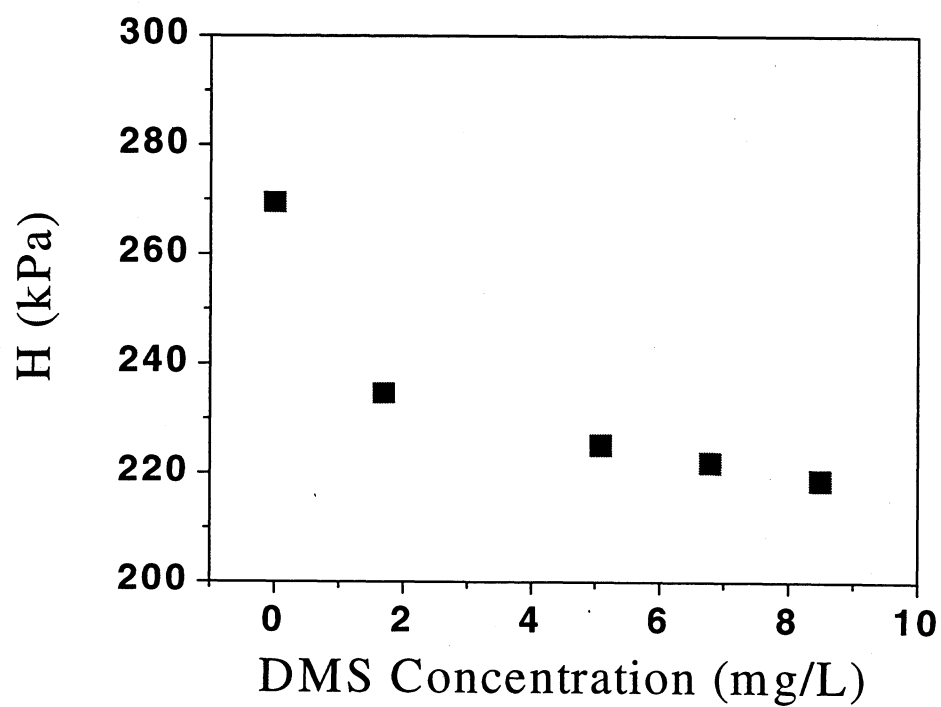


Fig. 7

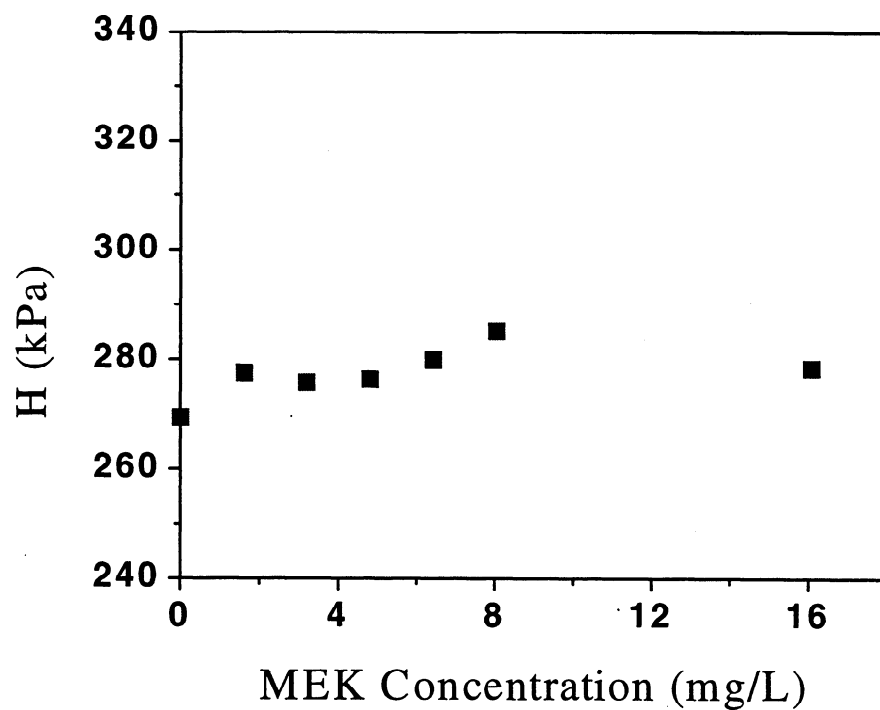


Fig. 8

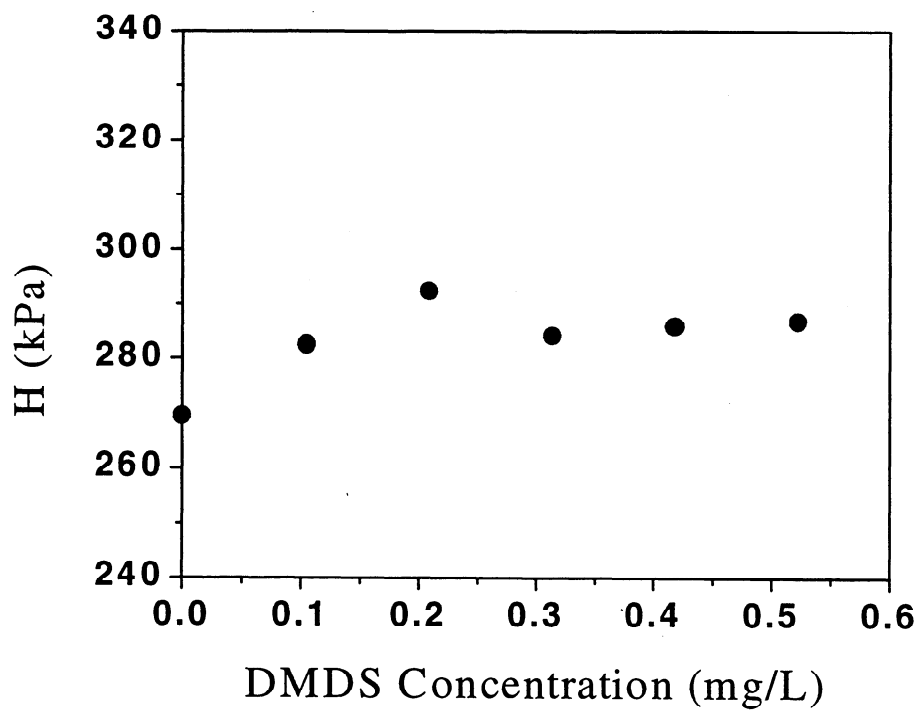


Fig. 9

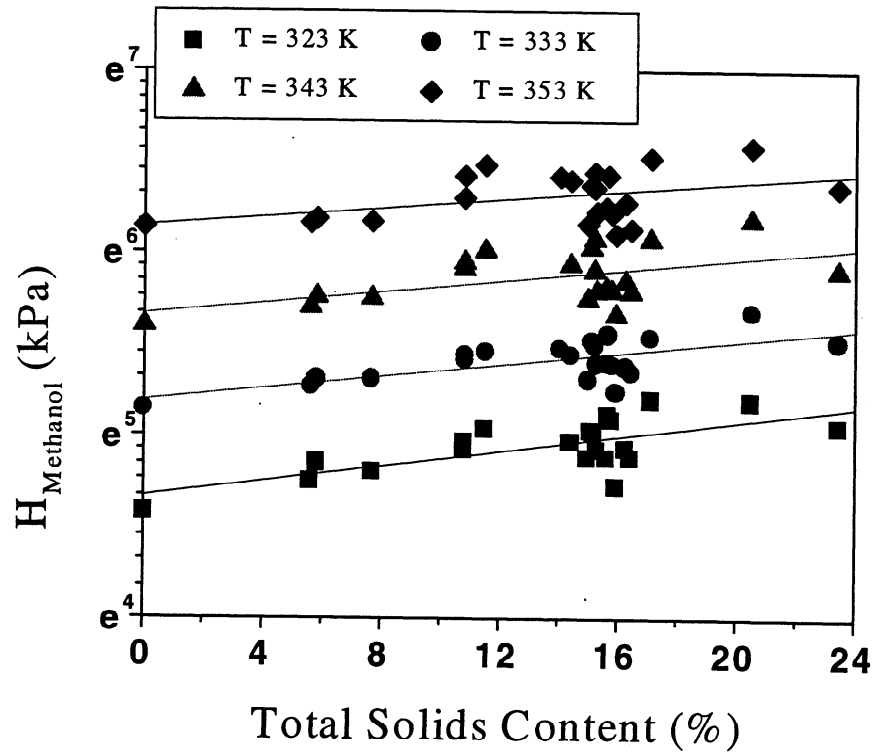
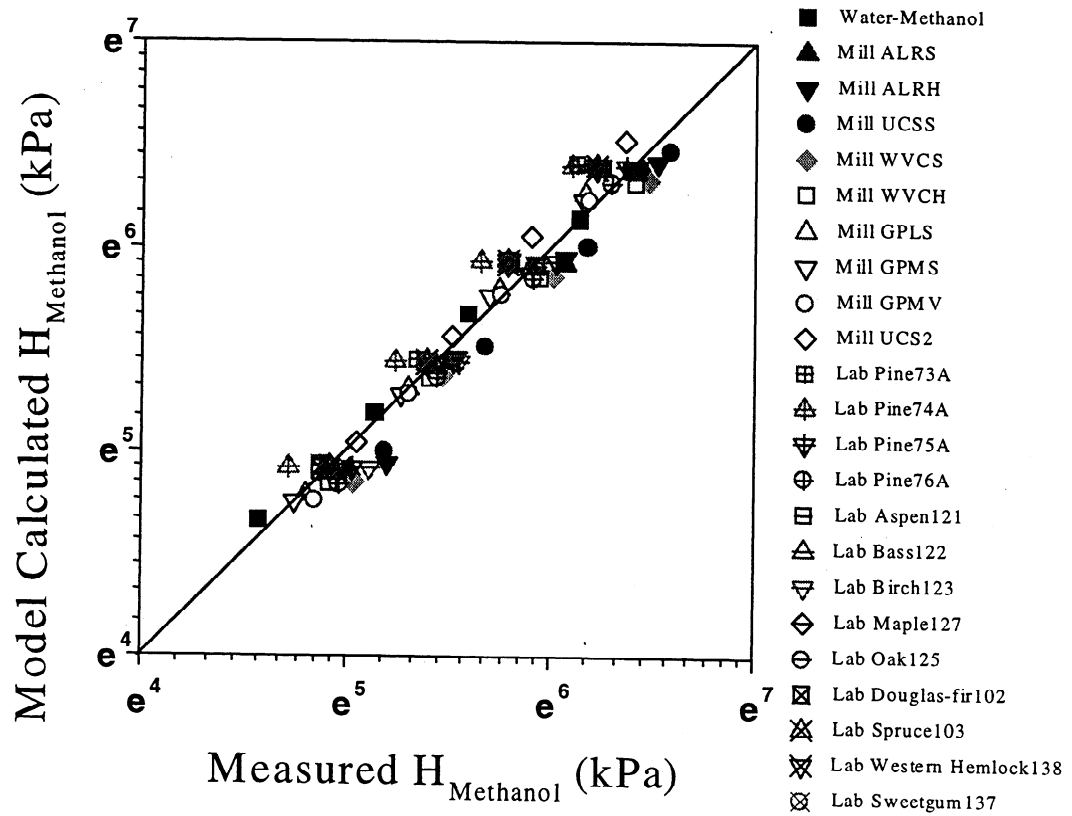


Fig. 10



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Table I: A list of fitting parameters of Eqn. (8) for a water-methanol mixture and black liquors.

Sample	a	b	Correlation Coefficient
Water-Methanol	-5878	22.766	0.9992
Mill ALRS	-5337	21.708	0.9996
Mill ALRH	-5164	21.024	0.9981
Mill UCSS	-5092	20.729	0.9996
Mill WVCS	-5179	20.835	0.9999
Mill WVCH	-5525	22.118	0.9980
Mill GPLS	-5119	20.988	0.9947
Mill GPMS	-5553	22.187	0.9983
Mill GPMV	-5734	22.648	0.9996
Mill UCS2	-5325	21.233	0.9997
Lab Pine73A	-5101	20.623	0.9999
Lab Pine74A	-4930	20.305	0.9991
Lab Pine75A	-4793	19.723	0.9991
Lab Pine76A	-5120	20.857	0.9996
Lab Aspen121	-5452	21.825	0.9997
Lab Bass122	-5767	22.733	0.9996
Lab Birch123	-4907	20.281	0.9976
Lab Oak125	-4305	18.366	0.9947
Lab Maple127	-5010	20.527	0.9996
Lab Douglas-fir102	-5175	20.903	0.9995
Lab Spruce103	-5128	20.787	0.9997
Lab Western Hemlock138	-4872	19.947	0.9998
Lab Sweetgum137	-4912	20.124	0.9996
Mean	-5190	21.01	0.9989
RSTD	6.9%	5.0%	0.15%

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Methanol Formation During Alkaline Wood Pulping

Project F03303/ or F01708 (Previously)

Report 6

A Progress Report

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu and X.S. Chai

November 1999

Previously Published Reports of This Project:

1. Zhu, J.Y., Yoon, S.-H., Liu, P.-H., Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VI. Methanol Formation During Alkaline Wood Pulping.**" (This report)
2. Zhu, J.Y., Liu, P.-H., Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part V. Henry's Constants of Methanol in Pulping Spent Liquors.**"
3. Zhu, J.Y., Chai, X-S, and Dhasmana, B., (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part IV. The Formation of Volatile Organic Compounds (VOCs) during Pulping.**"
4. Zhu, J.Y. and Chai, X-S, (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part III. Vapor-Liquid Phase Equilibrium Partitioning of Methanol in Black Liquors.**"
5. Zhu, J.Y. and Chai, X-S, (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part II. Protocol Development to Measure the Contents and Henry's Constants of VOCs in Kraft Mill Streams.**"
6. Zhu, J.Y., Chai, X-S, and Dhasmana, B., (1997), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part I. Method Development for Quantification of VOC contents in Liquids and Vapor-Liquid Phase Equilibrium Partitioning.**"

Upcoming Report of This Project (In Preparation)

Zhu, J.Y. and Chai, X.-S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VII. The Formation of Hexenuronic Acid Groups in Alkaline Wood Pulping.**"

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Part VI: Methanol Formation During Alkaline Wood Pulping

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EXECUTIVE SUMMARY

The release of volatile organic compounds (VOCs) in kraft mills has been an environmental concern. VOCs are formed in the wood pulping processes. Its formation depends on pulping time, temperature, hydroxide concentration, and wood species. Limited data has been reported on VOC formation (VOC yield) during pulping in the literature. In a previous study (Report No. 4), we investigated time-dependent VOC formation in alkaline pulping. Kappa number is generally used in pulp production; therefore, it will be beneficial to study the dependency of kappa number on methanol formation.

Because methanol has been identified as the main VOC species in kraft mill streams, this study investigated methanol formation in four pulping processes, i.e., soda, kraft, polysulfide, and multistage, and under various pulping conditions, i.e., different sulfidities and catalyst anthraquinone (AQ). The effects of pulp kappa number and wood species (both hardwood and softwood) on methanol formation were also studied. The results indicate that the alkaline hydrolysis of hemicellulose contributes to about 40% of the total methanol formation in kraft pulping of southern pine to bleachable grade. For a given active alkali (AA) charge and kappa number, soda pulping produces more methanol than kraft and polysulfide pulping processes do; furthermore, both the increase in sulfidity and the addition of catalyst AQ can reduce methanol formation.

Keywords: Methanol, Pulping, Headspace Gas Chromatography, Hexenuronic Acids

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METHANOL FORMATION DURING ALKALINE WOOD PULPING

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INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol, in kraft mills has been an environmental concern. Methanol has been identified as the major alcohol in pulp mill process streams [1-4]. Methanol is soluble in water and can increase the biochemical oxygen demand (BOD) [5]. Furthermore, it can also be released into the atmosphere at the process temperatures of kraft mill streams. The Cluster Rule [6] of the U.S. Environmental Protection Agency (EPA) now requires the control of the release of methanol in pulp and paper mills. Therefore, the understanding and quantification of methanol formation in pulp mills is of significant practical importance.

Methanol is primarily produced through the pulping process in digesters. Its formation during pulping depends on the pulping time, temperature, hydroxide concentration or alkalinity, and wood species [5]. Two different mechanisms of methanol formation in pulping processes are generally accepted [7-9]: the rapid alkali-catalyzed elimination of methanol from the rapid 4-O-methylglucuronic acid residues in hemicellulose [7] to form hexenuronic acid groups and methanol, and the demethylation of lignin [8, 9]. However, the amount of demethylated methoxyl groups in lignin in an alkaline pulping process is small according to Sarkanen et al. [9]. Therefore, it is reasonable to assume that a substantial amount of methanol is formed through the demethylation of xylan [7, 9]. Based on this argument, we conducted a methanol mass balance estimation in our previous study [10] and found that the complete (100%) elimination of methanol from xylan accounts for 70-75% of the total methanol formed (as measured from the final pulping spent liquor) in our laboratory batch pulping processes. As a result, lignin demethylation accounts for about 20% of the total methanol formed. Because most of the

methoxyl groups in lignin have not been demethylated during pulping [9], they can be hydrolyzed to form methanol in the downstream processes, such as bleaching and chemical recovery, whenever a set of favorable reaction conditions exists.

In our previous study [10], the time-dependent methanol formation during alkaline pulping of southern pine and birch to bleachable grade was investigated. In this study, we conducted various laboratory batch alkaline pulping processes to study the effect of kappa number, wood species, catalyst anthraquinone (AQ), and sulfidity on methanol formation.

Rapidly and accurately analyzing methanol concentration in pulping spent liquors and hexenuronic acid groups in pulps is critical to achieve the goals of the present research. It is not a trivial task to analyze methanol in black liquors due to the dissolved solids, in particular the inorganic salts, which makes it very difficult to apply gas chromatographic (GC) analysis through direct column injection because of fouling of the GC columns. In this study, methanol concentrations in the pulping spent liquors were analyzed by the method that we developed previously [3] using headspace gas chromatography. Although several methods have been developed to measure hexenuronic acids (HUA) in chemical pulps recently, all of these methods are time-consuming and require more than several hours to obtain one measurement. UV spectrophotometry through acid hydrolysis, used by Vuorinen [11], also suffers from the spectral interference of acid-soluble lignin in the UV range. NMR spectroscopy [12] and anion exchange chromatography [13] suffer from very low hydrolysis efficiency and therefore are very time consuming. The HPLC method developed by Gellerstedt and Li [14] uses a combination of hydrolysis by mercuric acetate and peroxide oxidation coupled with thiobarbituric acid, which complicates experimental procedures for quantifying hydrolysis products. In this study, a rapid UV-spectrophotometric method that we developed [15] was applied to determine the formation of HUA in chemical pulps.

EXPERIMENTAL

Pulping

The pulping experiments were conducted using eight rotating bomb digesters. The volume of each bomb digester was 500 mL. Fifty grams of oven-dry wood chips of four softwoods

(Douglas-fir, white spruce, western hemlock, and loblolly pine) and six hardwoods (aspen, bass, birch, maple, oak, and sweetgum) were used in each cook. The cooking liquor-to-wood chip ratio was 4.0 L/kg for southern pine and 3.7 L/kg for all the other wood species. Conventional kraft, soda, polysulfide kraft, and multistage kraft pulping processes to simulate RDH processes were conducted. The active alkali charge AA (as Na_2O) was maintained at 18% on wood for all the pulping processes except the multistage pulping. Three sulfidities of $S=10$, 20, and 30% and four AQ concentrations of 0, 0.025, 0.05, and 0.1% on wood were used in kraft pulping. A polysulfide concentration of 1.5% on wood and a sulfidity of $S=18\%$ were used in polysulfide kraft pulping. The multistage pulping processes were designed as follows: Stage 1 used black liquor with AA = 9 g/L (as Na_2O) and Na_2S = 12 g/L and lasted 20 minutes when pulping temperature was raised from 100 to 130°C, Stage 2 used black liquor with AA = 15 g/L and Na_2S = 12 g/L and lasted 20 minutes when pulping temperature was raised from 130 to 160°C, and Stage 3 used white liquor with AA = 18% and sulfidity $S = 30\%$ and lasted to the end of the cook and varied for different cooks. Therefore, some of the cookings may only have experienced Stage 1 or 2, depending on the total cooking time used to achieve the desired kappa number. For each set of pulping conditions selected, the pulping temperature was first linearly ramped from 100°C to 170°C in one hour and then maintained at 170°C to continue delignification. The pulping processes in different digesters were terminated at different pulping times to obtain the rate of formation of methanol and hexenuronic acid. By this approach, the effect of kappa number on methanol formation was obtained. The pulp kappa numbers were measured using the standard TAPPI Test Method (T236 cm-85) [16].

