



# Real Measurements Lead to Real Understandings and Better Operating Control of the Recovery Liquor Cycle

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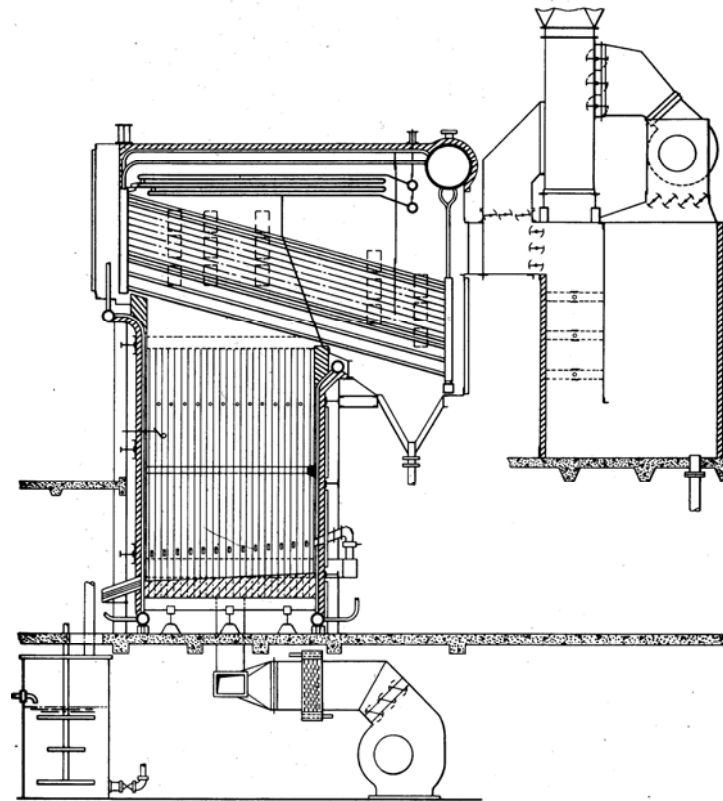
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From : Steam its generation and use,  
1992, 40th edition, Stultz, Steven C.  
and Kitto, John B. eds., 929 p. ISBN 0-9634570-0-4

## The First Tomlinson Recovery Boiler

- Approximately 90 years old
- The original Tomlinson boiler design included the combination of drying, combustion, and chemical recovery within a water-cooled unit.





## Many Improvements to the Original Design

- Increased spacing in tubes
- The addition of retractable sootblowers
- The conversion of economizers from a horizontal style to a vertical long flow
- Increased pressure and temperature
- The switch to a single drum to allow for the building of larger units
- At least 5 generations of air modifications
- Improved liquor delivery of high solids black liquor

(from Esa Vakkilainen “Kraft recovery boilers- Principles and practices” 2005 Helsinki)



## The Result

- The recovery boilers being built today are the largest and most efficient ever built
- The OKI boiler in Indonesia that started up in 2017 can process 12,000 tonnes of liquor a day and could theoretically supply a city of 1,000,000 people with the necessary power



# “But”

- The average age of recovery boilers in the U.S. is presently just over 44 years old (updated from BLRBAC 2022)
- The average age of a recovery boiler in Canada is almost 47 years old.
- North America still has the most recovery boilers in the world with Canada having 40 and the U.S. having 148 as of 2018. The world total in 2018 was approximately 600 ( Salmenoja )
- The average size of a recovery boiler, in 2018, was 1300 tds/d in the U.S. and 1410 tds/d in Canada. ( Salmenoja )
- The largest recovery boiler in the U.S. in 2018 was 3400 tons per day (Salmenoja)





## “And”

- Older mills and older recovery boilers still have operating issues that they have always had:
  - Fouling- the need to water wash a recovery boiler in between maintenance outages can easily result in a loss of over a million dollars
  - Corrosion- extended maintenance outage due to found corrosion can also result in a loss of millions
  - Environmental exceedances that can lead to restraints in operating production and possible fines
  - Physical upgrades to equipment need physical space, downtime and money



## A Better Understanding of Black Liquor

- Could lead to reduced variabilities, better operating control and fewer problems
- BUT
- Black liquor has been described as an impossible fuel (Rolf Ryham, 1993)
  - The AF&PA stated in 2003 that there are over 100 organic and inorganic properties that should be measured for a better understanding of this fuel and that “There is no analytical methodology available to characterize the composition of spent pulping liquor”
  - On-line testing is very limited and significant variability exists in manual testing