Methanol Analysis

The indirect headspace GC method for methanol analysis that we developed [3] uses the standard addition approach but relies on methanol material balance and liquid/vapor phase equilibrium in the sampling vial. Through the sampling of the vapor phase in the headspaces of two sampling vials (one with the standard addition of known amount of methanol), the method calculates the methanol concentration in the liquor from the ratio of the peak areas of the two headspace measurements. Therefore, calibration and direct sampling of the liquor are not required. It has been demonstrated that the method is reliable for determining methanol concentration in various kraft mill streams, including black liquors. A commercial headspace

gas chromatograph (HSGC, HP-7694 and HP-6890 Hewlett-Packard, Palo Alto, CA) was employed. GC conditions are: HP-5 capillary column at 30°C; carrier gas helium flow: 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: 25 minutes gentle shaking for equilibration of the sample, vial pressurization time: 0.2 min, and sample loop fill time: 1.0 min., loop equilibration time: 0.05 min. The sample preparation and measurement procedures were as follows: pipette duplicate 10 mL of sample solution into two 20 mL vials, add 10 µL of pure methanol solvent by microsyringe into one of the vials, then, close the vials and place them into the headspace sample tray for measurement.

Measurement of Hexenuronic Acid Groups

The UV-spectrophotometric HUA analysis method that we developed [15] uses a low absorptive mercuric chloride hydrolysis agent together with a spectral compensation technique to directly and rapidly (each measurement only takes 30 minutes) determine HUA concentration in chemical pulps. In this method, 22 mM (0.6 %) mercuric chloride and 0.7 % sodium acetate, of analytical grade from commercial sources, are used to make a hydrolysis solution. Then approximately 0.05 gram of air-dried pulp handsheet with a known moisture content is accurately weighed and put into a 20-mL vial with 10 mL of hydrolysis solution. The mixture is sealed in the vial by a septum. To obtain good mixing of the pulp with the hydrolysis solution, we shake the vial and then heat the mixture for 30 minutes in a water bath with a temperature range of 60-70°C. After the solution is cooled to room temperature, UV absorption measurements of the filtered solution are conducted in a 10-mm path length silica cell using a commercial spectrophotometer (UV-8453, Hewlett-Packard) at a wavelength range of 260 to 290 nm.

RESULTS AND DISCUSSION

Understanding Methanol Formation During Pulping

Figure 1 shows the time-dependent methanol and pulp kappa data of 3 replicate experiments of conventional kraft pulping of southern pine. The methanol data are presented as kilogram per metric ton of oven-dry pulp based on measured pulp yields and methanol

concentrations in the pulping spent liquors. The time-dependent methanol data show similar characteristics to those obtained in our previous study [10] using a different batch digester (ME&K), i.e., methanol formation is slow initially due to low cooking temperature, then increases rapidly as the temperature reaches 170°C, and finally levels out. A certain amount of methanol was formed instantly at the beginning of the pulping process. Although these 3 sets of experiments were conducted in a 6-month period, the results show remarkable repeatability.

We measured the amount of HUA in the pulp samples obtained in the kraft conventional pulping processes of southern pine with sulfidity $S = 30\%$ and active alkali charge $AA = 18\%$ to validate the mechanism of methanol formation through rapid alkali-catalyzed elimination of methanol from 4-O-methylglucuronic acid residues in hemicellulose [7]. According to the alkali-catalyzed methanol formation reaction of 4-O-methylglucuronic acid residues [7], the production of one mole of HUA will be accompanied by the formation of one mole of methanol. Figure 2 shows the correlation of the measured methanol in the pulping spent liquors and the measured HUA in the corresponding pulps. Because the methanol formation is not linearly dependent on cooking time, as shown in Fig. 1, the pulping temperature is not a linear function of methanol formation in Fig. 2. The data indicate that the amounts of methanol measured in the pulping spent liquors are linearly proportional to the amounts of HUA found in the pulps up to a methanol level of 53 mol/ODT-wood or 1.66 kg/ODT-wood ($R^2 = 0.9938$) when the pulping temperature reaches 160°C. Furthermore, the slope of the linear relationship is close to unity (0.90, to be exact, from least squares fitting of the first 3 data points, corresponding to pulping time of 65 minutes and temperature 160°C.) Therefore, the amount of HUA dissolution and the amount of methanol formation from lignin demethylation in the pulping liquor are negligible. This validates the 1:1 relationship of the amounts of methanol and HUA formed through the xylan degradation reaction. The slightly lower-than-unity (10%) slope of the linear relationship is perhaps due to the fact that some of the HUA formed associated with methanol formation is no longer with the pulp and is dissolved into the pulping spent liquors. It is noticed that the methanol-HUA linear line does not pass through the origin of the coordinate with a positive methanol intercept of 32 mol/ODT-wood (or 1.0 kg/ODT-wood) when HUA (measured) = 0. This is perhaps due to the fact that wood feedstock contains some methanol and it was released instantly at the beginning of cooking. We conducted cooking of southern pine wood chips using pure water heated up to 170°C to verify the natural presence of methanol in wood. From the

measurements in the final cooking solution, about 28 mol/ODT-wood (or 0.875 kg/ODT-wood, very close to the intercept of 1.0 kg/ODT-wood shown in Fig.2) methanol was obtained.

From the experimentally obtained unity slope of the methanol and HUA relationship, we can conclude that except for the methanol naturally present in wood that is released instantly at the beginning of the pulping process, the elimination of methanol from xylan is the only methanol formation mechanism during the initial pulping process and lignin demethylation does not contribute to methanol formation below pulping temperature 160°C (corresponding to a kappa number of 140). Figure 2 also shows that the methanol-HUA data deviate from the linear relationship as delignification continues after pulping temperature reaches 160°C. However, this deviation is not significant until the kappa number reaches about 120, indicating that lignin demethylation may start to contribute to methanol formation. With the completion of the methanol elimination reaction from xylan and further HUA dissolution into the solution, the HUA content measured in pulp decreases as pulping continues. One can extrapolate the maximum measurable amount of HUA content in wood (about 46 mol/ODT-wood) from the data presented in Fig.2. Based on the extrapolation, the contribution of methanol elimination from the xylan to methanol formation can be estimated to be about 51 (=83-32, calculated from the the least-square fitted equation shown in Fig. 2) mol/ODT-wood (or 1.59 kg/ODT-wood). The remaining 42 (=125-51-32, the total formation is 125) mol/ODT-wood (or 1.31 kg/ODT-wood) is the contribution from lignin demethylation. Based on this calculation, we can improve our previous estimation [10] by concluding that for bleachable grade pulping of southern pine, methanol formation from xylan is the major factor contributing to methanol formation in pulping processes, accounting for about 40% of the total methanol formed (as measured from the final cooking spent liquor). Lignin demethylation accounts for about 35%. The remaining 25% of the total methanol naturally present in wood released instantly at the beginning of the pulping process was also observed in our previous study [10], but was accounted for as originating from xylan degradation.

Effect of Sulfidity

Figure 3 shows the effect of sulfidity on methanol formation during kraft pulping of southern pine. The results plotted as methanol verses pulp kappa numbers clearly show that increasing sulfidity reduces methanol formation at a given pulp kappa number. There are two

factors that might explain this phenomenon. A longer cooking time is required in a lower sulfidity pulping process to achieve the same kappa number than that required in a higher sulfidity pulping process; a longer cooking time will increase methanol formation. Secondly, a lower sulfidity means a higher effective alkali concentration in the pulping liquor because the active alkali was maintained at 18% for all the pulping processes; an increase in effective alkali (or HO^- concentration) leads to an increase in methanol formation. The HUA data obtained in our previous study [17] of alkaline pulping of southern pine (not presented in the present paper) indicate that the amount of HUA in pulp decreased with the increase of sulfidity at the same kappa number, which verifies the second argument.

Effect of Catalyst Anthraquinone (AQ)

Figure 4 shows the effect of AQ addition on methanol formation in conventional kraft pulping. Although the data show some scattering, the results clearly indicate that AQ can reduce methanol formation. This reduction is not very significant at a low dosage application (a single curve was drawn for the two data sets of no AQ and 0.025% AQ addition in Fig. 4). However, at a high dosage application, i.e., 0.1%, the reduction of methanol formation is very significant. This phenomenon can be explained by the accelerated delignification due to the catalyst AQ, which reduces the cooking time to achieve the same kappa number. A dosage of 0.1% AQ may not be permitted in many mills; however, the results indicate that AQ can be used in mills not only to facilitate delignification but also to reduce methanol formation.

Effect of Pulping Processes

Figure 5 shows the effect of pulping processes on methanol formation as a function of pulp kappa number. Data with a kappa number greater than 130 were excluded in Fig. 5. The data clearly show the difference in methanol formation among various pulping processes. Soda cooking produces much more methanol than kraft cooking at a given kappa number. There are two factors that contribute to the higher methanol formation in soda pulping. Firstly, the delignification rate is lower in soda pulping than in kraft pulping. A longer pulping time is required to achieve the same kappa number in soda pulping than that required in kraft pulping. Secondly, the effective alkali is higher in soda pulping than in kraft pulping because the active

alkali was maintained at 18% for both the soda and kraft pulping processes; an increase in effective alkali (or HO^- concentration) results in more methanol formation.

The results in Fig. 5 also show that polysulfide kraft pulping processes consistently produce less methanol than in conventional kraft pulping processes. Polysulfide can reduce the degradation of hemicellulose through the peeling-off reactions of oxidation of end groups to carboxylic acid groups to reduce methanol formation. The methanol formation in RDH pulping processes is slightly less than that in kraft pulping. This may be explained by the lower effective alkali used in the first and second stages in an RDH pulping process.

Effect of Wood Species

Conventional kraft pulping experiments of various wood species were carried out to investigate the effect of wood species on methanol formation as shown in Figs. 6 and 7. The data are averaged over 2-5 replicate experiments. The specific number of replicate experiments varies with wood species. Figure 6 shows the results obtained from the pulping of softwoods. Four softwoods of Douglas-fir, white spruce, western hemlock, and southern pine were used. Both bleachable (kappa number around 30) and linerboard (kappa number around 60) pulps were produced. Figure 6 shows that western hemlock and southern pine produce the least (7.3 kg/ODT pulp) and most (9.3 kg/ODT pulp) amounts of methanol in bleachable grade pulping of softwoods, respectively. Figure 6 also shows that Douglas-fir and southern pine produce the least (5.6 kg/ODT pulp) and most (7.3 kg/ODT pulp) amounts of methanol in linerboard grade pulping, respectively. Furthermore, the difference in methanol formation between bleachable and linerboard pulping processes is the smallest (1.3 kg/ODT Pulp) for western hemlock and largest (2.7 kg/ODT Pulp) for Douglas-fir.

Figure 7 shows the methanol formation data during pulping of six hardwoods, aspen, bass, birch, maple, oak, and sweetgum. Bleachable (kappa number around 14), liner board (kappa number around 50, a little lower than the anticipated value of 60), and an intermediate kappa (kappa number around 25) grades of pulps were produced. For bleachable grade pulp, the methanol formation is highest (15.0 kg/ODT pulp) and lowest (9.6 kg/ODT pulp) when pulping sweetgum and aspen, respectively. The variation in methanol formation in linerboard grade pulping of various hardwoods is not very significant, ranging from 4.3 to 5.4 kg/ODT pulp.

However, the results show that the difference in methanol formation between bleachable and linerboard pulping is about 75-300%.

Overall, the results in Figs. 6 and 7 indicate that hardwoods produce more methanol than softwoods when producing an equivalent grade of pulp, which agrees with the results obtained in our previous study [10]. The total methanol formation varies from wood to wood mainly due to the variations in structure differences between softwood xylan and hardwood xylan and the variations of methoxyl group content in xylan and lignin of the woods.

CONCLUSIONS

We conducted laboratory pulping experiments using various wood species under various pulping conditions in bomb-type rotating batch digesters. We validated the methanol formation mechanism through alkali-catalyzed methanol elimination from 4-O-methylglucuronic acid groups in hemicellulose [7] of wood xylan by the direct measurements of hexenuronic acid groups in pulps. The results obtained from the pulping of bleachable grades from southern pine indicate that methanol formation from hemicellulose contributes to about 40% of the total methanol formed. About 25% of the methanol naturally present in wood is released instantly at the beginning of pulping. The remaining 35% of the methanol may be formed as a result of lignin demethylation reactions.

The results also indicate that increasing sulfidity reduces methanol formation for a given active alkali charge in kraft pulping. AQ addition in pulping can reduce methanol formation through increased delignification that results in a short reaction time. Soda pulping produces more methanol than kraft pulping at a given pulp kappa number and active alkali charge. Polysulfide kraft pulping produces less methanol than kraft pulping, possibly due to reduced hemicellulose degradation. Wood species can have a significant effect on total methanol formation. The study further confirms our previous work [10] that hardwoods produce more methanol than softwoods do.

ACKNOWLEDGEMENTS

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List of Figures:

- Fig. 1 Time-dependent methanol formation during conventional kraft pulping processes.
- Fig. 2 The relationship of measured methanol in pulping liquors and hexenuronic acid groups in pulps in a set of conventional kraft pulping processes.
- Fig. 3 The effect of sulfidity on methanol in conventional kraft pulping of southern pine.
- Fig. 4 The effect of catalyst AQ on methanol in conventional kraft pulping of southern pine.
- Fig. 5 The effect of pulping processes on methanol formation.
- Fig. 6 The measured methanol formation data in conventional kraft pulping of four softwoods (the first number in the bar is the methanol formation, and the second number after the slash is the pulp kappa number).
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Fig. 1

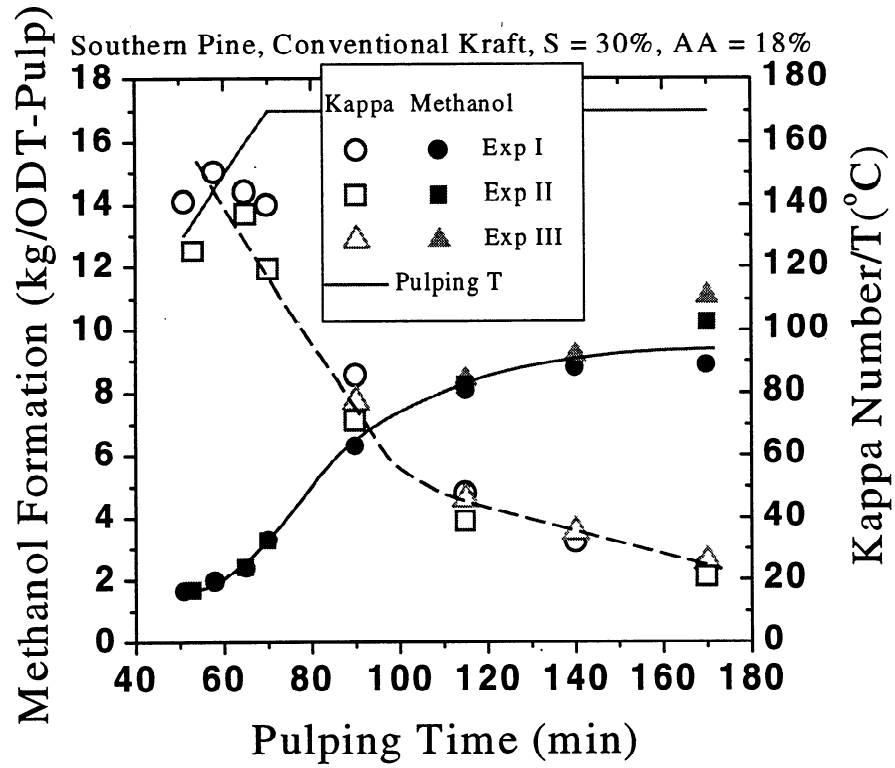


Fig. 2

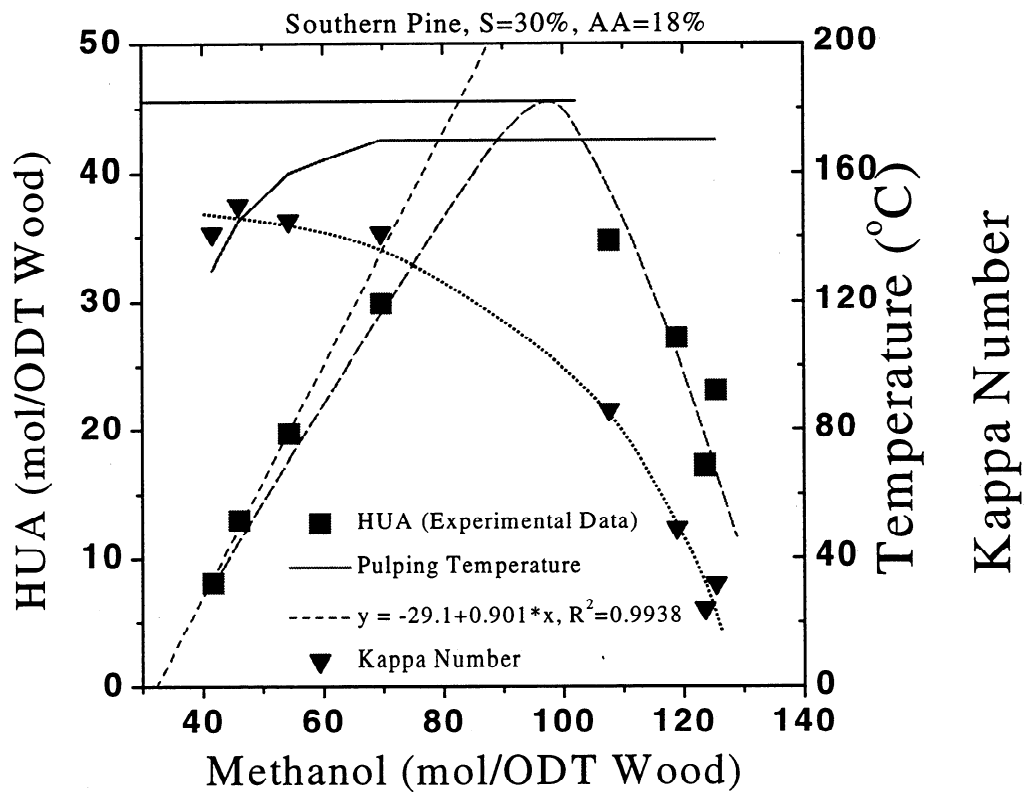


Fig. 3

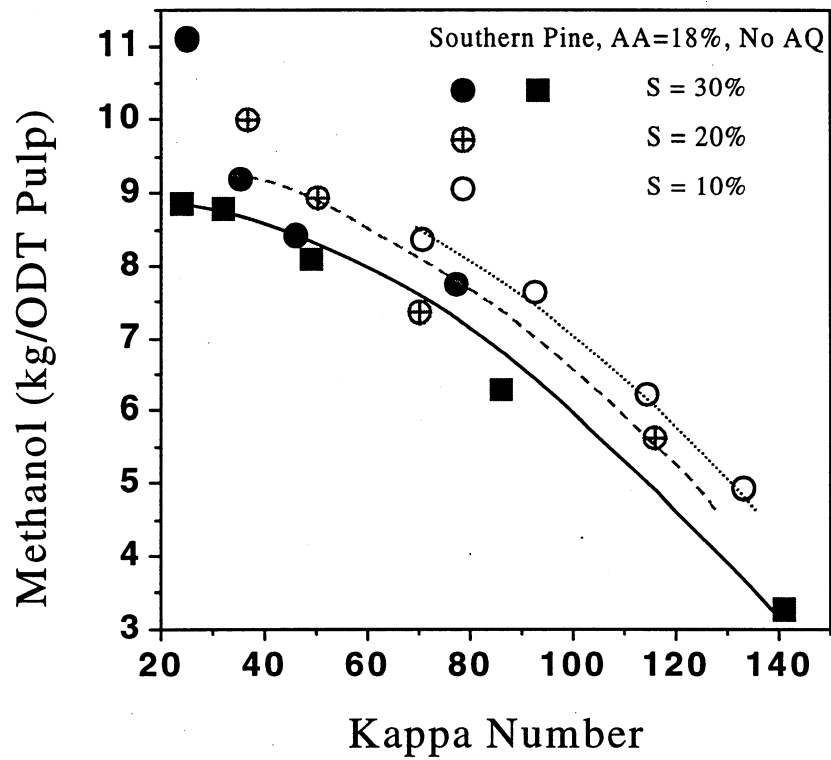


Fig. 4

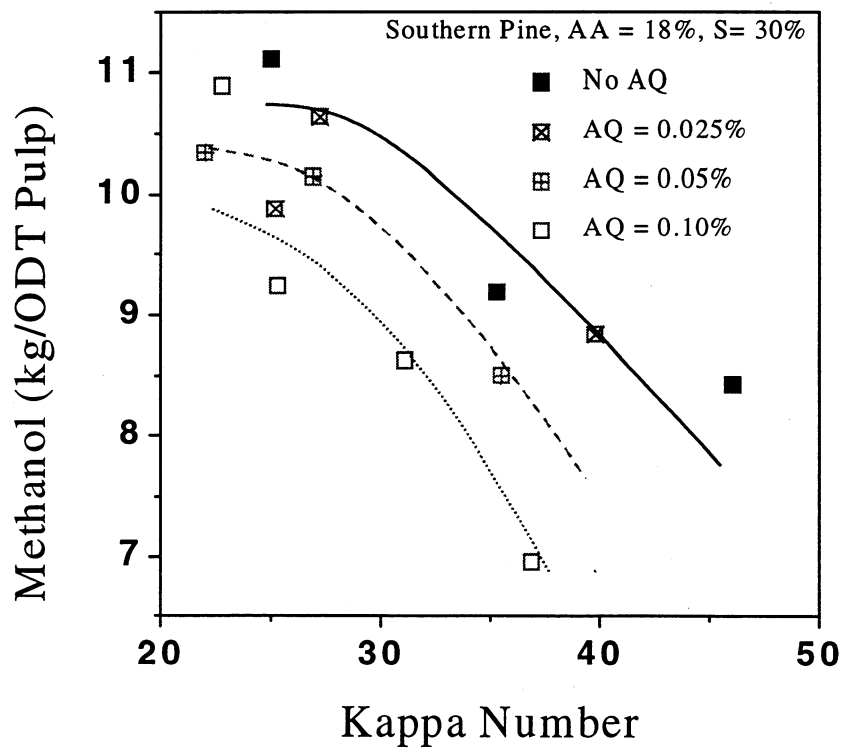


Fig. 5

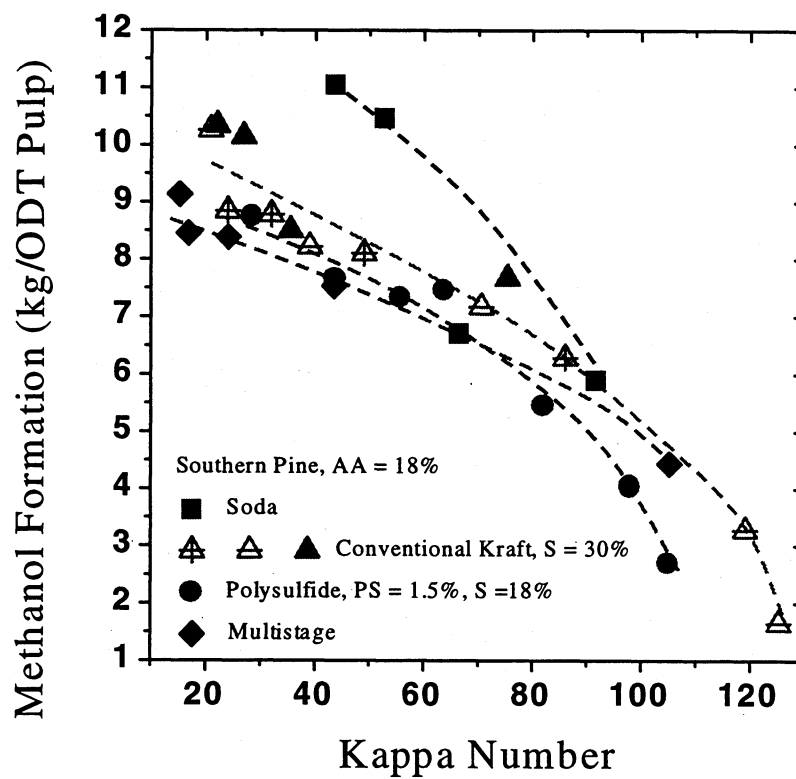


Fig. 6

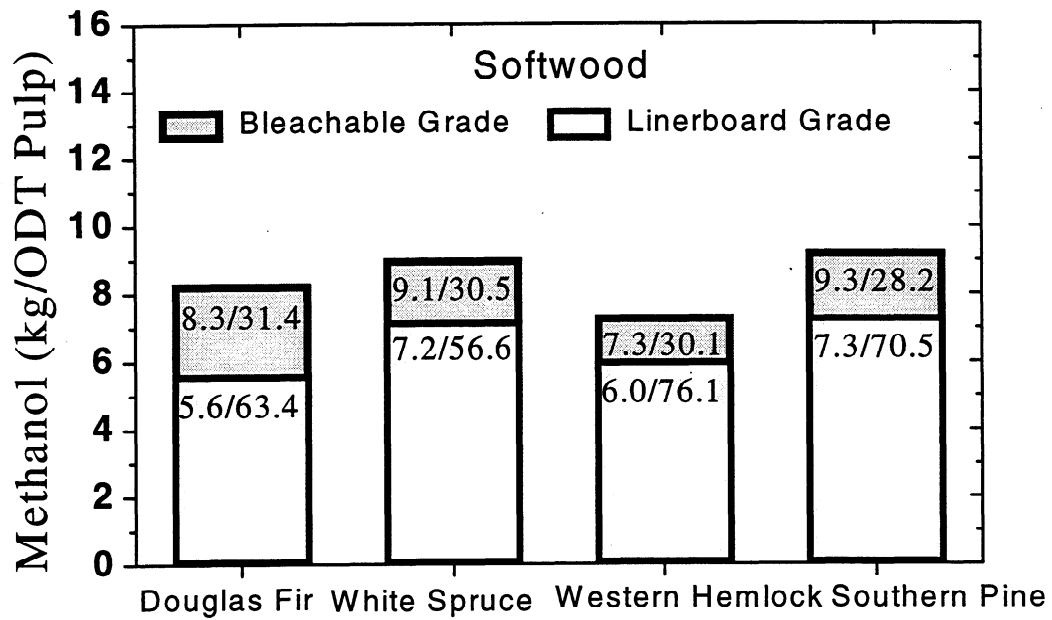
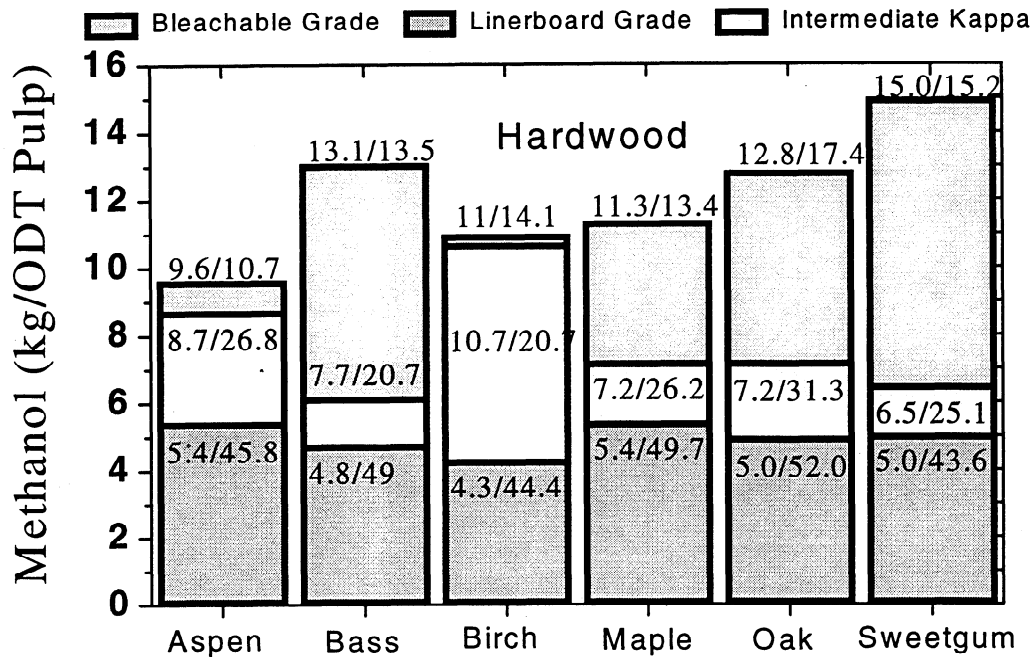


Fig. 7



INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

**The Fate of Hexenuronic Acid Groups during Alkaline Pulping of
Southern Pine**

**Project F03303
(Previously F01708)**

**Report 7
A Progress Report
to the**

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu, X.S. Chai, S.H. Yoon, and J. Li

January, 2000

Previously Published Reports of This Project:

1. Zhu, J.Y., Chai, X.S. Yoon, S.-H., Li, J. (2000), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VII. The Fate of Hexenuronic Acid Groups during Alkaline Pulping of Southern Pine.**" (This report)
2. Zhu, J.Y., Yoon, S.-H., Liu, P.-H., Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VI. Methanol Formation during Alkaline Wood Pulping.**"
3. Zhu, J.Y., Liu, P.-H., Chai, X.S., (1999), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part V. Henry's Constants of Methanol in Pulping Spent Liquors.**"
4. Zhu, J.Y., Chai, X-S, and Dhasmana, B., (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part IV. The Formation of Volatile Organic Compounds (VOCs) during Pulping.**"
5. Zhu, J.Y. and Chai, X-S, (1998), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part III. Vapor-Liquid Phase Equilibrium Partitioning of Methanol in Black Liquors.**"
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Upcoming Reports of This Project (In Preparation)

Zhu, J.Y., Liu, P.-H., and Chai, X.S., (2000), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part VIII. Methanol Formation in Black Liquor Storage Tanks**"

Zhu, J.Y., Liu, P.-H., and Chai, X.S., (2000), "Volatile Organic Compounds (VOCs) in Kraft Mill Streams: **Part IX. Methanol Formation in Black Liquor Evaporation**"

Volatile Organic Compounds (VOCs) in Kraft Mill Streams -

Part VII: The Fate of Hexenuronic Acid Groups during Alkaline Pulping of Southern Pine

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EXECUTIVE SUMMARY

The formation of hexenuronic acid groups (HexA) during alkaline wood pulping has recently been a concern in the pulp industry because of its detrimental effects on bleaching operations, such as increased bleaching chemical consumption, bounding with transition metals, and reduced pulp brightness ceiling. Thus, research in this area has been very active in the last several years.

This study conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. The study found that the maximum HexA formation rate is linearly dependent on hydroxide ion (effective alkali) concentration and the rates of HexA formation and degradation reactions are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-stage cooking is directly related to the amount of effective alkali (EA) consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species. The study demonstrated that the amounts of HexA in the pulps obtained in the early stages of pulping are linearly proportional to the amounts of methanol found in the corresponding pulping liquors with a slope close to unity, which validates the accuracy of the rapid HexA measurement method employed in this study.

Keywords: Hexenuronic acid; xylan degradation; kraft; soda; pulping; AQ; kappa number; pulp yield; methanol.

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INTRODUCTION

The formation of hexenuronic acid groups (HexA) during alkaline wood pulping has recently been a concern in the pulp industry because of its detrimental effects on bleaching operations, such as increased bleaching chemical consumption, bounding with transition metals, and reduced pulp brightness ceiling. Thus, research in this area has been very active in the last several years. One area of research is developing analytical methods to determine HexA content [1-5], which will assist the studies on the issues related to HexA that leads to the control of bleaching plant operations. The other two areas are developing HexA-removal processes prior to bleach plant [1] and understanding the impact of HexA on different bleaching stages and sequences [6-8]. However, little research activities have been reported on the effect of various parameters, including alkali charge, temperature, pulping time, wood species, pulp yield, and pulping additives (AQ and polysulfide), on HexA formation during chemical pulping. Such information is critically needed because it can demonstrate whether HexA removal during kraft cooking is possible or not.

Although a number of studies have reported that the HexA content in pulp is a strong function of the pulping process [9-10], limited studies have been reported on the effects of pulping parameters on the formation of HexA [11-12]. Buchert et al. [12] studied the effect of two parameters, cooking time and alkali charge, on HexA formation using a limited amount (12-36%) of pulp xylan peeled by xylanase. They found that the maximum amount of HexA was formed at the end of the heating-up period, and the HexA content was reduced by over 50% when active alkali charge was increased from 18 to 22%. More recently, Gustavsson et al. [13] reported that the HexA content at kappa number of 20 in Scots pine pulp could be predicted as functions of cooking time, initial $[HS^-]$, and $[HO^-]$. They found that HexA formation is increased with the increase of initial sulfide concentration and the decrease of initial NaOH concentration. Furthermore, they found that the effect of cooking time was negligible, i.e., only to the power of 0.06. These two studies [12, 13] were conducted using high liquor-to-wood ratio, 6:1, and two stage-cooking with fresh liquors in each stage, which has limited applications in conventional pulping process.

Recently, Tenkanen et al. [14] presented a detailed comparison of three HexA measurement methods [1, 3, 5]. In general the three methods can give consistent measurements of HexA. However, all these three methods are tedious and time consuming (all take several hours to complete one measurements), which is probably why a systematic study on HexA formation in various pulping processes has not been conducted. In this study, a detailed characterization of HexA in chemical pulps obtained during various pulping processes was conducted using a simple and rapid method [15]. The effects of effective alkali (EA) charge, EA consumption, pulping process, and addition of AQ on time-dependent HexA content in pulp were investigated. The relationship of HexA content with pulp kappa number and yield was also analyzed. The HexA content is also quantitatively correlated with methanol content in the corresponding pulping liquor.

EXPERIMENTAL

Pulping

All pulping experiments were carried out in 500-mL bomb digesters. Eight bombs were mounted on a rotating drum, and heated with glycol oil. Fifty grams (ODW) of loblolly pine chips were charged in each bomb. Active alkali (AA) charge was varied between 15 and 18% on wood. Sulfidity was changed from 0 to 30%. Liquor-to-wood ratio was 4:1. The cooking temperature was ramped at 2.1°C/min from 23°C in 70 minutes and then maintained at 170°C. Cooking time was varied for a set of digestions in different bombs conducted under the same pulping condition to obtain time-dependent formation data of HexA and methanol. The pulp was completely disintegrated in a laboratory blender and thoroughly washed with tap water in a basket with 200-mesh screen. Pulp pads were then prepared in a handsheet machine for the measurement of pulp yields, kappa numbers, and HexA. The pulp yield, kappa number, and chemical strength of the cooking liquor, such as EA, and sulfidity, were measured according to the standard TAPPI test methods [16].

Measurement of HexA in Chemical Pulps

In a previous study [15], we developed a reliable, simple, and rapid technique for HexA measurements in chemical pulps; therefore, it is particularly suitable for the present systematic

study. In this method, 22 mM (0.6 %) mercuric chloride and 0.7 % sodium acetate are used to make a hydrolysis solution. The mercuric chloride (HgCl_2) and sodium acetate trihydrate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) of analytical grade were from commercial sources. Accurately weigh about 0.05 gram of air-dried pulp handsheet with known moisture content and put it into a 20 mL vial with 10 mL of hydrolysis solution. The mixture is sealed in the vial by a septum. To obtain good mixing of the pulp with the hydrolysis solution, we shake the vial and then heat the mixture for 30 minutes in a water bath with a temperature range of 60-70°C. After the solution is cooled to room temperature, we conducted UV absorption measurements of the filtered solution in a 10 mm path length silica cell using a by spectrophotometer (UV-8453, Hewlett-Packard) at a wavelength range of 260 to 290 nm. Detailed description on the measurement procedure can be found in our previous publication [15].

Measurement of methanol concentration in pulping liquors.

Accurate quantification of methanol concentration in pulping liquor is not trivial because of the complex sample matrix and the presence of inorganic salts in the liquor. In this study, methanol measurements in pulping liquors were conducted using an indirect headspace GC method that we developed [17] using a commercial gas chromatograph (HP-6890, Hewlett-Packard) and an automatic headspace sampler (HP-7694, Hewlett-Packard). The method uses the standard addition approach but relies on methanol material balance and liquid/vapor phase equilibrium in the sampling vials. Through the sampling of the vapor phase in the headspaces of two sampling vials (one with the standard addition of known amount of methanol), the method calculates the methanol concentration in the liquor from the ratio of the peak areas of the two headspace measurements. Therefore, calibration and direct sampling of the liquor are not required. It has been demonstrated that the method is reliable for determining methanol concentration in various kraft mill streams, including black liquors [17].

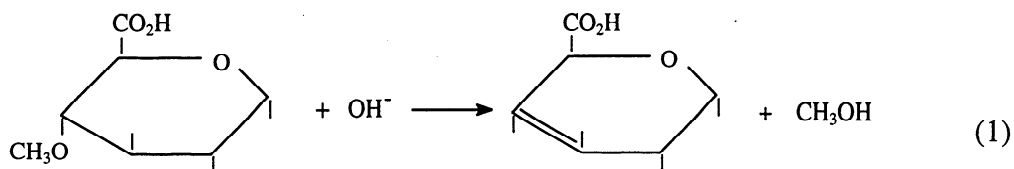
RESULTS AND DISCUSSIONS

Time-dependent Formation and Degradation of HexA

Figure 1 shows the HexA content in pulp as a function of cooking time for conventional kraft cooking with a sulfidity of 30%. The HexA content in pulp increased very rapidly as the

digester temperature linearly ramped to the final cooking temperature of 170°C. Shortly after the temperature reached the final cooking temperature, it started to decrease continuously. Similar results were reported by Buchert et al. [12].

The fundamental chemistry of HexA formation in pulp has well been established [18]. During alkaline pulping, hydroxide ions in the cooking liquor attack the methoxyl groups in the xylan chain through the following rapid hydrolysis reaction, leading to formation of HexA in pulp and methanol in the pulping liquor:



As the temperature increases, the HexA content in pulp increases until all the methoxyl groups in xylan chains are completely eliminated. Meanwhile, the degradation of xylan also takes place, leading to the reduction of HexA content in pulp. The HexA degradation from pulp will outpace HexA formation after the temperature reaches the final cooking temperature. Thus, HexA content in pulp begins to decline.

According to reaction (1), the same molar amount of methanol and HexA will be formed during the hemicellulose hydrolysis reaction. Figure 2 shows the amounts of methanol found in the pulping liquors and of HexA found in the corresponding pulps for cooks that were terminated at the different early stages of the cooking, i.e., before final pulping temperature of 170°C was reached. A linear relationship between methanol and HexA was obtained as shown.

Furthermore, the slope of the linear relationship is 1.1, very close to unity, suggesting that almost all the methanol is formed from the hydrolysis of 4-O-methylglucuronoxylan, leading to the formation of the same amount of HexA. The close-to-unity slope of the methanol and HexA linear relationship also validates the accuracy of the HexA measurement method we developed [15]. The slightly higher than unity slope of 1.1, could be due to the small systematic errors in the measurements of methanol and (or) HexA, and could also be due to the dissolution (degradation) of HexA-containing xylan in the cooking liquor. Nevertheless, the result indicates that the degradation of xylan is not significant during the early stage of the cooking. The positive

intercept of 32.3 mmol/kg-ODW of the linear relationship indicates that methanol can also be released in the early stage of the pulping through mechanisms other than xylan hydrolysis.

Effect of Effective Alkali Charge on HexA Formation

Figure 3 shows the time-dependent HexA formation in different pulping processes. The data clearly show that the addition of AQ does not affect the formation and degradation of HexA. Although the profiles for HexA in various pulps obtained in different pulping conditions (soda and kraft with low and high active alkali charge and different sulfidities) are quite different, the same maximum amount of about 65 mmol/kg-OD pulp) of HexA was yielded during all the pulping processes immediately after the the pulping temperature reached 170°C. This indicates that the hydrolysis reaction is rapid [18] and perhaps results in a 100% conversion of 4-O-methylglucuronoxylan to methanol and HexA. Therefore, the final amount of HexA formed does not vary with pulping process for a given wood species.

According to reaction (1), the HexA formation rate can be written as follows:

$$\frac{d[HexA]}{dt} = k \cdot \text{Exp}(-E_a / RT) \cdot [(OCH_3^+)_{-xylan}] [OH^-] \quad (2).$$

Therefore, the effective alkali (EA or OH⁻ concentration) is a key factor controlling the formation of HexA for a given cooking temperature and wood species. Figure 4 shows that the maximum HexA formation rate is linearly proportional to the initial EA concentration in the cooking liquors or the first order in hydroxide ion concentration. Data also clearly show that a higher initial EA does lead to a fast HexA formation.