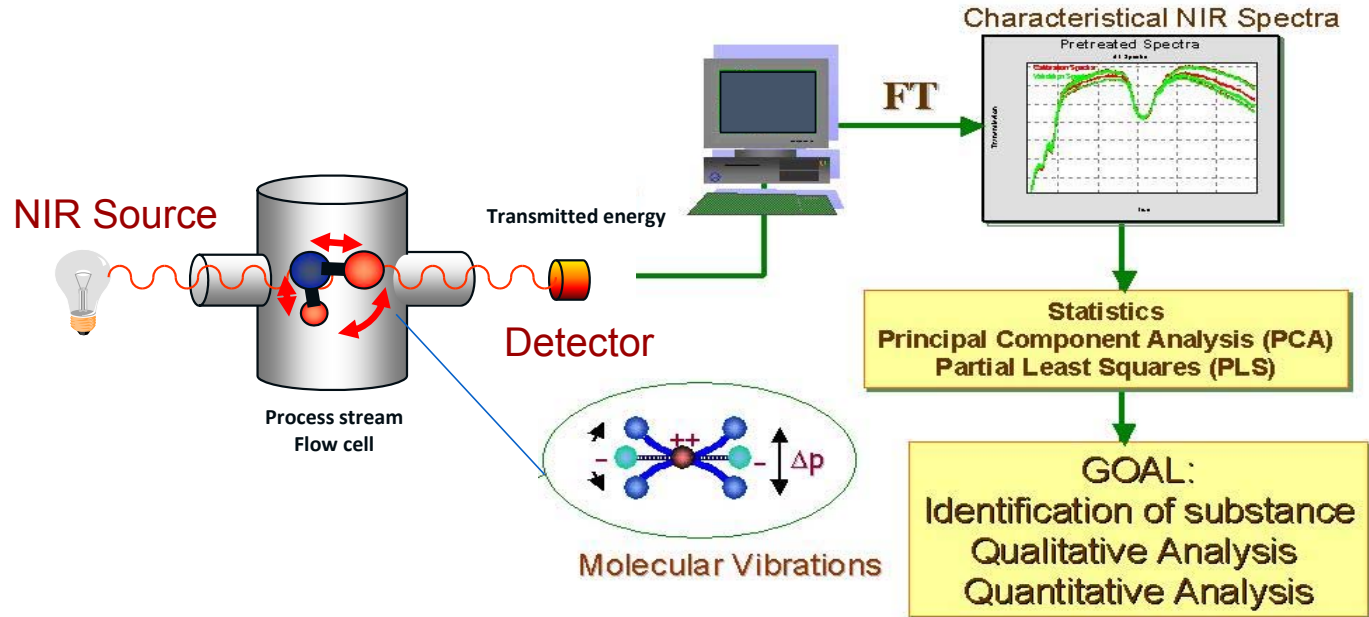
## Measurement Issues

- Many measurements are still inferential- pressure, temperature, density
- Many mills have limited on-line measurements
- Some measurements such as reduction efficiencies are done infrequently-once a week in many mills
- Significant variability between different forms of measurement for the same liquor property
- Some measurements such as REA vary in different parts of the world
- Some measurements such as lignin, inorganic and organic content along with soap are only measured in a handful of mills in the world



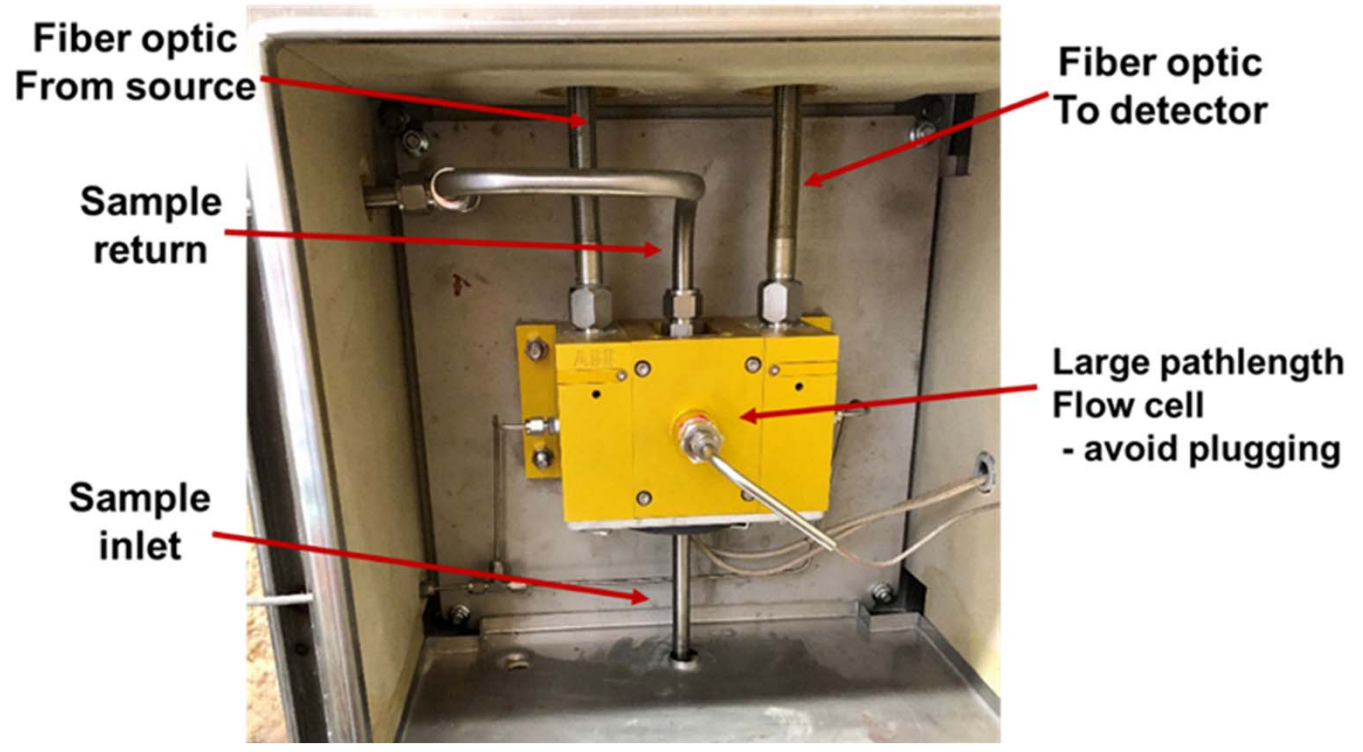
# How does FT-NIR work?