An interesting phenomenon was found when we plotted the HexA content vs the consumption of EA. As shown in Fig. 5, HexA profiles for different pulping processes fall to a single curve. Although a quantitative interpretation of this result is not presently possible, a few implications can be drawn from it. Firstly, the fate of HexA in pulp, formation and degradation, is only a function of hydroxide ion. Secondly, all the reactions during pulping that consume a major part of the hydroxide proceed to the same degree as that of reactions associated with HexA in all pulping processes. It is known that the hydroxide is mainly consumed in the neutralization of organic acid groups in original wood components, and that the acids are generated during

degradation of carbohydrates and lignin. Because depolymerization of lignin is strongly accelerated by the presence of sulfide and AQ in kraft cooking, the data shown in Fig. 5 suggest that lignin degradation by sulfide and AQ does not generate a large amount of acid groups, which otherwise would consume a measurable amount of alkali. Finally, the results shown in Fig. 5 and Fig. 1 also suggest that the xylan redeposited onto the fiber surface during the final cooking stage when residual alkali concentration becomes very low does not contain, or at least not a measurable amount of HexA. Otherwise, we should see increased HexA content during the end of cooking. Buchert et al. [12] measured the total xylan content in pulps based on O.D. weight of wood and found that these pulps contained higher xylan, but less HexA.

The results in Fig. 5 can be used to estimate the amount of HexA content in pulp with EA data without conducting HexA measurements. If one can determine the amount of EA consumed for any type of one-stage cook, e.g., kraft with different sulfidity, soda, with and without AQ, one can determine the amount of HexA in pulp using the data shown in Figure 5 without conducting HexA measurements. To facilitate this estimation, we conducted a least-square fit of the data to obtain the following equation for HexA determination,

$$HexA = \frac{a \cdot w}{5(EA_{consum} - 0.42)^2 + w^2} + b(EA_{consum})^2 \quad (3)$$

where $a = 9.1$, $w = 0.15$, and $b = 43$. Eqn (3) is purely a mathematical fit of the data and specific for southern pine. Eqn. (3) fits the data well, in particular at large EA consumption as shown in Fig. 5. But the accuracy of Eqn. (3) decreases outside the region where there are no experimental data points.

The data shown in Fig. 5 were obtained in the pulping of southern pine. The profile of HexA vs EA-consumed may be different for different wood species. The validity of the results in Fig. 5 and Eqn. (3) for other wood species will have to be investigated in the future. Furthermore, the results in Fig. 5 were obtained in one-stage pulping processes, i.e., no liquor exchange or addition during cooking. The validity of the results in Fig. 5 and Eqn. (3) for complex pulping processes, such as EMCC and RDH, will also be investigated in the future. In these complex processes, determination of EA consumption may require a lot more effort than

just simply determining HexA in pulp. Therefore, the practical importance of Fig. 5 may be limited as the measurement of HexA will be easier than the determination of EA consumption.

Relationship of HexA Content in Pulp with Kappa Number and Yield

Because HexA formation through hydrolysis and degradation reactions proceed simultaneously with delignification, correlating HexA with pulp number may have some practical applications. We plotted the HexA formation as functions of pulp kappa number and yield for both soda and kraft cooks with or without AQ as shown in Figs. 6 and 7, respectively. HexA content in pulps with AQ addition is slightly higher than that in pulp without AQ addition. These results do not contradict the findings presented in the previous section, i.e., HexA formation is mainly affected by hydroxide ion concentrations, not by the presence of AQ or sulfide. However, the addition of AQ facilitates delignification and thus reduces the required pulping time, which results in high yield of HexA. The results shown in Figs. 6 and 7 clearly demonstrate that sulfidity has no effect on HexA formation and degradation.

For a given pulp kappa number or yield, HexA in kraft pulp is much higher than that in soda pulp as shown in Figs. 6 and 7. The difference in HexA content between soda and kraft pulp at a given yield cannot be explained by the negative effect of higher hydroxide concentration on pulp yield, and can only be attributed to that fact that hydroxide concentration has a much stronger effect on HexA degradation than on pulp yield. The difference between HexA content in soda and kraft pulps at a given kappa number is due to the difference in delignification selectivity. Kraft cooking not only has lower EA concentration at the same active alkali charge, but also requires much lower H factor to reach a given kappa number. Both lower H factor and EA concentration will result in less HexA degradation.

CONCLUSIONS

We conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. Our study found that the maximum HexA formation rate is linearly dependent on (first order) hydroxide ion (effective alkali) concentration and the rates of HexA formation and degradation reactions are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-

stage cooking is directly related to the amount of EA consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species, regardless of the pulping processes and conditions. HexA content as a given yield or kappa number was different at different sulfidity or AQ addition, which is a result of the increased delignification rate by these additives. Finally, the study demonstrates a linear relationship with unity slope between the amounts of HexA in the pulps obtained in the early stages of pulping and the amounts of methanol found in the corresponding pulping liquors, which validates the hydrolysis reaction theory [18] as well as the accuracy of the technique for rapid HexA measurements that we developed [15].

PRACTICAL IMPLICATIONS

Two possible practical implications could be derived from the information generated from this study. The first one is that the HexA content in pulp could be estimated by knowing the EA consumption of the cooking process for one-stage cooking. For multi-stage cooking processes, e.g., EMCC and RDH, the existence of the relationship has to be investigated in the future. The second implication is that it is unlikely to find suitable procedures or conditions to reduce HexA content during pulping process. This is because the amount of HexA removal is directly proportional to the EA consumption, and not by any other conditions. The amount of EA consumption is basically linked to the amount of carbohydrate degradation. Therefore, any attempts to reduce HexA during pulping will likely result in higher carbohydrate degradation, leading to lower yield or/and lower strength. Any improvement in delignification selectivity will lead to higher HexA content in pulp as is shown by the presence of sulfide and AQ. Finally, the HexA measurement method we developed [15] is not only simple and rapid (it only takes 30 minutes to obtain one measurement), but also accurate. Therefore, the method [15] has significant advantages over most of the existing techniques [1-5, 14] (all take several hours to obtain one measurement) in practical applications.

ACKNOWLEDGEMENT

This research was supported by the United States Department of Energy (Grant No. DE-FC07-96ID13438) and the State of Georgia (Grant No. PP99-MP9).

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Fig. 4 Effect of initial EA concentration on the maximum formation rate of HexA in various pulping processes.

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Fig. 6 The relationship between HexA content in pulp and the corresponding kappa number.

Fig. 7 The relationship between HexA content in pulp and the corresponding pulp yield.

Fig. 1

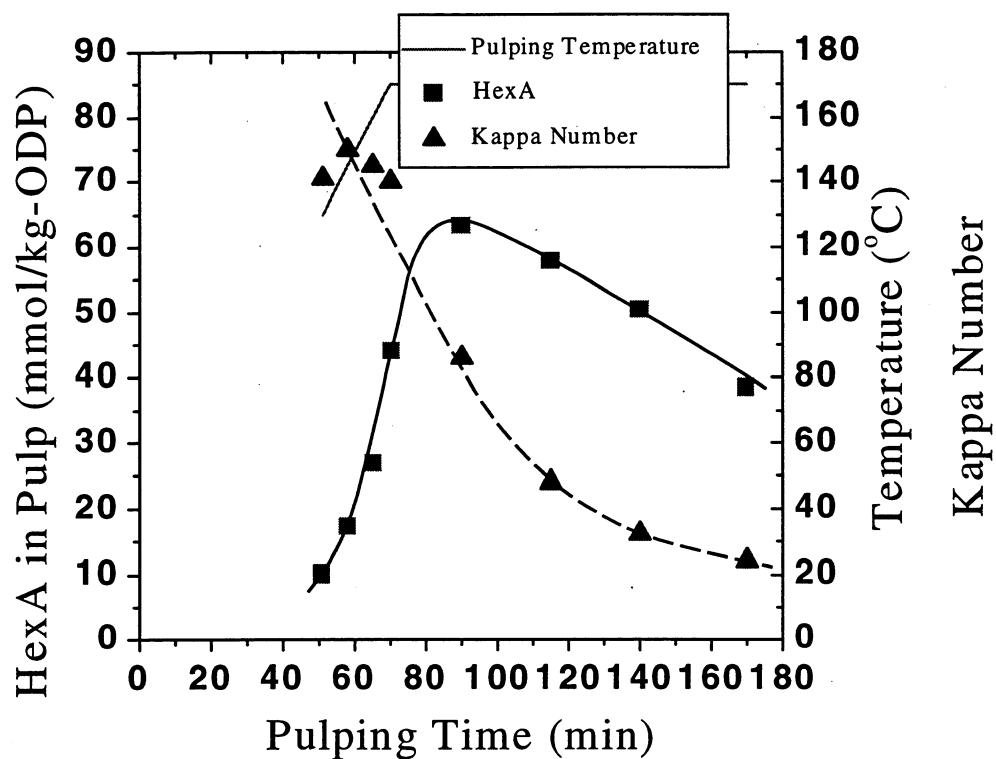


Fig. 2

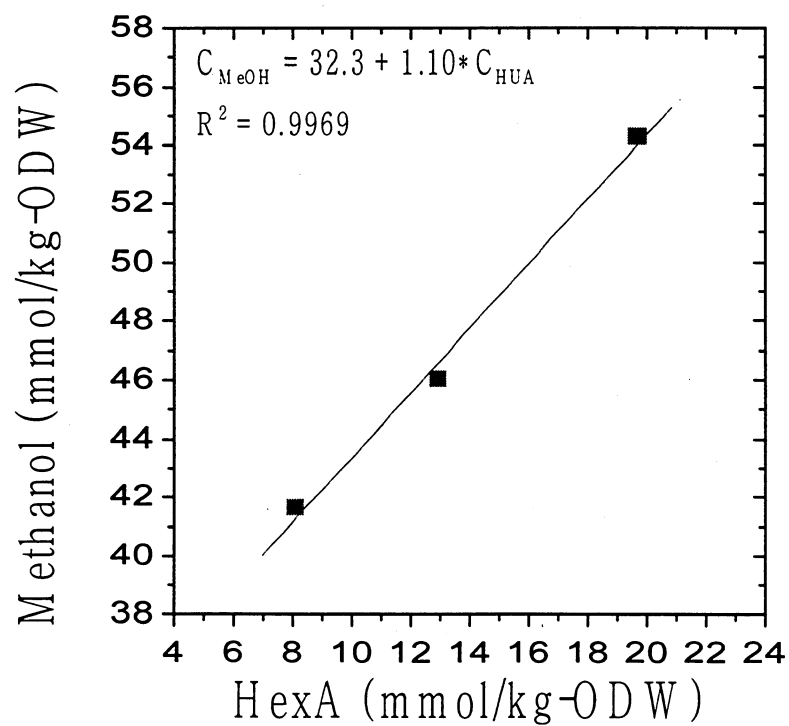


Fig. 3

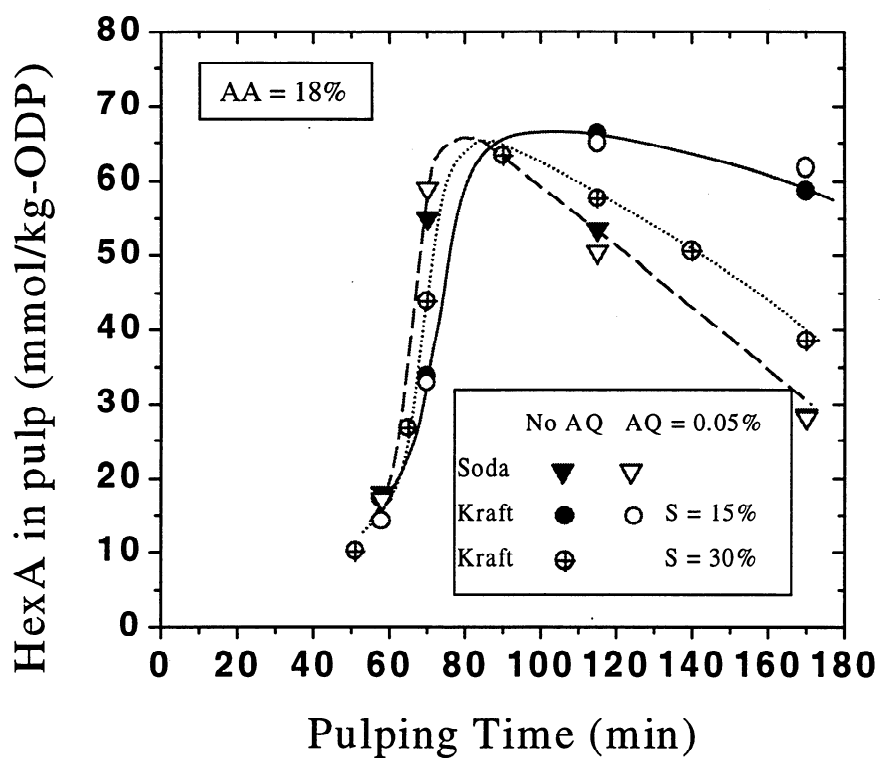


Fig. 4

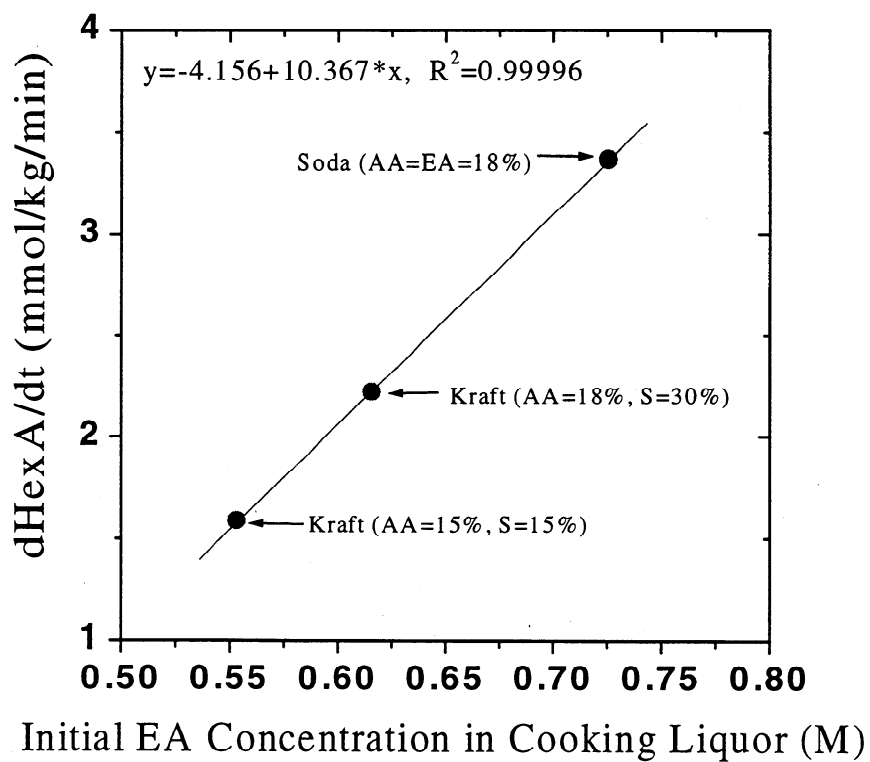


Fig. 5

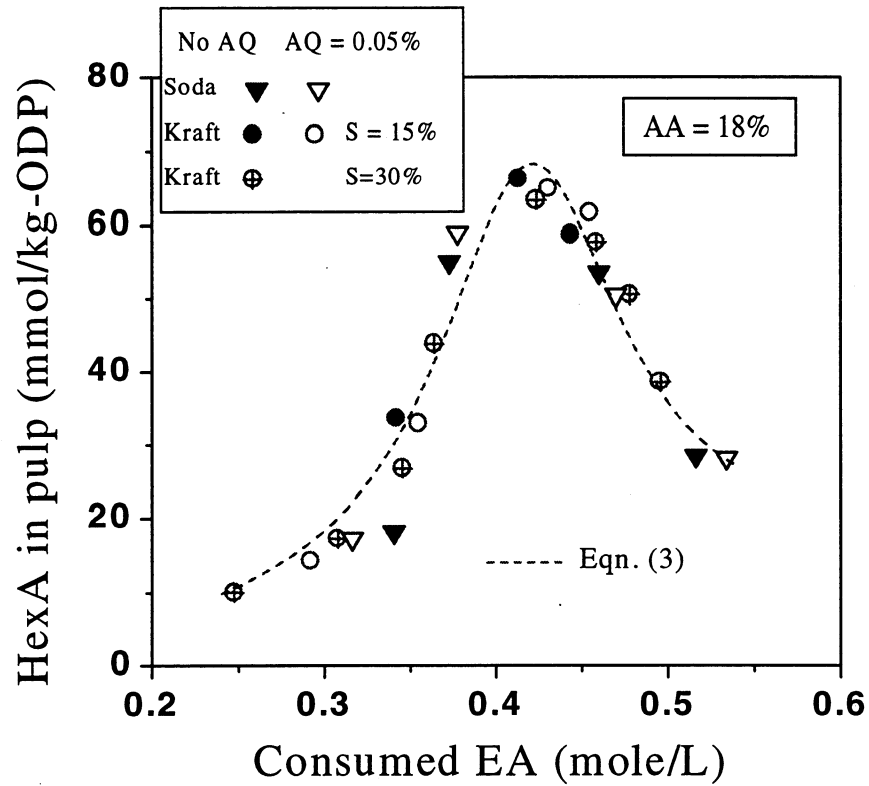


Fig. 6

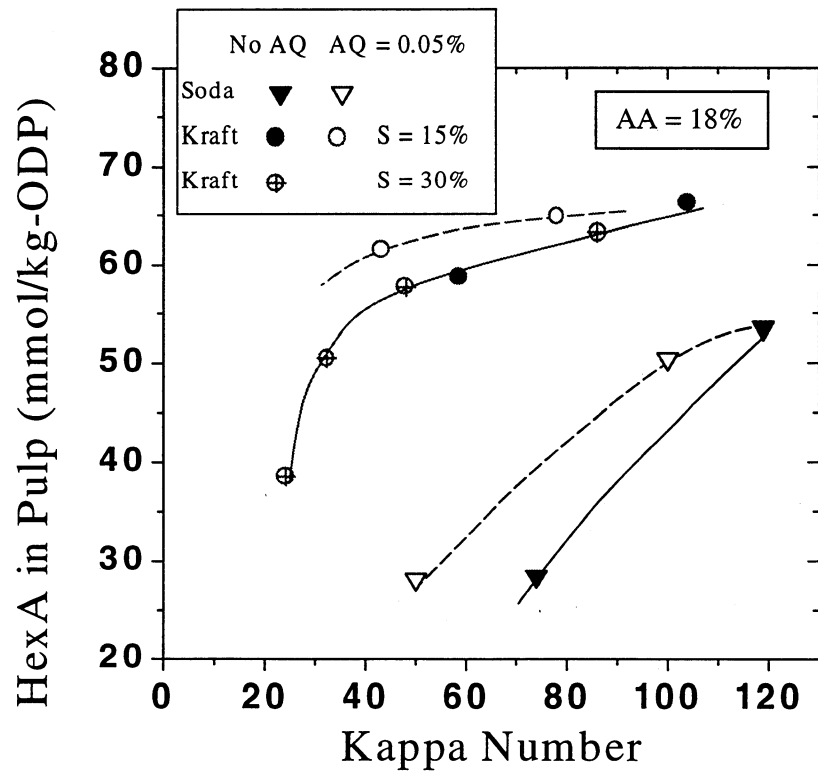
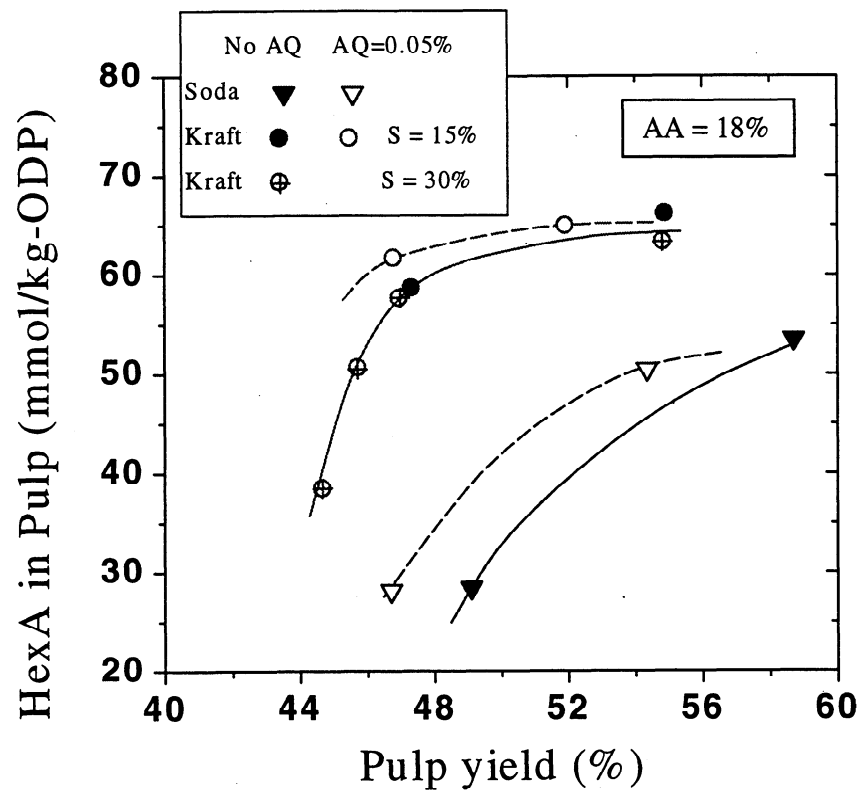


Fig. 7



DUES-FUNDED PROJECT SUMMARY

Project Title: In-Digester Odor reduction
Project Code:
Project Number: F03305
PAC: Chemical Recovery PAC

Project Staff

Principal Investigator: J.Y. Zhu
Co-Investigators: X.S. Chai, J.Li
Research Support Staff: Garry Heedick

PAC Subcommittee None

FY 99-00 Budget: \$51,641
Allocated as Matching Funds: 0

Time Allocation:

Principal Investigator: 9%
Co-Investigators: 8%
Research Support Staff: 34%

Supporting Research:

Special Students:
External (Where Matching Is Used):

RESEARCH LINE/ROADMAP: Line – 6. Environmental Performance: Develop economically viable pulping technology to produce kraft equivalent pulp which ensures no odor at mill boundaries. Develop technologies to eliminate odor formation

PROJECT OBJECTIVE:

The overall objective is to develop an **In-Digester Reduction (IDR) technology** through modified kraft pulping process to significantly reduce the formation of odorous compounds and/or destroy these compounds before pulp discharge, while preserving or improving cooking selectivity, such as pulp yield.

PROJECT BACKGROUND: Kraft mill odor has long been an environmental and public relations issue for the pulp and paper industry. Much of the work on TRS reduction has been focused on the implementation of these technologies in the later 70s to the 90s. Significant odor reduction has achieved. Further reduction of TRS emission using post odor formation control technologies, e.g., oxidation, scrubbing, etc., will be very difficult and costly. Unfortunately, limited research has been conducted on developing new technologies or taking new approaches to reduce kraft mill odor. In this study, we present a completely innovative approach, i.e., odor reduction at its sources, i.e., before TRS gases are formed – In-Digester Odor Reduction (IDOR) technologies through modifications of the pulping processes without the sacrifice of the pulp yield and quality.

MILESTONES:

1. Analytical Technique: Successful
2. Completed conventional kraft pulping of southern pine
3. Completed conventional kraft pulping of other wood species
4. Completed Data analysis of 2 and 3
5. EMCC pulping
6. RDH pulping
7. Subsequent delignification sequences

DELIVERABLES:

- Analytical technique for rapid and accurate measurements of organic sulfur compounds in pulping liquors (Report I issued)
- **In-Digester Reduction (IDR) technology** demonstrated in a laboratory scale digester (Report II issued, attached).
- **In-Digester Reduction (IDR) technology** demonstrated for advanced pulping processes (Report to be issued)
- **Subsequent delignification sequence** developed to achieve desired pulping property and quality.

STATUS OF GOALS FOR FY 99-00:

In progress: In-Digester Reduction (IDR) technology development – EMCC, RDH pulping processes.

SCHEDULE:

Task Descriptions (example)	1999 Apr - Jun	1999 July - Sept	1999 Oct - Dec	2000 Jan - Mar	2000 Apr-Jun
Analytical Technique			→		
Conventional Kraft Pulping Process				→	
Wood Species Effect				→	
EMCC					→
RDH					→

SUMMARY OF RESULTS:**See Member Company Reports I-II Issued**

- Rapid, automated, and accurate techniques for organic sulfur compound analysis in pulping liquors (Report I Issued)
- PTP low odor cooking technology (Report II issued)
- AQ effect on odor reduction (report II issued)

SUMMARY OF KEY CONCLUSIONS:

See Member Company Reports I-II Issued. PTP cooking technology developed for odor reduction without capital investment.

DISCUSSION:

See Member Company Reports I-II Issued

1. Topic 1

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

E. References

F. Tables

G. Figures

2. Topic 2

A. Significance

B. Approach

C. Results

D. Conclusions

- *Scientific Conclusions*
- *Economics*
- *Deliverables*

E. References

F. Tables

G. Figures

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

IN DIGESTER ODOR REDUCTION –

**Part I: Analysis of Volatile Organic Sulfur Compounds in Kraft Liquors
by Full Evaporation Headspace Gas Chromatography**

Project F03305

A Progress Report 1

to the

MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

By

J.Y. Zhu, X.S. Chai, J. Li, and E.W. Malcolm

November, 1999

Analysis of Volatile Organic Sulfur Compounds in Kraft Liquors by Full Evaporation Headspace Gas Chromatography

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EXECUTIVE SUMMARY

Kraft mill odor has long been a public relations problem for many kraft mills. Reduction of the odorous gas emission in kraft mills will significantly improve the environmental competitiveness of the U.S. pulp and paper industry, and will also improve public relations, with surrounding communities. When it is more economically feasible, **odor reduction**, instead of **odor elimination**, can significantly improve the air quality and the environment of a kraft mill since it will reduce the radius of the area being impacted by the odor emission.

The overall objective of the present research is to develop an In-Digester Reduction technology for reducing odor at its source – during kraft pulping without sacrificing pulp yield and quality. For example, a bleaching sequence may be designed differently now with the odor gas formation data. The next step will be to examine the overall performance in terms of total reduced sulfur (TRS) formation and pulp productivity and quality with the knowledge gained in the present study.

In Part 1 of the study, we demonstrated a full evaporation (FE) technique for direct organic sulfide analysis in kraft pulping liquors using headspace gas chromatography (HSGC). A very small volume (10 μ L) of liquor sample is introduced into a sampling vial of about 20 mL and heated to an elevated temperature. Near-complete analyte transfer from the condensed phase to the vapor phase (headspace) is achieved in a very short period of time because of the small sample size and overheating; therefore, HSGC analysis provides the direct measurements of the analytes without sampling the liquid phase. The FE HSGC eliminates the matrix effects on the calibration for quantitative analysis. Furthermore, calibration using an external gas standard can be applied when the liquid standard is not available. The method is simple, rapid, and accurate. It provides environmentally sound and technologically superior alternative to the only tested method reported some 30 years ago (now prohibited due to restricted environmental regulations) using tedious and time-consuming solvent (such as carbon tetrachloride) extraction to measure organic sulfur compounds in kraft liquors.

Key words: Headspace, Gas Chromatography, Pulsed Flame Photometric Detector, Sulfide, Full Evaporation, Pulping Liquor.

* Principle Investigator

INTRODUCTION

The odorous sulfide compounds generated during kraft pulping processes have been an environmental concern. The quantification of the volatile organic sulfide compounds in pulping processes can lead to a better understanding of the formation mechanisms and, in turn, to a reduction in their formation. Unfortunately, it is not trivial to accurately determine the organic sulfide compounds in the cooking liquors because they are corrosive in nature and have a complicated sample matrix containing many inorganic salts that prevent direct gas chromatographic (GC) analysis through direct injection of the liquor sample.

To avoid interference from the sample matrix and GC column damage by the corrosive materials, sample pretreatment has to be adopted. Andersson and Bergstrom [1] used carbon tetrachloride as a solvent to extract the organic sulfur compounds for GC analysis. Later Prakash and Murray [2] found that toluene was best for extraction of hydrogen sulfide (H_2S) and methyl mercaptan (MM), while carbon tetrachloride was best for extraction of dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). Therefore, different chemicals have to be used for optimum analysis. Because the efficiency of a given solvent extraction procedure varies with both the solvent and the species to be extracted, calibration is required for quantitative analysis. However, calibration always leads to a more complicated and time-consuming experimental procedure and compromises the measurement accuracy. Furthermore, the tailing effect of the solvent signal peak (usually a huge peak) on the GC chromatogram may require the use of empirical methods [1] to calculate the peak area of organic sulfides of interest, which can also significantly affect the measurement accuracy. Finally, carbon tetrachloride is now prohibited in the laboratory as a solvent due to environmental regulations in many countries.

Because the odorous organic sulfides are very volatile, direct gas extraction has also been used. Rayner et al. [3] used a stripping method to quantify MM, DMS, and DMDS in contaminated pulping waters. In their method, a specially designed stripping cell was used to strip the sulfur compounds into a collection column. Sulfuric acid was used to neutralize the black liquor to yield mercaptan from mercaptide ions. The stripping procedure was time-

consuming and was not applied to black liquors. Moreover, the presumed 100% stripping efficiency of organic sulfides can be a problem when it is applied to black liquors. Nevertheless, O'Connor and Genest [4] adopted a similar gas extraction approach using a commercially available glass sparger system (a specially designed stripping cell) to strip sulfide gases. They claimed that 93-110% recoveries of TRS compounds in various mill streams including weak black liquor were achieved. The measurement requires cooling of the system for sample addition, heating and purging (for 30 minutes at a nitrogen flow rate of 250 mL/min) for stripping, collection of the stripped gas using a bag, and analyzing the sample in the bag using a GC system. Therefore, it suffers from the same difficulties of any other gas-stripping technique, i.e., complicated, tedious, and time-consuming.

Partial gas extraction using headspace gas chromatography (HSGC) has also been applied to the analysis of volatile organic compounds in solutions [5, 6]. This partial gas extraction HSGC method is based on standard addition and headspace phase equilibrium so that the species concentration in the liquid phase can be determined from two measurements in the vapor phase (headspace) before and after standard addition without sampling the liquid phase. We have applied this HSGC method to analyze volatile organic compounds such as methanol and methyl ethyl ketone (MEK) in kraft black liquors in a previous study [6]. Because no liquid form of MM can be used for standard addition under standard laboratory conditions, it is difficult to measure MM using the ordinary HSGC method even with a highly sensitive detector, such as the pulsed flame photometric detector (PFPD) used in the present study. The method also presents another problem because it assumes that the species to be analyzed is at infinite dilution in the solution so that the liquid-vapor partition coefficient is a constant before and after standard addition.

The full evaporation (FE) technique used in the present study was initially developed by Markelov and Guzowski [7]. It uses a very small sample size to achieve a near-complete transfer of analytes from a condensed matrix into a vapor phase in a very short period of time; therefore, it does not require sample pretreatment and it eliminates the unknown extraction efficiency problem. When integrated with headspace gas chromatography, it not only eliminates the standard addition procedure required in the ordinary HSGC method (partial gas

extraction), but also offers the advantages of automation in measurements and the elimination of the matrix interference from nonvolatile compounds. It should be pointed out that complete evaporation of the condensed analyte is not necessary [7], it only requires the near-complete transfer of the analyte into the vapor phase. The present study applied the full evaporation technique to measure organic sulfur compounds in pulping liquors, namely, MM, DMS, and DMDS, using a headspace gas chromatograph equipped with a pulsed flame photometric detector (PFPD). The objective of the study is to demonstrate a simple and accurate FE HSGC method for organic sulfide analysis in kraft pulping liquors. With some of the high extraction efficiency solvents, e.g., carbon tetrachloride, being prohibited in many countries due to environmental regulations, the present study provides a technically superior and environmentally sound alternative to the only tested method reported some 30 years ago using tedious and time-consuming solvent extraction [1; 2].

METHODOLOGY

A material balance of an analyte dispensed into a sampling vial can be described by the following equation after thermal equilibrium of the sample [7]:

$$C_G = M_0 / (KV_R + V_G) \quad (1)$$

where C_G is the equilibrium concentration of the analyte in the vapor phase (headspace), M_0 is the initial mass of the analyte in the sample, $K = C_L/C_G$ is the analyte phase partition coefficient, V_R is the sample residual volume after thermal equilibrium (the volume of the condensed phase may change significantly after thermal equilibrium due to heating), V_G is the volume of the vapor phase (headspace).

Because the response of a GC detector is proportional to the analyte concentration in the headspace C_G , it will be influenced by the partition coefficient of the analyte K in the sample according to Eqn. (1). In the case of near-complete evaporation, however, the term of KV_R is significantly smaller than the headspace volume V_G , i.e., $KV_R \ll V_G$, and, hence,

$$C_G \approx M_0 / V_G \quad (2)$$

Therefore, the effect of K (a sample matrix-dependent parameter) is eliminated.

Detailed analysis of an appropriate sample size with respect to thermal equilibrium temperature, analyte, and its partition coefficient in a system was presented by Markelov and Guzowski [7]. In this study, we will experimentally demonstrate that a near-complete analyte transfer can be achieved in the analysis of organic sulfide in kraft pulping liquors.

EXPERIMENTAL

Chemicals

All chemicals used in the experiment were from commercial sources. The concentration of MM in a standard gas (Holox, SN: SA9275) is 100 ppm by volume. A standard DMS-water solution with a concentration 169 mg/L was prepared in-house with the addition of 0.5 M NaOH solution.

Black Liquors

Conventional soda and kraft pulping of southern pine with two sulfidity levels of 15 and 30% were conducted using a bomb-type batch digester to obtain black liquors. To obtain the rate of MM, DMS, DMDS formation under a selected set of pulping conditions, the pulping process was terminated at different pulping times. By this approach, the effect of pulp kappa number or cooking H factor on organic sulfide compound formation can be obtained. The volume of the bomb digester was 500 mL. Each cook used 50 grams of oven-dry wood chip. Special procedures were followed in the collection of the black liquor to avoid the oxidation of MM. The bomb digester was cooled down immediately after the completion of each cook using an ice bath. Then the black liquor (stock liquor) was dispensed into a sampling vial that was thoroughly purged with nitrogen. The vial with the stock liquor was then air sealed with a septum and stored in a refrigerator. When analysis was needed, another sampling vial, which was thoroughly purged with nitrogen was used as the testing vial. A predetermined exact known amount of black liquor was dispensed into the

testing vial using a syringe. The volume of the testing vial, as measured, was 21.6 mL. The black liquor was then acidified before GC measurements to yield MM from mercaptide ions.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.). GC conditions were: HP-5 capillary column at 30°C, carrier gas helium flow rate of 1.1 mL/min. A pulsed flame photometric detector [8, 9] (PFPD, O.I. Analytical, TX, U.S.A.) was employed with hydrogen and air flow rates (the system requires two air flows) of 11.5, 10, and 15 mL/min, respectively. The PFPD has the unique characteristic of high selectivity of sulfur compounds over hydrocarbons ($10^5:1$), which is very suitable for analysis of organic sulfur compounds in a mixture containing a high amount of hydrocarbons, such as black liquor. Headspace operating conditions were: 5 minutes strong shaking for equilibration of the sample, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min.

The sample vials were purged by nitrogen gas in order to minimize the effect of oxygen on the MM determination. The sample preparation and measurement procedures were as follows: Inject 10 μ L of sample solution into a closed 21.6 mL vial by micro syringe and place it in the headspace sample tray for HS-GC measurements. For quantifying total MM, 50 μ L of 0.5 M sulfuric acid was added into the vial for the acidification of the black liquor.

RESULTS AND DISCUSSION

Effect of Sample Size and Sample Matrix

As indicated by Eqn. (1), both the sample size and the partition coefficient of the analyte can affect measurement accuracy when using the FE HSGC method. We used a DMS-water solution to test the valid sample size range (the partition coefficient K_{DMS} of DMS is greater than that of MM). Several FE HSGC measurements of DMS in small testing

samples were conducted at a headspace temperature of 80°C. The sample sizes varied; however, the total mass of DMS in these testing samples was kept constant by diluting the standard DMS-water solution. The PFPD signals were recorded. It was found that the PFPD signals essentially remained constant for sample sizes ranging from 6 to 21 μL . The relative standard deviation of the recorded signal from six measurements with different sample sizes is only 1.6%, as listed in Table I. This indicates that a sample size of about 10 μL used in the present study is valid to achieve near-complete analyte transfer from the liquid solution to the vapor phase (headspace). The valid sample size can be increased with the increase in temperature.

Black liquors obtained from the soda pulping process were then used to study the effect of the sample matrix. The liquors were obtained by terminating the soda cooking process at various cooking times so that the solids contents of the liquors are different. The soda liquors should have very similar sample matrices to those of kraft liquors under the same delignification conditions, except that soda liquors do not contain sulfur compounds. A known amount (1 μg) of DMS was added into each soda liquor sample with a sample size of 12 μL , and the DMS signal of the PFPD was recorded at a headspace temperature of 80°C. It was found that the PFPD signal count is independent of the liquor sample (or solids content) and is a constant. The relative standard deviation of the recorded signal from seven measurements with solids content varying from 1 to 17.6% is only 4.1%, as listed in Table II, indicating that the black liquor sample matrix does not affect the validity of the FE HSGC measurements of sulfur compounds in black liquors.

To further demonstrate the validity of sulfur compounds measurements using FE HSGC in kraft black liquors at a temperature of 80°C, we conducted several FE HSGC measurements of a kraft liquor with different sample sizes. The total solids content of the liquor was 15%. It was found that the square root of the PFPD signal of DMS was linearly proportional to the sample size (or total DMS mass) up to a sample size of 400 μL as shown in Fig. 1. Therefore, a sample size of 60 μL that includes 50 μL of acid solution (to yield MM) was used for all black liquor analysis in this study.

Effect of Sample Size on Equilibrium Time

One advantage of FE HSGC over ordinary HSGC is the fast analyte transfer from the condensed phase to the vapor phase (headspace). We conducted several equilibration tests with various sample sizes to quantitatively validate this argument and to give experimental guidance for future applications. A methanol-water solution was used to investigate the effect of sample size on the time needed to achieve thermal equilibrium. As shown in Fig. 2, it was found that the equilibration time was reduced from about 30 minutes for a sample size of 10 mL to less than 2 minutes for a sample size less than 50 μ L. Therefore, near-complete analyte transfer is very rapid with FE HSGC when a small sample size is used.

Effect of Oxygen on the MM Measurement

Thiols are readily oxidized by molecular oxygen. This oxidation reaction can be accelerated by alkalinity [10]. It was reported that MM in aqueous solutions can be easily oxidized to form DMDS [3]. This reaction is significant when the MM level is very low. Bentvelzen et al. [11] found that both oxygen and quinones in the lignin structure can oxidize MM to DMDS. Their study also indicated that the presence of sodium sulfide (as low as 0.2 g/L) can effectively inhibit the reaction of MM with quinones under oxidation temperatures below 100°C. According to Bentvelzen et al. [11], the oxidation of MM by quinones in black liquors in the present study was effectively avoided because the sodium sulfide concentration in the black liquors was always greater than 2.0 g/L and a headspace temperature of 80°C was used. However, MM oxidation in black liquors was still very significant, which was perhaps due to oxygen. For example, when 10 μ L of a black liquor sample was added into a 21.6 mL vial with air at 80°C, the MM in an acidified black liquor could be completely eliminated by the oxygen present in the headspace air within 5 minutes. Therefore, it is extremely important to avoid contact between the black liquor and air throughout the entire experiment. The testing vials were thoroughly purged using nitrogen to eliminate the oxidation of MM before dispensing black liquor for GC measurements. The purge nitrogen flow rate was 130 mL/min. Figure 3 shows the PFPD signal of MM measured in several testing vials that were purged with nitrogen for different periods of time and dispensed with the same amounts of a

kraft black liquor. The result indicates that a 2-minute purge was sufficient to obtain a constant MM signal, meaning that the oxygen was completely purged out of the 21.6 mL sample vial. The near-zero DMDS signal measured, as shown in Fig. 3, further demonstrates the complete elimination of MM oxidation by oxygen as well as quinones.

Effect of acidification on the MM measurements

MM is present in pulping spent liquors in the form of mercaptide ions. To quantify total organic sulfur compounds, the pulping liquor needs to be acidified to yield MM from mercaptide ions. As discussed early, 50 μL of sulfuric acid is added into 10 μL of pulping spent liquor. Table III listed the effect of acidification on the measured MM in 8 pulping spent liquors collected in the same kraft pulping process but at different cooking stages. The results indicate that acidification is needed to yield the total organic sulfur compounds.