## Principle of NIR Measurements





# A Sample Cell





# The Sampling Station connected to a Spectrometer

Remote Measurement Fibre optic



Field Sampling Station (FSS)



Spectrometer (SRS)





# Advantages of the FT-NIR System

- Uses spectroscopy to measure the frequency of liquor properties
- No Chemicals and it is non-destructive
- No sample preparation-except time for settling
- Fast -128 scans in 50 seconds
- It can analyze more than one liquor parameter with one sample.
- One sampling station can analyze numerous samples.
- One spectrometer can handle several sample stations
- Can lead to a dynamic look at an “impossible fuel”





## How Can an Improved Understanding of Black Liquor Improve Operations?

- Many older boilers can't operate continually above 70 % solids
- The evaporator or recovery boiler physical design doesn't allow for it
- Viscosity is a key hurdle in operating at higher solids
- REA and Lignin content are primary determinants on black viscosity
- Most mills do not measure REA and lignin on-line and these liquor parameters constantly change - especially between species
- Low solids operations (62-70%) can lead to increased corrosion, environmental emissions, lower thermal efficiencies





## Corrosion and Low Solids

- “Acidic sulfates, mainly sodium bisulphate ( $\text{NaHSO}_4$ ) and sodium pyrosulfate ( $\text{Na}_2\text{S}_2\text{O}_7$ ) are thought to be the main cause of fireside fouling and severe tube wastage in the generating bank and economizer regions of kraft recovery boilers”
- “Solid  $\text{Na}_2\text{S}_2\text{O}_7$  which is non- corrosive may revert to the corrosive liquid  $\text{NaHSO}_4$  if the  $\text{H}_2\text{O}$  in the flue gas exceeds a critical value”.
- The critical value of  $\text{H}_2\text{O}$  is 33% (Tran) which would be a combination of water in black liquor and the water from the steam from sootblowing.

“The effect of  $\text{H}_2\text{O}$  on acidic sulfate corrosion in kraft recovery boilers” by Tran, Mapara, and Barham, November 1996 Tappi Journal.

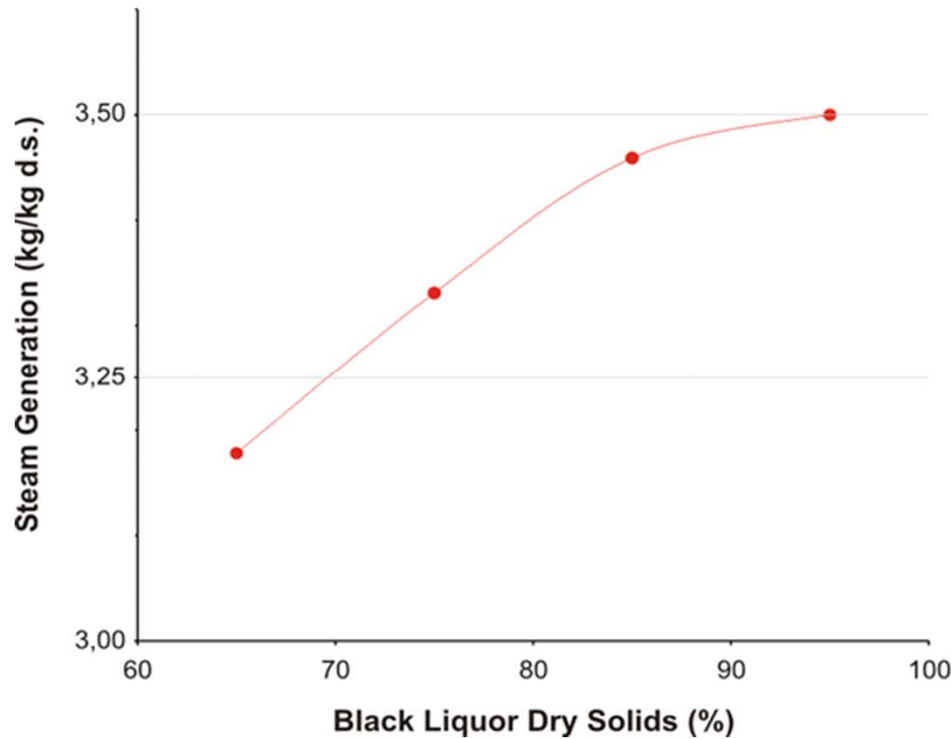


## Environmental Excursions and Low Solids

- “Long term fouling of a recovery boiler operating at 66 to 68% solids has been studied previously. At this solids, the sulfur emissions are 100 to 500 ppm at 3% O<sub>2</sub>. In high solids operation the outlet flue gas SO<sub>2</sub> can be continuously kept close to zero.” (Vakkilainen 1992)
- “Both the sulfur dioxide (SO<sub>2</sub>) and hydrogen sulfide (H<sub>2</sub>S) were practically zero when high dry solids firing was in operation.” (Salmenoja 2019)



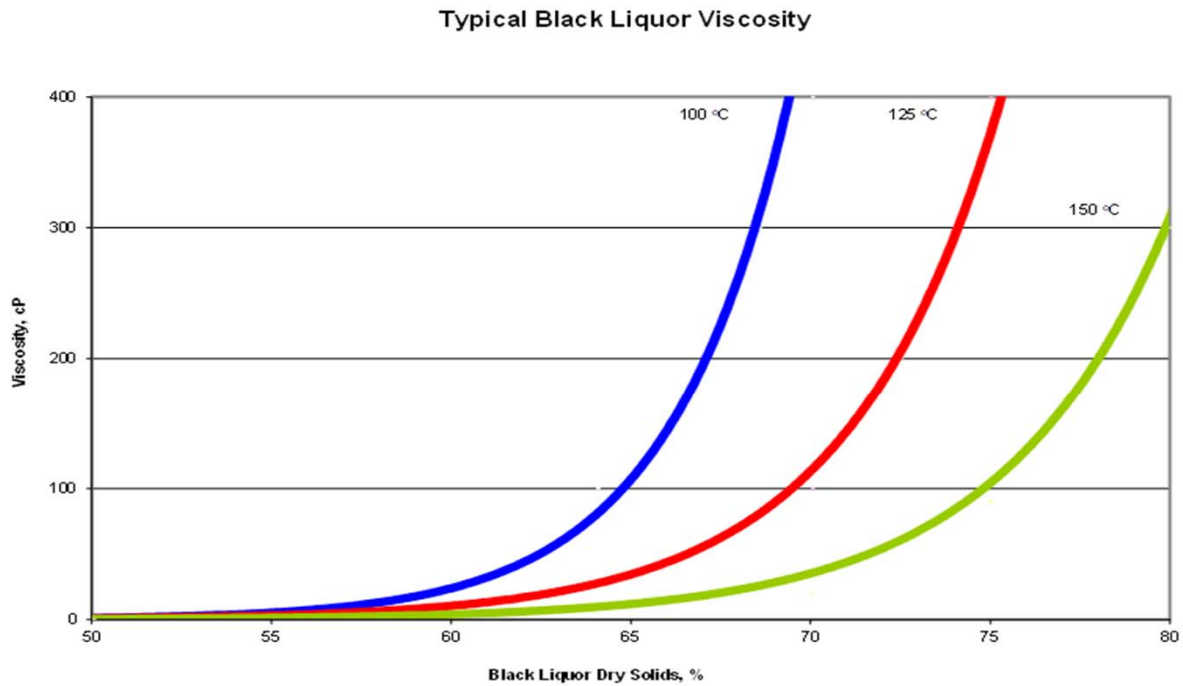
# Thermal Efficiency is Dependent upon the Amount of Water in the Black Liquor



Boiler size	= 5000 tds/d
$T_{\text{STEAM}}$	= 500°C
$T_{\text{FEEDWATER}}$	= 115°C
$T_{\text{FLUE GASES}}$	= 180°C
Excess $O_2$	= 3% in dry gases
HHV	= 14 MJ/kg