Experimental Calibration

An external calibration standard was used in this study. Because near-complete analyte transfer or full evaporation was achieved in the present FE HSGC measurements, MM was calibrated using a gas standard from a commercial source. On the other hand, DMS and DMDS were calibrated using a liquid standard for simplicity. Both the DMS- and DMDS-water solutions were prepared under alkaline conditions to increase their solubilities in the water. The calibration ranges of MM, DMS, and DMDS were chosen differently on purpose to match the ranges of the actual amounts of these sulfur compounds present in the black liquors. Figure 4 shows the calibration curves of MM, DMS, and DMDS obtained. The results indicate that the square root of the PFPD signal is linearly proportional to the total mass in the testing samples as shown in Eqn. (3).

$$m = Q + k\sqrt{A} \quad (3)$$

where m is the mass of the species to be measured, A is the PFPD peak area, k ($= 9.747, 7.353, 7.619$ for MM, DMS, and DMDS, respectively) is the calibration constant, and Q ($=$

10.5, -26.5, -11.4 for MM, DMS, and DMDS, respectively) is a small intercept of the calibration curves due to experimental errors ($Q = 0$ in theory).

Experimental Validation

Because soda liquors are free of sulfur compounds but have similar sample matrices to that of kraft liquors, different known amounts of DMS were added to a soda black liquor of solids content 15% to validate the FE HSGC measurements. The testing sample volume was 10 μ L, and the measurements were carried out at 80°C. The present method measures the amount of DMS according to Eqn. (3) in this set of soda liquors that were spiked with DMS. The measured DMS in these samples was then compared to the known amounts spiked. For a given DMS range of 100-1015 ng, the measured DMS data are in excellent agreement with those spiked as shown in Fig. 5. The maximum relative standard difference is 8.1%.

Chromatograms and PFPD Signals in Kraft Black Liquors

It should be pointed out that MM, DMS, and DMDS can be detected using a flame ionization detector (FID). However, when using a PFPD the sensitivity for the sulfur compound measurement will be much higher than a FID. On the other hand, the signal response in a PFPD to non-sulfur compounds is extremely low, therefore, the interference from non-sulfur compounds in the black liquors can be significantly reduced. Figure 6 shows a typical chromatogram of a kraft black liquor sample obtained using a PFPD in a FE HSGC measurement. The first huge peak (separable with dilution) was hydrogen sulfide and sulfur dioxide (H_2S and SO_2), which are formed from sulfide and thiosulfate due to the acidification of the liquor. Because the present study is concerned with the measurements of organic sulfide compounds, the measurement of inorganic sulfur compounds such as H_2S was not attempted. It will be the objective of a future study. It can be seen from Fig. 6 that the signal peaks of the three organic sulfur species (MM, DMS, and DMDS) can be well separated by the present GC column. Most volatile non-sulfur organic species have no response except for methanol that has an extremely high concentration in black liquor.

Application

We measured the MM, DMS, and DMDS concentrations in two sets of kraft liquors obtained in high (30%) and low (10%) sulfidities with and without catalyst AQ (0.05%) pulping processes. The active alkali charge was 18% for both pulping processes. The black liquors were acidified first to yield MM from the mercaptide ions in the liquors. The measured MM, DMS, and DMDS concentrations as a function of kappa number are shown in Figs. 7 and 8. Little DMDS was found, as shown in Fig. 7, in the fresh black liquor samples, which agrees with the results reported by Andersson [12]. This indicates that DMDS was not produced in the pulping process, but rather in the oxidation process after the liquor is contacted with oxygen. The results in Fig. 7 also show that DMS was not formed until the temperature was raised to the final cooking temperature of 170°C or kappa number reaches 100. As expected, less MM will be formed under low sulfidity pulping conditions as shown in Fig. 7. However, this low sulfidity effect on the formation of DMS is not obvious. The data rather suggest that sulfidity has little effect on the formation of DMS. The catalyst AQ can significantly reduce both MM and DMS formation for a given pulp kappa number as shown in Fig. 8.

CONCLUSIONS

We successfully demonstrated the full evaporation technique for measurements of organic sulfur compounds in kraft black liquors by headspace gas chromatography equipped with a pulsed flame photometric detector. The FE HSGC measurements greatly simplified organic sulfide analysis in kraft liquors by eliminating the conventional solvent extraction or gas-stripping procedure and using either gas or liquid in an external calibration standard. With the combination of the full evaporation technique and headspace chromatography, the measurements completely eliminated sample matrix interference for organic sulfide analysis in kraft liquors. The full evaporation technique also greatly reduced the thermal equilibrium time in conventional HSGC by using a very small sample size. The present full evaporation HSGC method is simple, rapid, and accurate. It eliminates the use of hazardous solvents for extraction, such as carbon tetrachloride; therefore, the method is also environmentally sound. It also provides a better alternative to the gas-stripping technique. The method is very

suitable for sulfur analysis in various kraft mill and environmental streams and other applications in petrochemical industry.