# Viscosity is the Hurdle in Front of Higher Solids



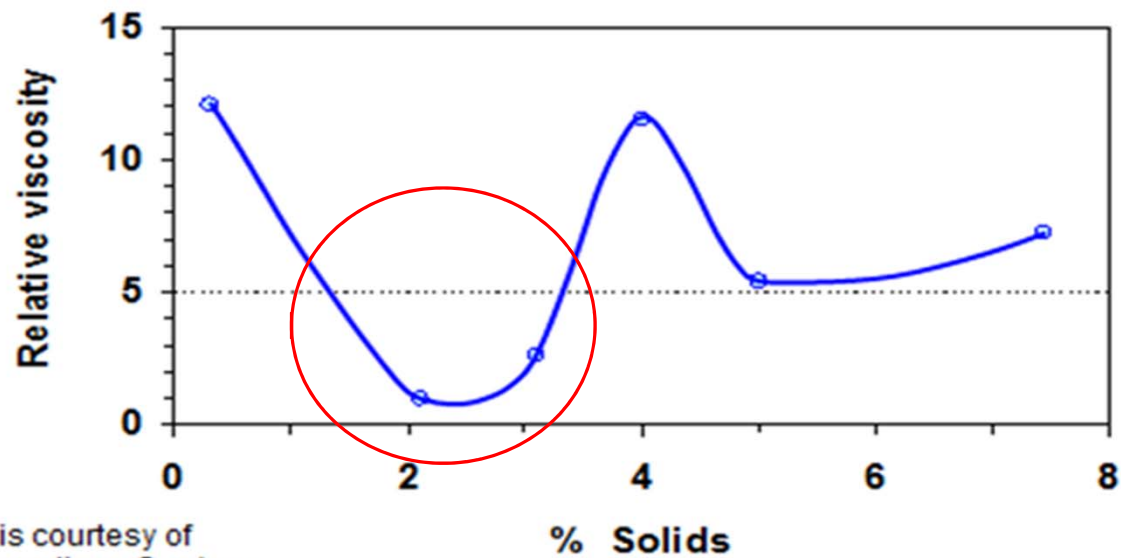
A typical black liquor solids / viscosity / temperature relationship (Reproduced from a slide by Marr and Adams )





# REA and Black Liquor Viscosity

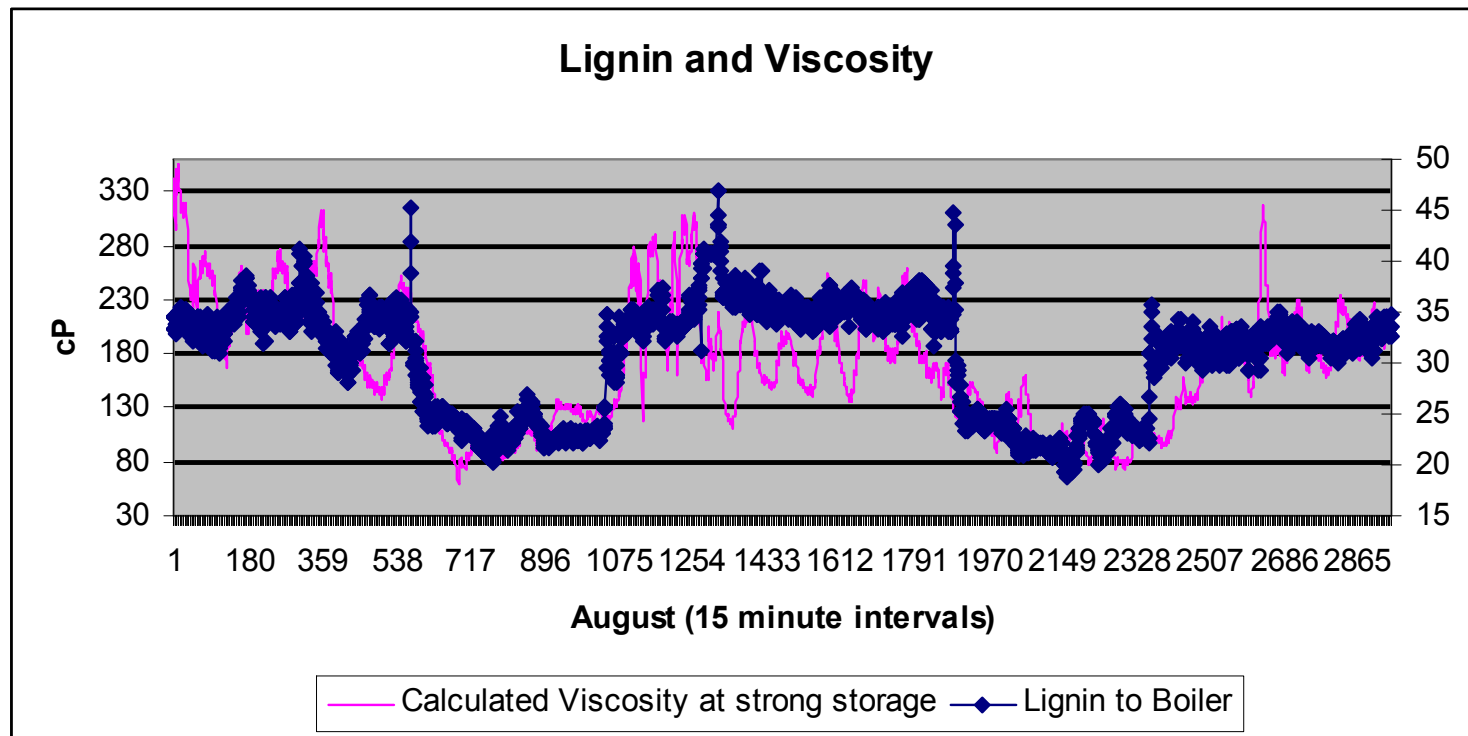
Effect of REA on Viscosity for a 70% Solids  
Jack Pine Black Liquor at 100°C, SR =  
0.85/s



Slide is courtesy of  
FPInnovations Quebec  
ICRC 2007

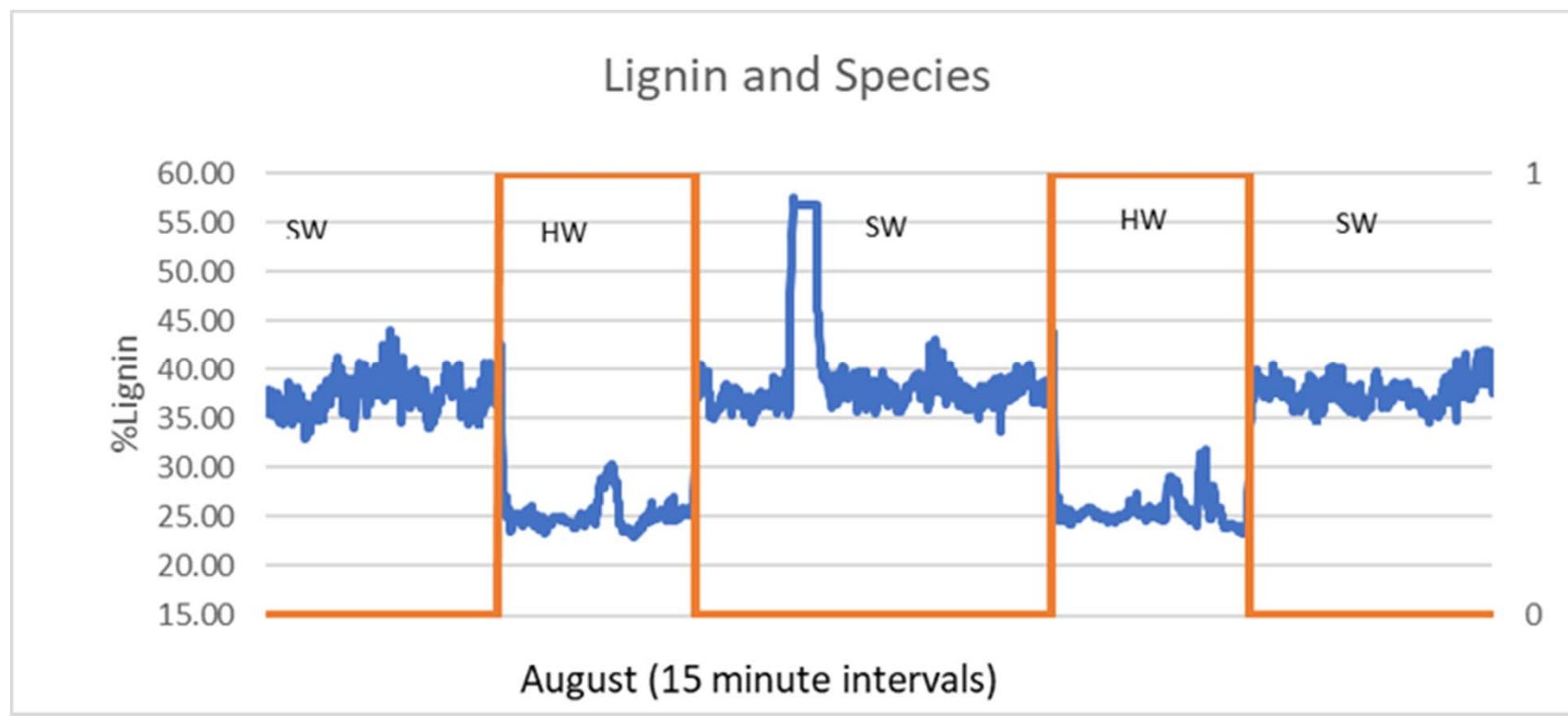


# Lignin and Viscosity