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Fig. 1

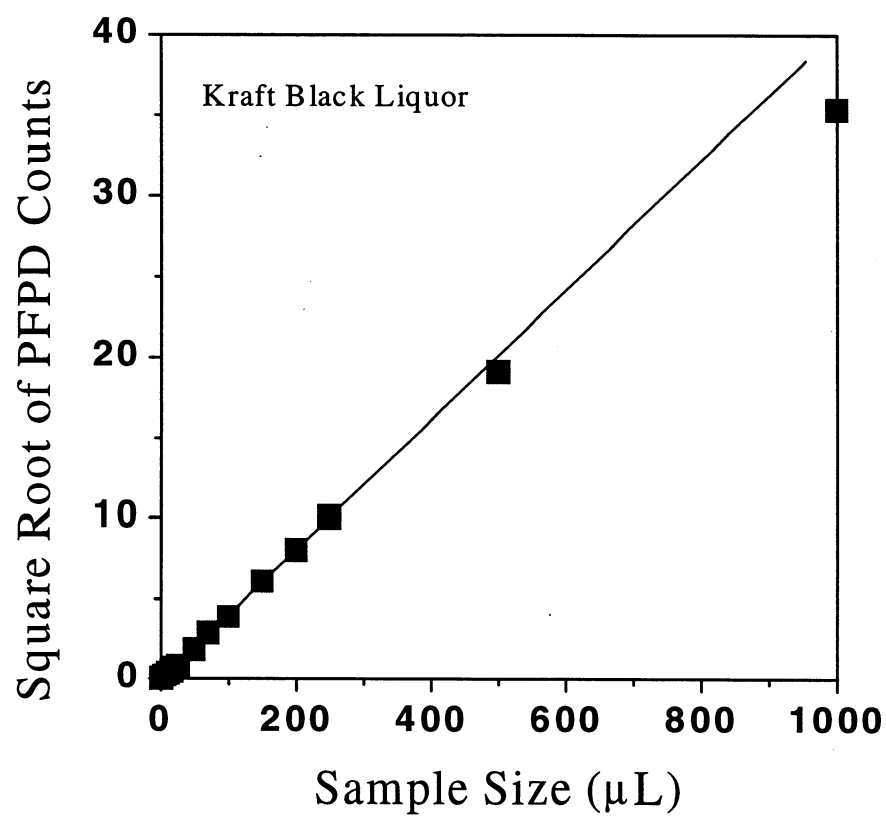


Fig. 2

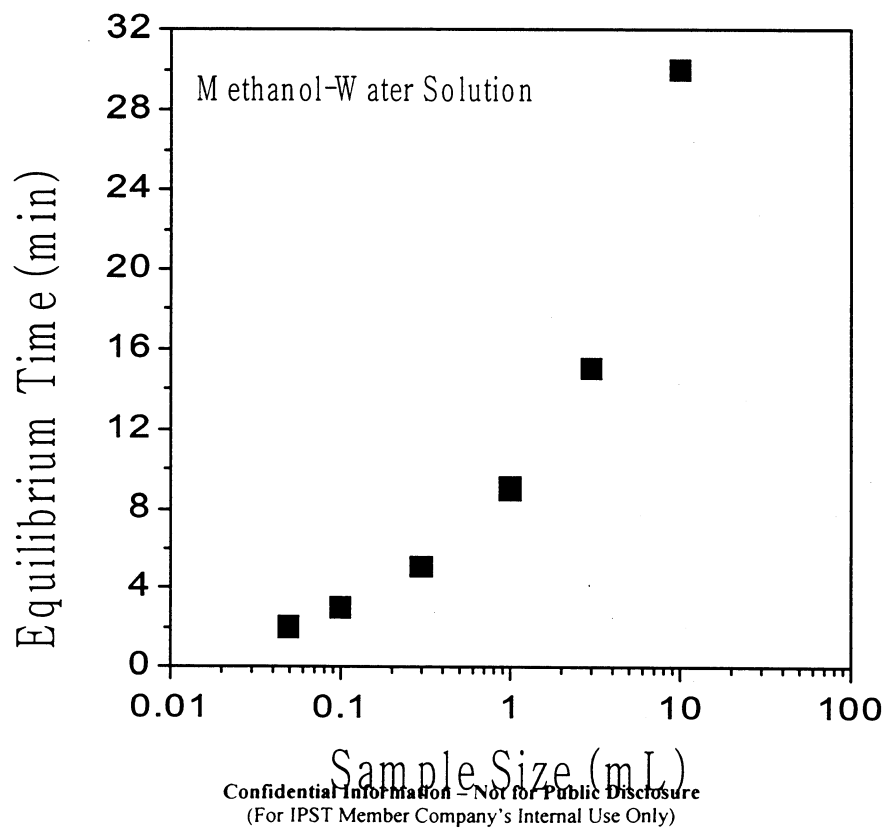


Fig. 3

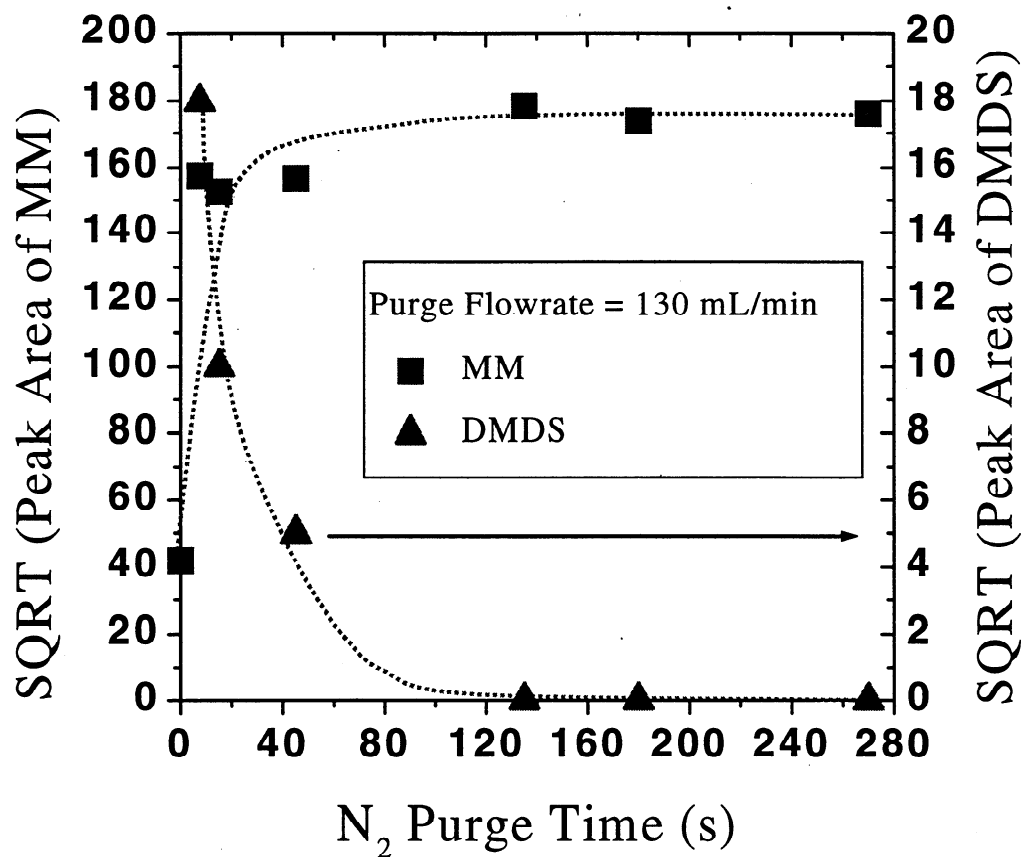


Fig. 4

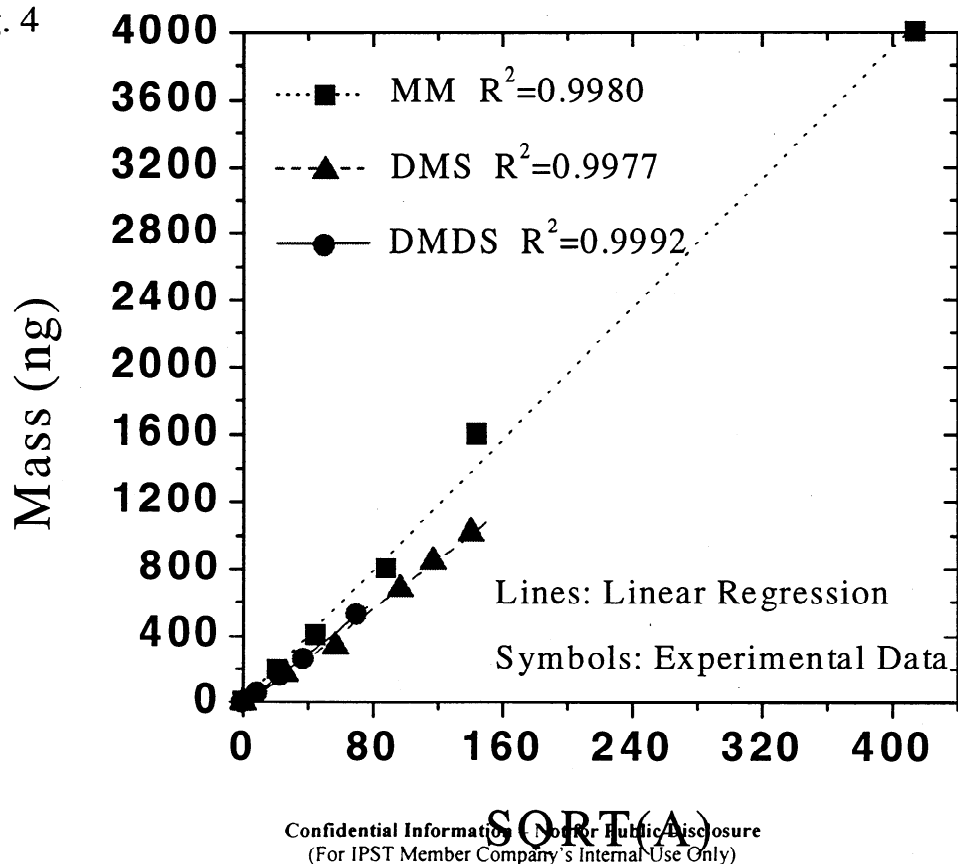


Fig. 5

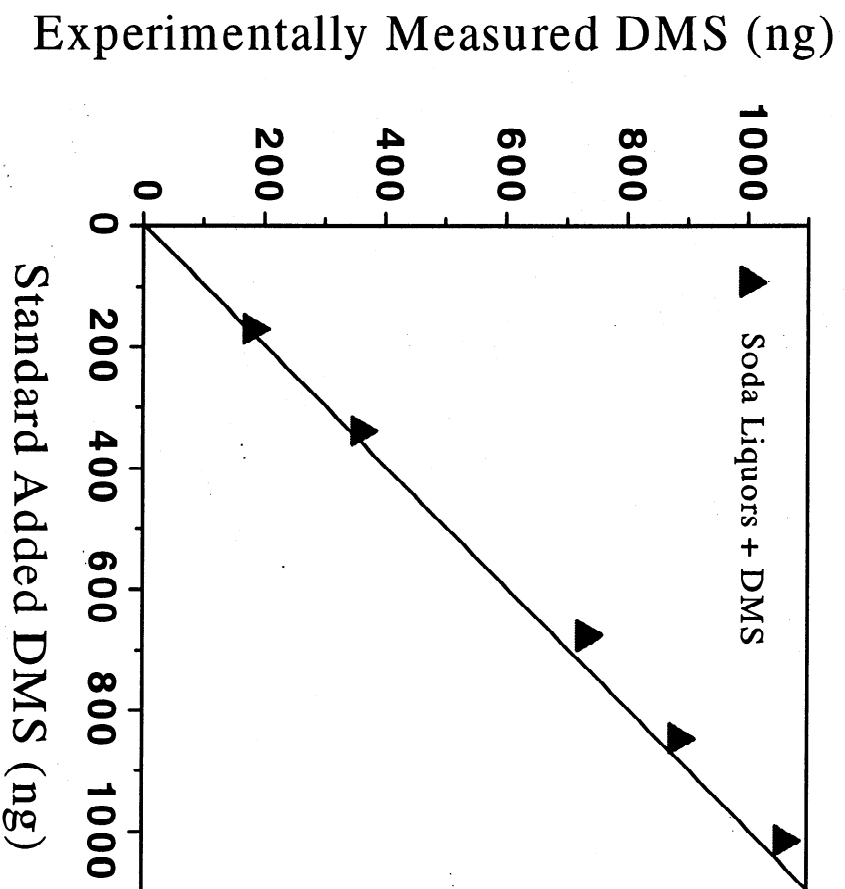


Fig. 6

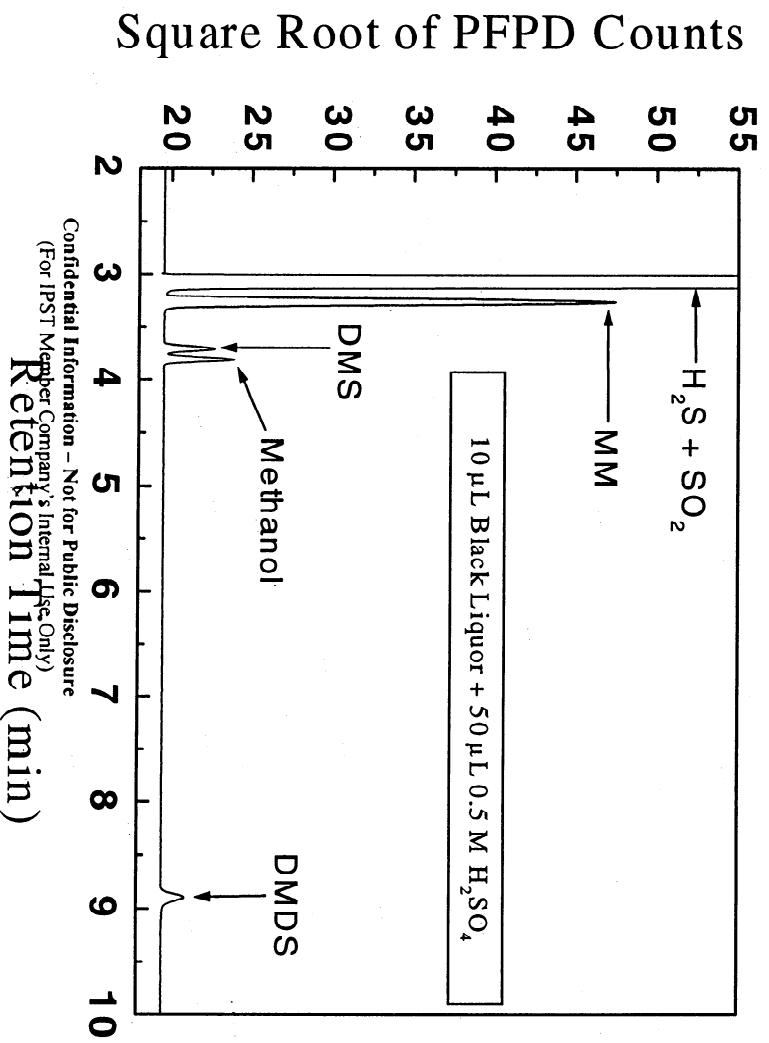


Fig. 7

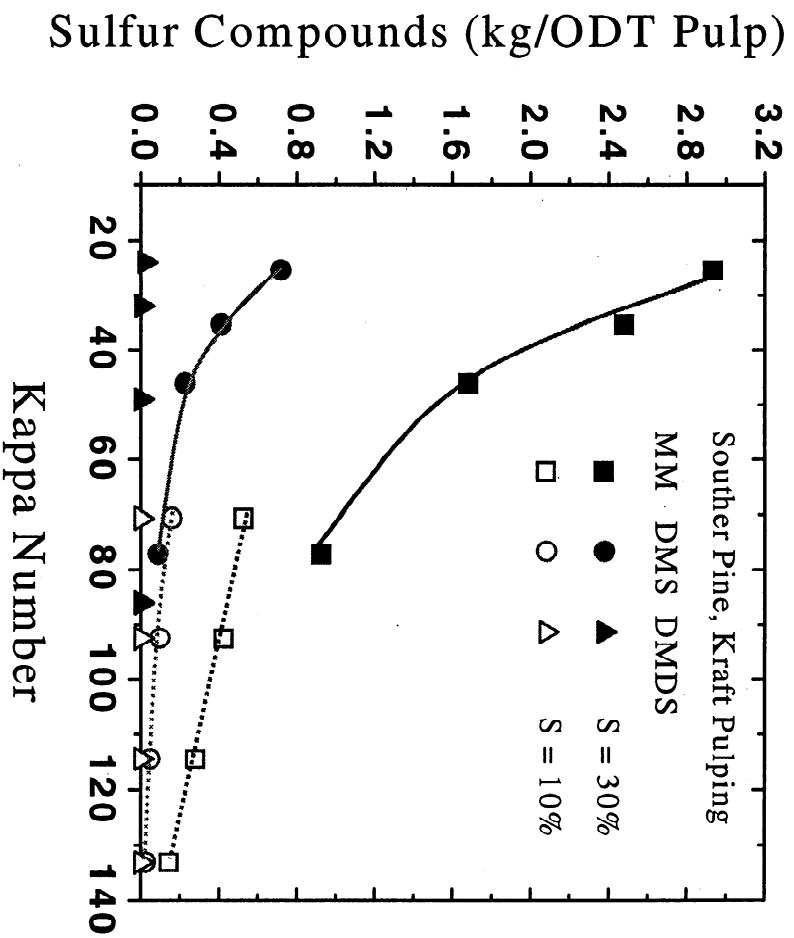


Fig. 8

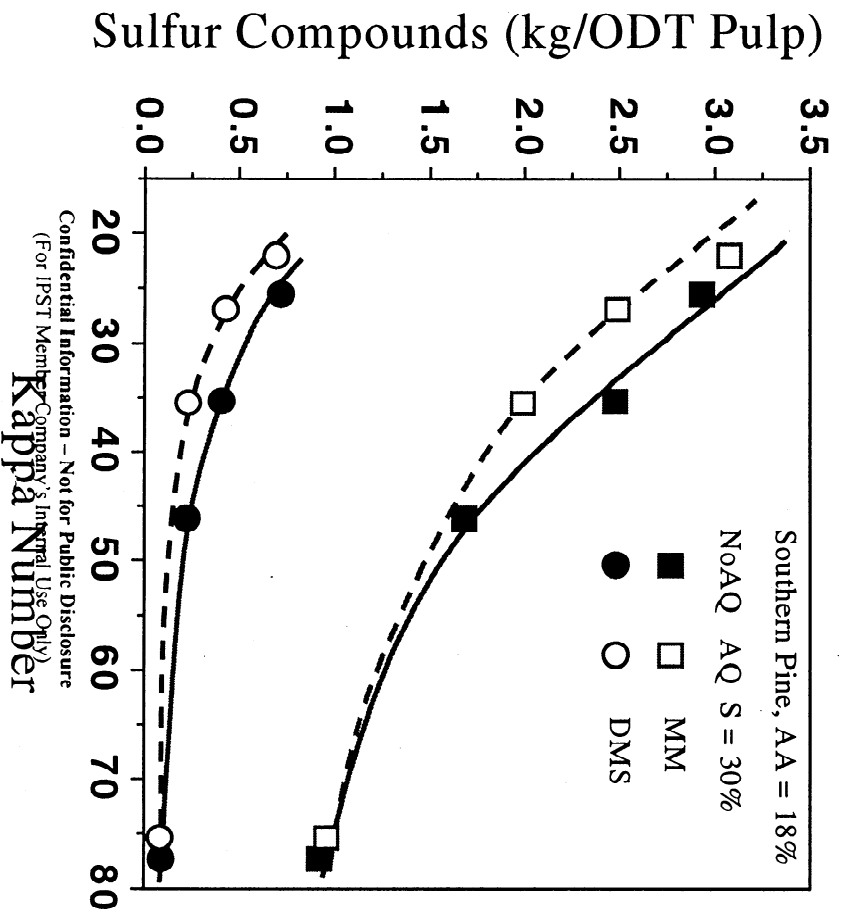


Table I. Effect of sample size on FE HSGC measurements of DMS.

Sample No.	Sample Size (μL)	DMS mass (μg)	DMS (ppm)	NaOH (Mole)	PFPD counts
1	6	1.01	169	0.50	13219
2	9	1.01	113	0.33	13618
3	12	1.01	84.5	0.25	13221
4	15	1.01	67.6	0.20	13059
5	18	1.01	56.3	0.17	13297
6	21	1.01	48.3	0.14	13024
RSTD					1.6%

- The sample volume is varied from 6 to 21 μL.

Table II. Effect of sample matrix on the determination of DMS in different soda liquors.

Sample No.	DMS mass, μg	Total solids, %	PFPD counts
1	1.00	1.00	11676
2	1.00	5.39	11067
3	1.00	7.45	12075
4	1.00	8.22	12510
5	1.00	11.71	11842
6	1.00	15.62	11321
7	1.00	17.57	11634
			RSD = 4.1%

* All sample volume sizes are 12 μL.

Table III. Effect of acidification on MM measurements.

Sample No	MM (mg/L, acidified)	MM (mg/L, nonacidified)
1	6.2	0
2	6.3	0
3	11.0	3.9
4	22.8	5.7
5	63.6	30.8
6	122.0	71.0
7	132.0	85.0
8	167.0	102.0

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY

Atlanta, Georgia

IN DIGESTER ODOR REDUCTION -
Part II: In-Digester Odor Reduction in Kraft Pulping

Project F03305

A Progress Report 2

to the

**MEMBER COMPANIES OF THE INSTITUTE OF PAPER SCIENCE AND
TECHNOLOGY**

By

J.Y. Zhu, X.S. Chai, and J. Li

January, 2000

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1. Zhu, J.Y., Chai, X.S., and Li, J. (2000), "In-Digester Odor Reduction: **Part II: In-Digester Odor Reduction in Kraft Pulping.**" (This Report)
2. Zhu, J.Y., Chai, X.S., J. Li, and E.W. Malcolm, (1999), "In-Digester Odor Reduction: **Part I: Analysis of Volatile Organic Sulfur Compounds in Kraft Liquors by Full Evaporation Headspace Gas Chromatography.**"

Upcoming Reports of This Project (In Preparation)

Zhu, J.Y., Chai, X.S., and Li, J. (2000), "In-Digester Odor Reduction: **Part III: In-Digester Odor Reduction in Advanced Kraft Pulping Processes.**"

IN DIGESTER ODOR REDUCTION -

Part II: In-Digester Odor Reduction in Kraft Pulping

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ABSTRACT

Kraft mill odor has long been a public relation problem for many kraft mills. With the increasingly restrictive environmental regulations posed by the federal agencies, gaining environmental competitiveness in pulp and paper mill operation is of strategic importance to the success of the pulp and paper industry. Reduction of the odorous gas emission in kraft mills will significantly improve the environmental competitiveness of the U.S. pulp and paper industry, and will also improve public relation, with surrounding communities. When it is more economically feasible, **odor reduction**, instead of **odor elimination**, can improve significantly the air quality and the environment of a kraft mill since it will reduce the radius of the area being impacted by the odor emission.

The overall objective of the present research is to develop an In-Digester Reduction technology for reducing odor at its source – during kraft pulping without sacrificing pulp yield and quality. The data on odor gas formation during pulping in various pulping processes obtained in this study can be used to optimize the operation process to achieve minimum odor production. For example, a bleaching sequence may be designed differently now with the odor gas formation data. The next step will be to study the overall performance in terms of total TRS formation and the pulp productivity and quality with the knowledge gained in the present study.

In Part 2 of the study, we relate the formation of organic sulfur compounds to delignification in kraft pulping from the first time. The study discovered a phase transition point (PTP), below and above which the formation of total organic sulfur compounds, with respect to delignification, changes significantly. The transition point occurs at about kappa number 35 and 20 for softwoods and hardwoods, respectively. The transition point is directly related to the phase transition of kraft delignification from bulk to residual delignification. Significant in-digester odor reduction can be achieved using phase transition cooking (PTC), i.e., limiting delignification to bulk delignification phase or PTP. The study also discovered that anthraquinone (AQ) as a catalytic additive can reduce in-digester organic sulfur compound formation. The reduction of sulfur compound formation is linearly proportional to the square root of the level of AQ addition (in percent). A 70–90% reduction of in-digester reduction in TRS formation can be achieved by using PTC and AQ in kraft pulping.

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In-Digester Odor Reduction in Kraft Pulping

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INTRODUCTION

Kraft mill odor has long been an environmental and public relations issue for the pulp and paper industry. The kraft mill odor is caused predominantly by malodorous reduced sulfur compounds, or total reduced sulfur (TRS), namely, methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and hydrogen sulfide (H_2S). MM, DMS, and DMDS are the main volatile organic sulfur compounds and are formed in the pulping process, while hydrogen sulfide is formed in the recovery furnaces. Although significant reduction of TRS emission has been achieved in the pulp and paper industry in the last decade with advanced odor abatement technologies, subjective odor nuisance at very low concentrations still causes odor problems in surrounding communities of a kraft mill. Furthermore, because of the enhanced sensitivity of the human nose to sulfur compounds due to the variability of odor emission from day to day, kraft mill TRS emission will always be a sensitive subject in dealing with the public and surrounding communities.

TRS formation in kraft pulping was studied as early as in the 50s, 60s, and 70s [1-9]. Much of these research efforts were devoted to quantification and kinetics [4-8] of the organic sulfur compound formation. The general formation mechanism of the TRS has been described elsewhere [7-9] and recently in Jarvensivu et al. [10]. The formation

of MM and DMS is through the reaction of mercaptide ions and the methoxyl groups present in the pulping liquor [4, 6, 9]. DMDS is not formed in the pulping process but rather through the oxidation of MM when black liquor is in contact with air [4-6, 9]. Hydrogen sulfide is not formed under the normal pulping pH conditions, but rather in the downstream processes where the pH of the streams are reduced below 10 through the dissociation of sodium sulfide [10, 11]. Other significant sources of H₂S formation are lime mud reburning, black liquor pyrolysis, and molten smelt dissolution processes [10, 12-15].

There are two general approaches to abate odor currently implemented in kraft mills: thermal oxidation and absorption using scrubbing technologies. Thermal oxidation of TRS is achieved by two steps: collecting non-condensable gases (NCGs) in various emission vents and eliminating odorous compounds in the NCGs through combustion in lime kilns, power boilers [16-18], or special incinerators [11, 19] to convert them into non-odorous compounds. Absorption is mainly implemented to destroy H₂S and MM in diluted NCGs through scrubbing using a spray tower or packed column [20-22].

Much of the work on TRS reduction has been focused on the implementation of these technologies in the late 70s to the 90s. Significant odor reduction has been achieved. Further reduction of TRS emission using post-odor-formation control technologies, e.g., oxidation, scrubbing, etc., will be very difficult and costly. Unfortunately, limited research has been conducted on developing new technologies or taking new approaches to reduce kraft mill odor. Kringstad et al. [23] conducted indigester oxidation (IDO) of kraft black liquor using oxygen and found that both MM and DMS can be reduced with the application of a large amount of oxygen into the pulping

liquor. Tormund and Teder [24] found that significant amounts of MM and DMS formed during pulping can be converted to non-volatile compounds by reaction with polysulfide or polythionate immediately before blow (post-formation in-digester reduction). Neither of these two technologies has been implemented in kraft mills.

In this study, we present a completely innovative approach, i.e., odor reduction at its sources, i.e., before TRS gases are formed. This approach – In-Digester Odor Reduction (IDOR) technologies – works by modifying the pulping processes without sacrificing pulp yield and quality. The present IDOR approach provides kraft mills a new and economical way to significantly improve the air quality, the environment, and public relations with the surrounding communities. Because no new capital is required with IDOR technologies, IDOR will be much more economical than any existing odor reduction technologies.

EXPERIMENTAL

Kraft Pulping

Conventional kraft pulping experiments were conducted using 8 rotating bomb digesters in an oil bath. The rotating speed of the digesters was 6 rpm. Four different softwood species of Douglas-fir, white spruce, western hemlock, and loblolly pine, and six hardwood species of aspen, bass, birch, maple, oak, and sweet gum were used in the experiments. Fifty grams (ODW) of wood chips in each bomb were subjected to a conventional kraft digestion. In the pulping of southern pine, a pulping liquor-to-wood ratio of 4, an 18% active alkali charge, and four AQ concentrations of 0, 0.025, 0.05, and 0.1% were used. In the kraft pulping of southern pine and maple, three sulfidity levels of

10, 20, and 30% were used. For the pulping of the rest of the wood species, the pulping liquor-to-wood ratio was 3.7, active alkali charge was 17%, and sulfidity was 31%. Cooking temperature was ramped from a room temperature of 23°C to 170°C in 70 minutes or at a rate of 2.1°C per minute. Cooking times at the preset maximum temperature of 170°C were varied to study the time-dependent formation of organic sulfide compounds in pulping. Each bomb was quenched in an ice bath immediately after the completion of the cook. Pulps obtained from each cook were disintegrated in a blender and thoroughly washed on a 200 mesh screen with a flowing of cold water. Thick pulp pads were prepared and air-dried for the measurement of pulp yields and kappa numbers using TAPPI standard methods. Black liquor samples collected from each digester were analyzed for the determination of chemical strength and the TRS concentrations, i.e., MM, DMS, DMDS (H_2S was not formed in pulping due to high pH).

TRS Analysis

Accurate determination of organic sulfide compounds in kraft pulping spent liquors is key to the present research. Unfortunately, there are a limited number of methods available for sulfur compounds analysis in pulping spent liquors. The most commonly used solvent extraction technique [25, 26] is not only tedious and time-consuming but also gradually becoming outdated because many high-extraction-efficiency solvents, e.g., carbon tetrachloride, are being prohibited for laboratory usage due to environmental regulations. The direct gas extraction (stripping) technique was used for sulfur analysis in kraft mill condensates [27-29]. The technique also suffers from the pitfalls of tedious and time-consuming operations with very limited applications to sulfur analysis in pulping liquors. In this study, the full-evaporation headspace gas

chromatographic (FE-HSGC) method that we developed in a previous study [30] was employed. The FE-HSGC method is based on the principle of near-complete analyte transfer from the liquid phase into the vapor phase when a very small sample is heated in a sample vial; therefore, the analyte in the liquid phase can be analyzed by direct headspace gas chromatography without sample pretreatment requirements. It is simple, rapid, and accurate as demonstrated in our published study [30].

The measurement apparatus consist of an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.) and a pulsed flame photometric detector [31, 32] (PFPD, O.I. Analytical, TX, U.S.A.). GC conditions were: HP-5 capillary column at 30°C, carrier gas helium flow rate of 1.1 mL/min. The PFPD was run with hydrogen and air flow rates (the system requires two air flows) of 11.5, 10, and 15 mL/min, respectively. The PFPD has the unique characteristic of high selectivity of sulfur compounds over hydrocarbons ($10^5:1$), which is very suitable for analysis of organic sulfur compounds in a mixture containing a high amount of hydrocarbons, such as black liquor. Headspace operating conditions were: 5 minutes strong shaking for equilibration of the sample, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min. The sample vials were purged by nitrogen to minimize the oxidation of MM to obtain accurate MM analysis. The sample preparation and measurement procedures were as follows: Inject 10 μ L of sample solution into a closed 21.6 mL vial by micro syringe and place it in the headspace sample tray for HS-GC measurements. For quantifying total MM, 50 μ L of 0.5 M sulfuric acid was added into the vial for the acidification of the black liquor.

RESULTS AND DISCUSSIONS

Time-Dependent Organic Sulfur Compound Formation

Figure 1 shows the time-dependent formation of organic sulfur compounds, namely MM and DMS, in a set of conventional kraft pulping processes of southern pine. The sulfidity was 30%. We did not find DMDS in the pulping spent liquor, which agrees with the conclusions reported in the literature [4-6, 9]. The time-dependent data show that the formation of MM and DMS was slow at the beginning of the pulping process due to low temperature and low methoxyl group concentration, but increased exponentially as the pulping process continued. The formation rate transition point (FRTTP) occurs right as the pulping temperature reaches 170°C (the 4th data point corresponding to a pulping time of 70 minutes). The formation of MM is much earlier than that of DMS. Figure 1 also shows that the present data agree in general with those obtained by Andersson [9] in 1970 (about 30 years ago). The discrepancy at the early stage of the pulping is due to the difference in the cooking temperature profile, as shown. Because Andersson [9] used a sulfidity of 33%, higher than the 30% used in the present work, a little more MM was formed in his study.

The time-dependent volatile organic sulfur compound formation data provide detailed information about the formation kinetics and have been well documented in the literature [4-9]. The data clearly show that the formation of organic sulfur compounds experiences a slow stage at the beginning of the pulping and a rapid increase stage after the cooking temperature reaches 170°C. However, the data did not provide any information about the degree of delignification and its relation to the formation of organic sulfur compounds. Research on the correlation between the formation of organic sulfur

compounds and delignification has not been reported in the literature. From a practical point of view, it will be very interesting and beneficial to correlate organic sulfur compound formation to delignification. It is this approach, adopted in the present study, that leads to the development of the present IDOR technologies.

Phase-Transition Pulping (PTP) for In-Digester Odor Reduction

To relate the formation of organic sulfur compounds with delignification, we determined the kappa number of each pulp sample for data presentation in the present study. Figure 2 shows the correlation of sulfur compound formation to the kappa number for a set of kraft conventional pulping processes of southern pine (the time-dependent formation data are presented in Fig. 1). The results demonstrate that the formation of organic sulfur compounds linearly increases with the reduction of kappa number. Further reduction of kappa number as delignification continues results in a rapid increase of the formation of sulfur compounds. The transition point occurs at about a kappa number of 35 (between the 6th and 7th data points corresponding to a pulping time of 120 minutes). We call this transition point phase transition point (PTP) based on the assumption that the pulping process enters residue delignification from the bulk delignification phase. The phase transition point (PTP) differs from the formation rate transition point (FRTP) in terms of the corresponding pulping time, kappa number, physical meaning, and practical importance. The FRTP (at 70 minutes in the pulping process) has no practical importance because it is derived from the time-dependent measurement with no relation to delignification. Furthermore, the kappa number corresponding to the FRTP is about 140, meaning that the wood chips essentially have not been pulped or only a very small amount of lignin has been removed through pulping. However, the kappa number at PTP

has been reduced to about 35 for conventional kraft pulping of southern pine, meaning a significant amount of lignin (bulk lignin) has been removed. Therefore, PTP is significantly important to mill practice.

The PTP concept is developed through the idea that environmental consideration does not necessarily mean a sacrifice in productivity. This idea led us to examine the relationship between the formation of sulfur compounds and delignification. It is well known that kappa number reduces rapidly in the early stage of bulk delignification. This rapid lignin-removal process cannot be sustained in any chemical pulping processes; therefore, further cooking in the later stage of residual delignification only results in a slight kappa reduction. Figure 3 demonstrates this characteristic of delignification with a kraft pulping of southern pine where the transition from bulk to residual delignification occurs at a kappa number around 35 (exactly the same kappa at PTP). To obtain a fixed kappa reduction, one would have to cook for longer time or use more energy once the delignification enters the residual phase ($\text{kappa} < 35$ for southern pine), which results in more formation of organic sulfur compounds (even though their formation rates remain unchanged as shown in Fig. 1). Therefore, if the pulp and paper industry has to pay environmental costs, then, we propose PTP pulping to achieve in-digester odor reduction (IDOR), i.e., to cook southern pine to PTP or a kappa number of 35 to remove the bulk lignin to significantly reduce the formation of organic sulfur compounds and reduce mill odor. Furthermore, we propose to use other non-odor producing technologies, such as oxygen delignification, to remove the residue lignin and achieve required delignification (kappa number around 25 for a bleachable grade of softwood pulp).