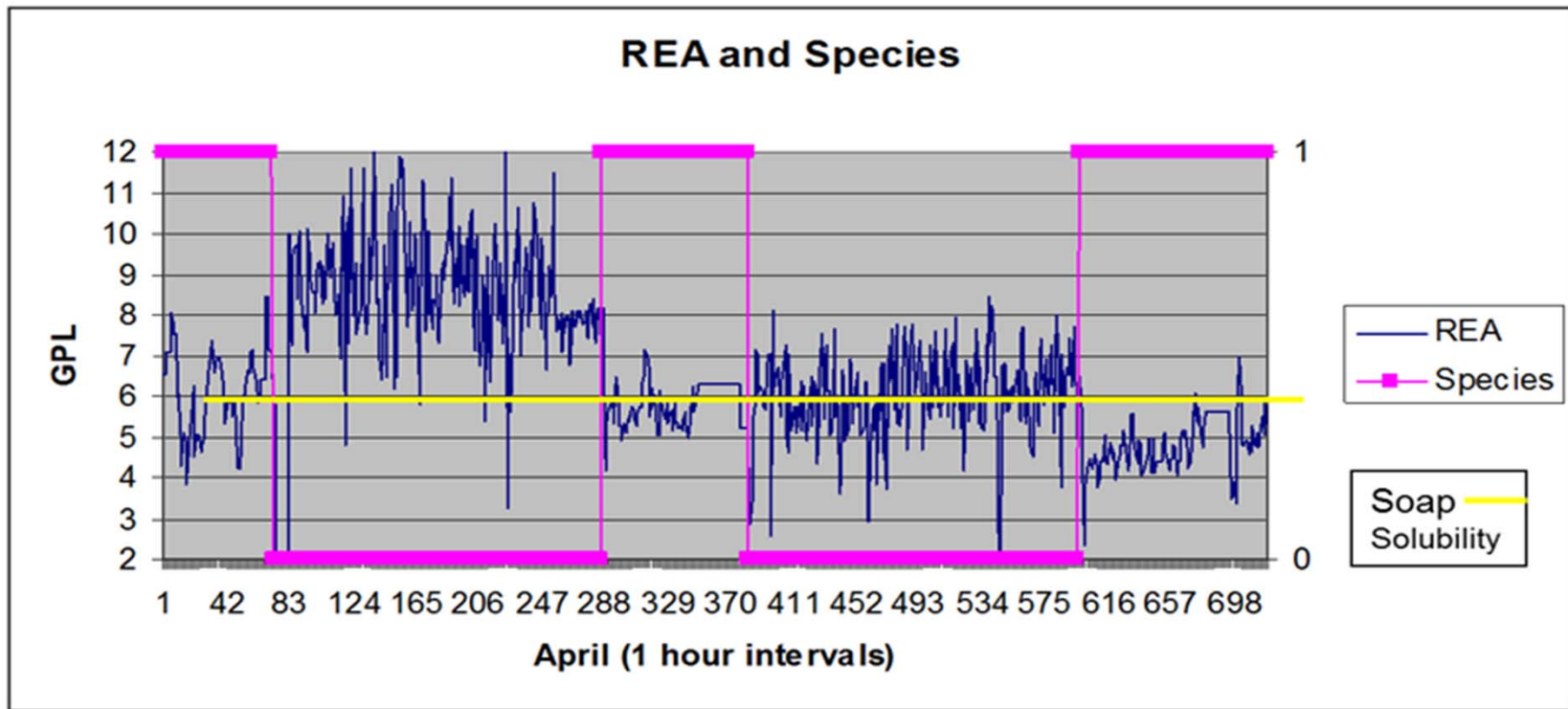


# Lignin and Viscosity and Species



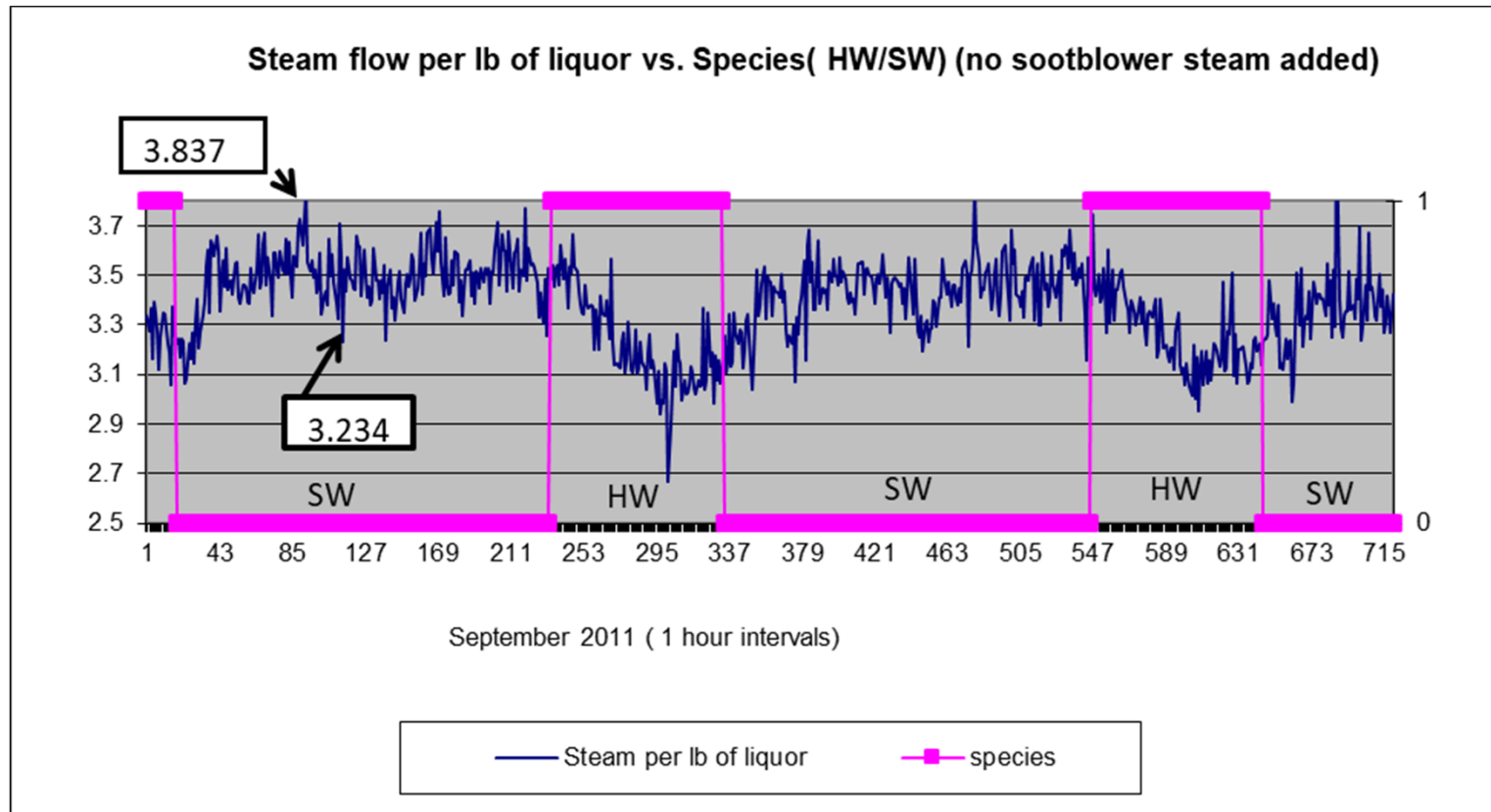