To demonstrate that the PTP pulping concept is universally valid, we conducted kraft conventional pulping of 4 softwoods and 6 hardwoods. Figure 4 shows the formation of total reduced sulfur compounds, i.e., MM plus DMS, in relation to delignification pulp kappa number. The sulfidity was 30% for southern pine and maple and 31% for the rest of the wood species, as stated in the experimental section. The results indicate that kraft pulping of softwoods produces many more organic sulfur compounds than that of hardwoods at a given kappa number. The results also show that the total organic sulfur compounds formed from pulping of all softwoods and all hardwoods fall into a single curve, respectively, regardless of the specific wood species within the general categorization of hardwood and softwood. Furthermore, the slopes of the two TRS formation curves experience an abrupt change at a critical kappa number, respectively, meaning that a PTP exists in both hardwood and softwood pulping. The kappa number at the PTP is 35 and 20 for softwoods and hardwoods, respectively. When kraft cooking is terminated around the critical point for the purpose of odor reduction, we refer to it as the phase transition cooking (PTC). It is our understanding that the transition point is directly related to the phase transition of kraft delignification from bulk delignification to residual delignification. Thus, when the different cooking processes, e.g., RDH or EMCC, are used, the actual kappa number of the transition may be different. In most cases, it may be a lower kappa number.

The data in Fig. 4 indicate that the total organic sulfur compounds formed during the post-PTP cooking stage are 70% and 50%, respectively, for bleachable grade hardwood pulping with a final kappa number of 10 and bleachable grade softwood with a final kappa number of 25. Therefore, it is feasible to significantly reduce TRS formation

in kraft pulping by limiting the degree of delignification to the PTP at which the pulp kappa number is 20 and 35 for hardwoods and softwoods, respectively. The increased amount of residue lignin can be removed through other means, such as oxygen delignification in which odor compounds will not be formed because sulfur compounds are not used.

AQ Addition

AQ has been well known to possess a marked capability of accelerating the delignification while at the same time stabilizing the carbohydrates toward alkaline degradation in the alkaline pulping process [33]. During pulping, AQ is reduced to anthrahydroquinone (AHQ) by carbohydrate-reducing end groups, which, in turn, are oxidized to alkali-stable aldonic acid groups. The AHQ now acts as an effective nucleophile with regard to the lignin $\beta - O - 4$ linkages and is simultaneously oxidized to AQ. As a result of this reduction-oxidation cycle, AQ could have a significant effect on delignification as well as pulp yield gains. From the reaction kinetics [4-8], one can easily find that catalyst AQ does not affect organic sulfur compound formation, which is verified in the present study. As shown in Fig. 5, the TRS formation rate does not change with the addition of 0.05% of AQ in kraft pulping of southern pine and maple. Only when we correlate TRS formation with delignification have we discovered that AQ can change the correlation between the formation of organic sulfur compounds and delignification due to improved delignification. Therefore, we believe that TRS formation can be reduced by using a reduced pulping time with AQ to achieve an equivalent delignification (or kappa number). Considerable reduction in TRS formation with AQ

addition in kraft pulping of southern pine and maple was shown in Figs. 6 and 7 over a wide range of sulfidity variations from 10 to 30%. Even in such a wide sulfidity range of 10-30%, the PTP remains the same, i.e., 20 and 35, for maple and southern pine, respectively.

To further demonstrate the effect of AQ addition on TRS formation reduction, we varied the level of AQ addition in pulping. We found that the TRS formation decreases linearly with the square root of the AQ (in percent) added in kraft pulping of southern pine, as shown in Fig. 8. We found that TRS formation can be reduced by 20 and 30% with the addition of 0.05% AQ in the kraft pulping of southern pine to kappa numbers of 30 and 40, respectively. The difference in the percent of reduction of TRS formation between kappa number 30 and 40, perhaps, is due to the fact that the PTP is at a kappa number of 35, indicating that the addition of AQ is perhaps more effective to the bulk delignification phase of pulping.

Combined Effects of Pre-PTP Cooking and AQ-Addition

From the results shown above, it can be strongly postulated that by using both pre-PTP cooking and AQ-addition, approximately 70-90% TRS emission can be reduced from the kraft digester. TRS reduction effect by this in-digester odor control technology will be even higher in hardwood than softwood cooks.

CONCLUSION

We conducted the first experimental study on the relationship between the formation of organic sulfur compounds with delignification in kraft pulping. The overall objective of the study was to develop in-digester control technologies for kraft odor

reduction. The results show that the formation of organic sulfur compounds increases as delignification proceeds. Further removal of lignin results in a rapid increase of the formation of sulfur compounds. The transition point occurs at about a kappa number of 35 and 20 for softwoods and hardwoods, respectively. Furthermore, all the softwoods and hardwoods have the exact same sulfur compounds formation with delignification relationship. Therefore, the transition point is directly related to the phase transition of kraft delignification from bulk delignification to residual delignification. We define this transition point as phase transition point (PTP). When kraft cooking is terminated around the critical point for the purpose of odor reduction, we define it as the phase transition cooking (PTC). The results also indicate that anthraquinone (AQ) as a catalytic additive can be used for the purpose of TRS reduction during kraft digestion. The reduction of sulfur compound formation is linearly proportional to the square root of the level of AQ addition (in percent). Based on data obtained, we found that it is possible to reduce 70 – 90% of total TRS formation during kraft pulping simply by combining the following two methods: limiting the degree of delignification to the bulk delignification phase (using PTC) and using AQ as a catalytic additive in kraft pulping.

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Fig. 1

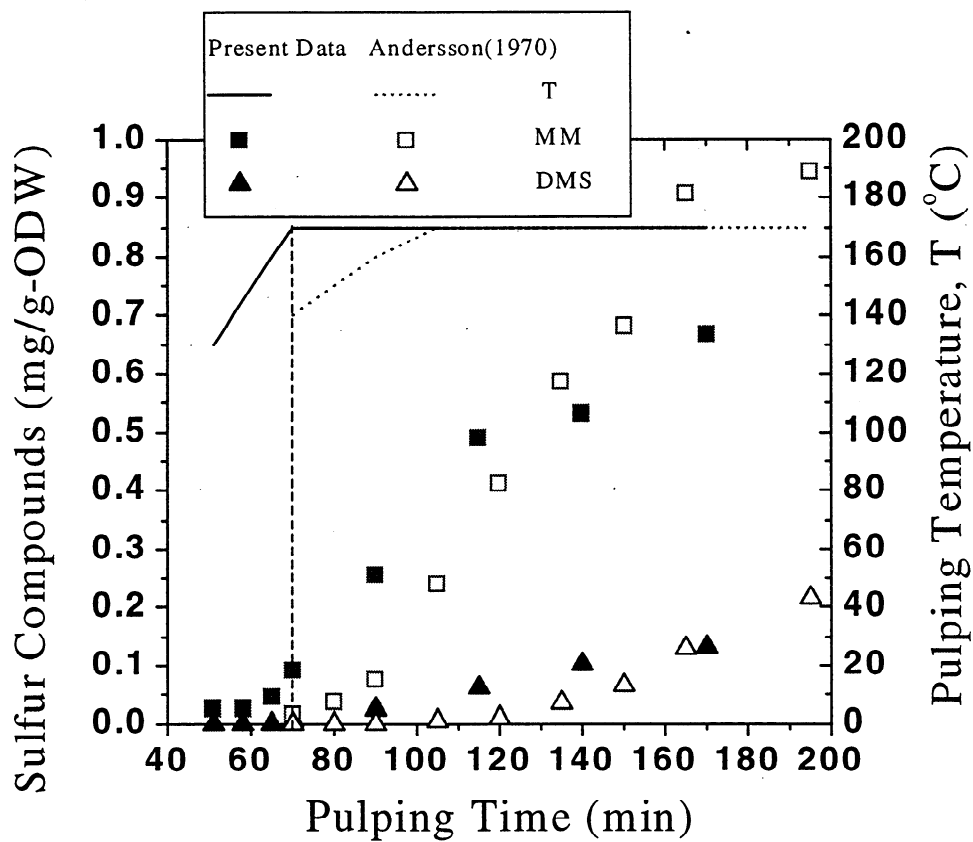


Fig. 2

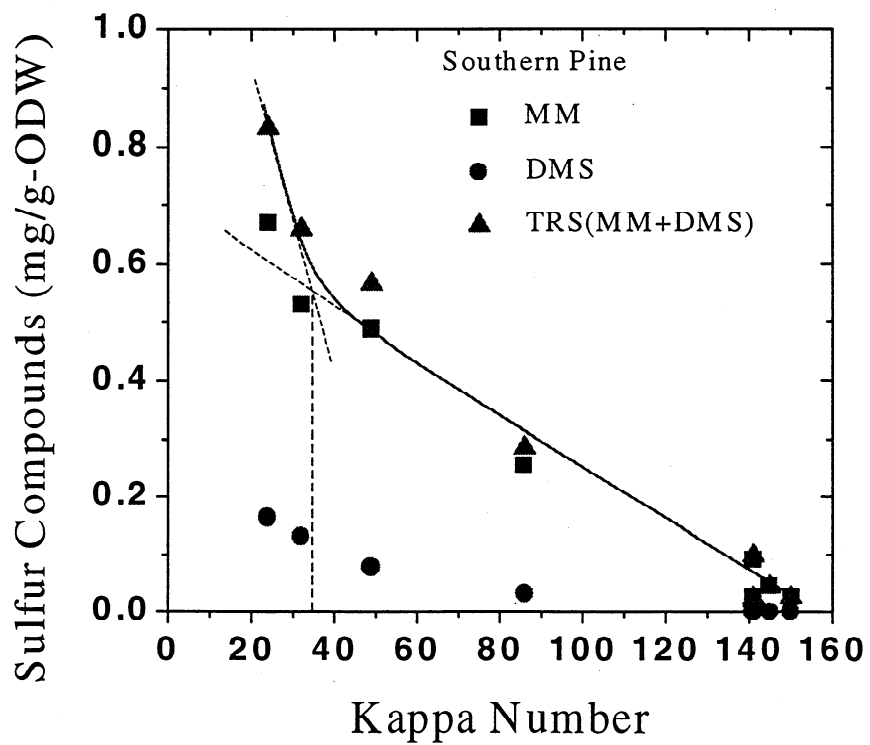


Fig. 3

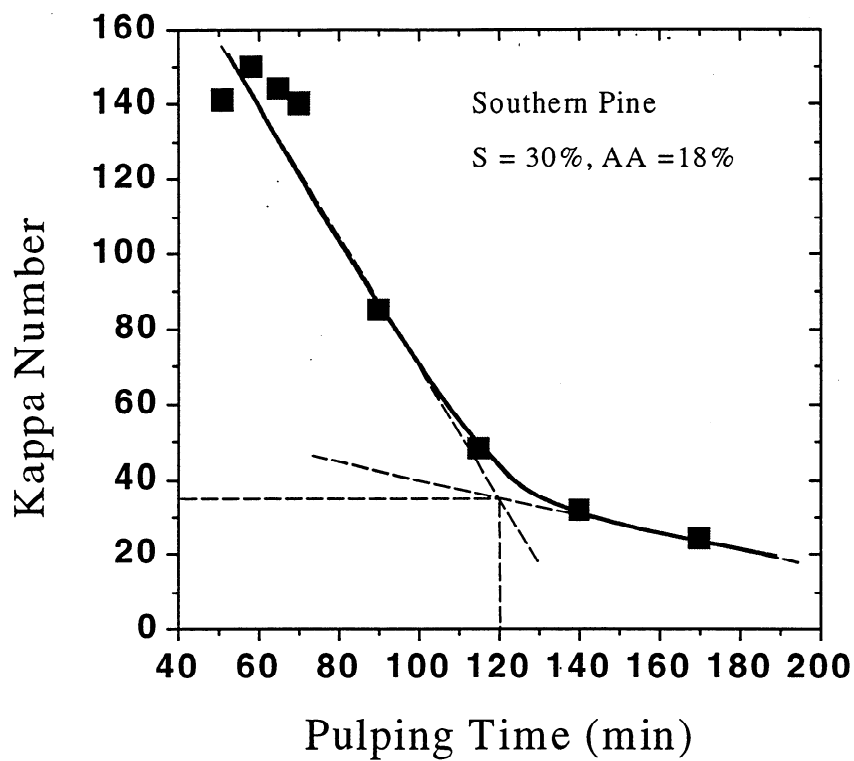


Fig. 4

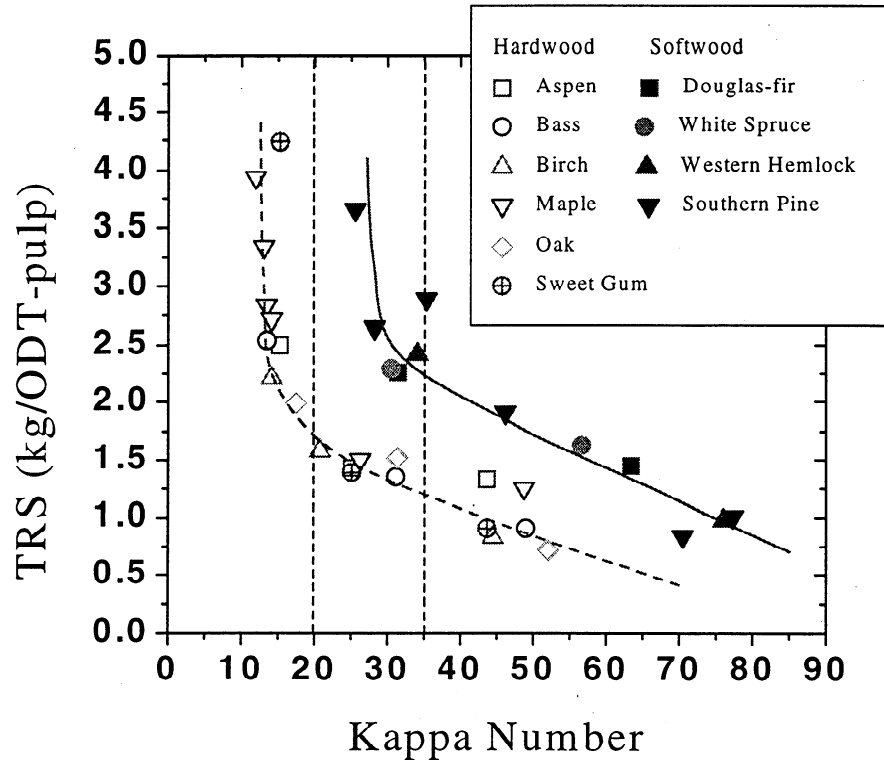


Fig. 5

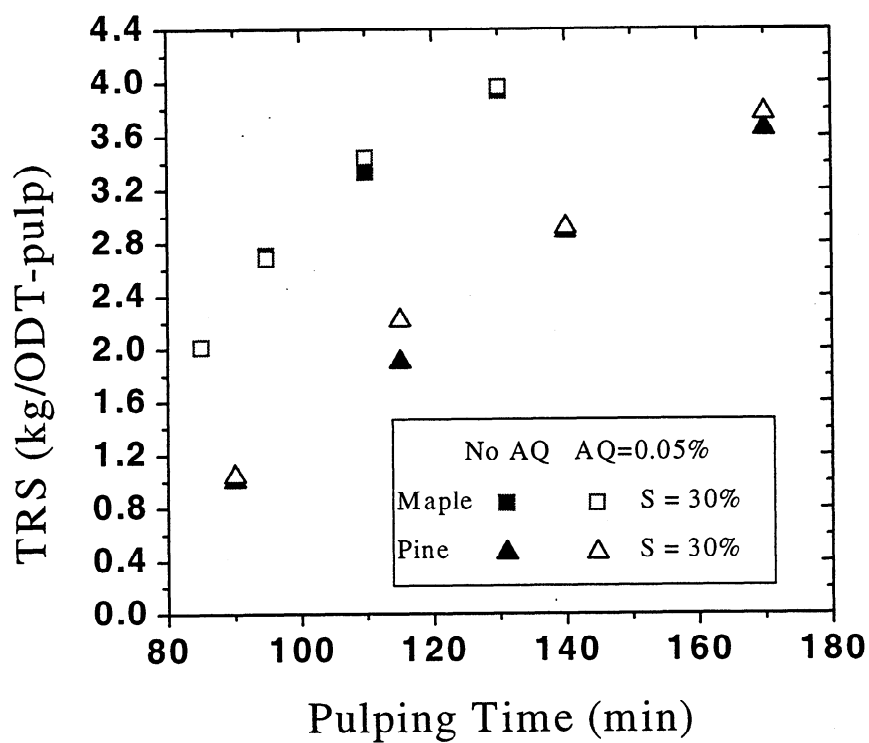


Fig. 6

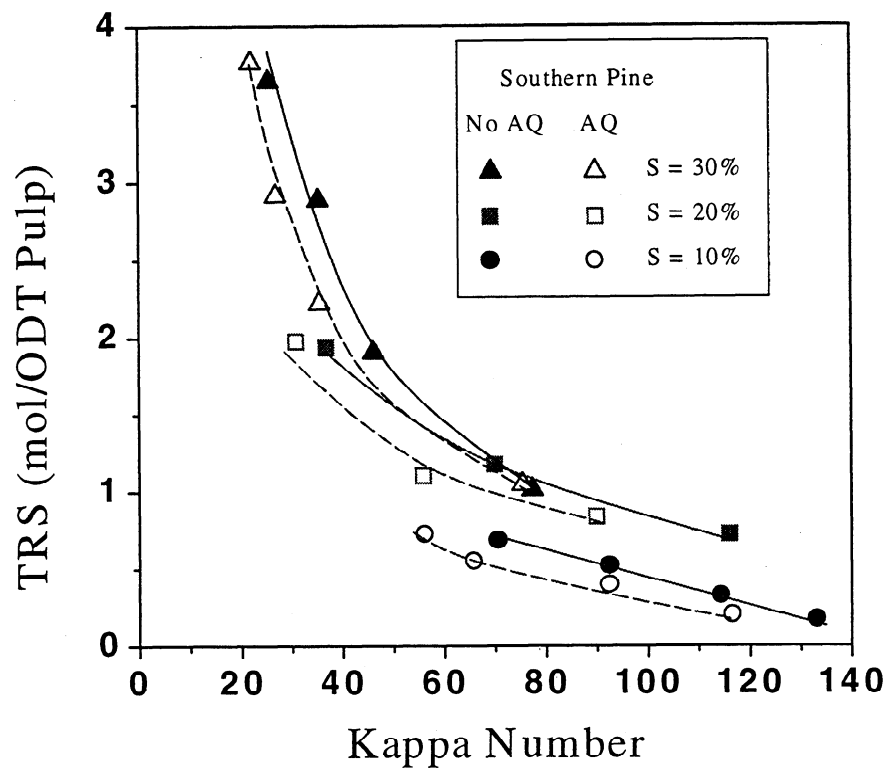


Fig. 7

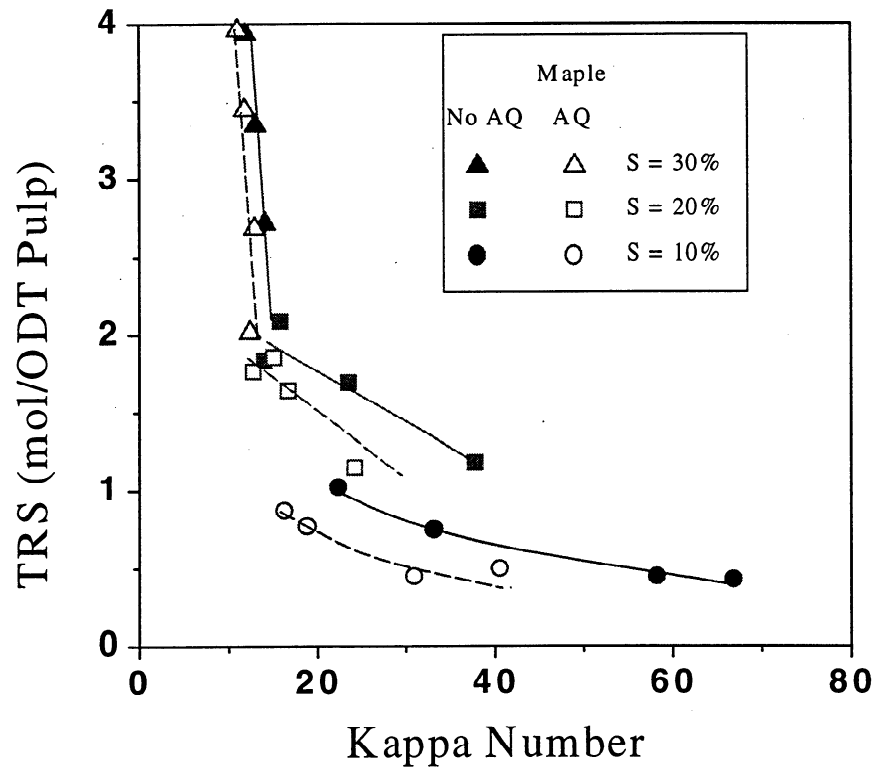


Fig. 8