# REA and Soap Solubility





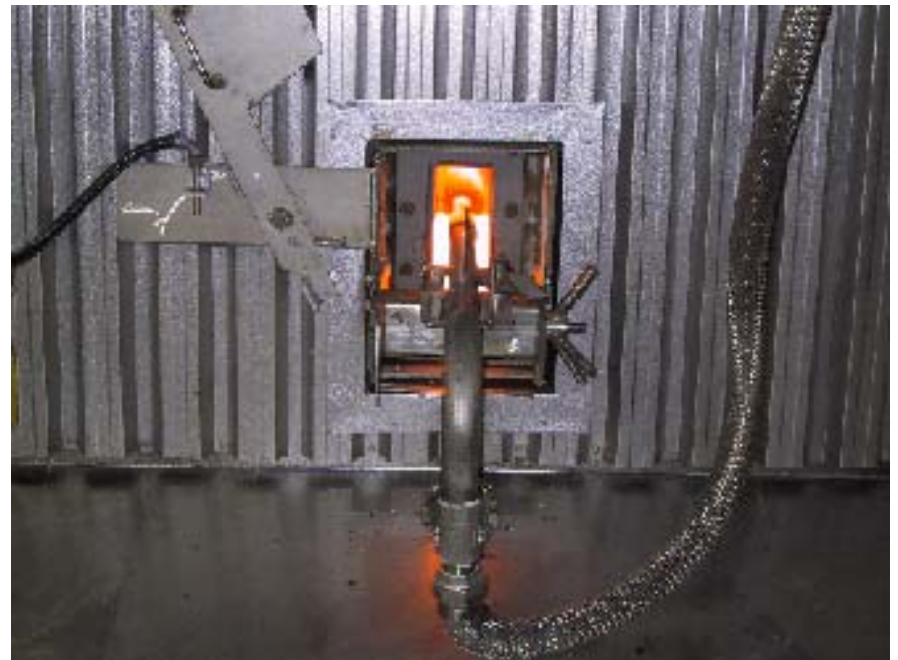
# Variable Soap and Variable Lignin Lead to Variable Steam Flow





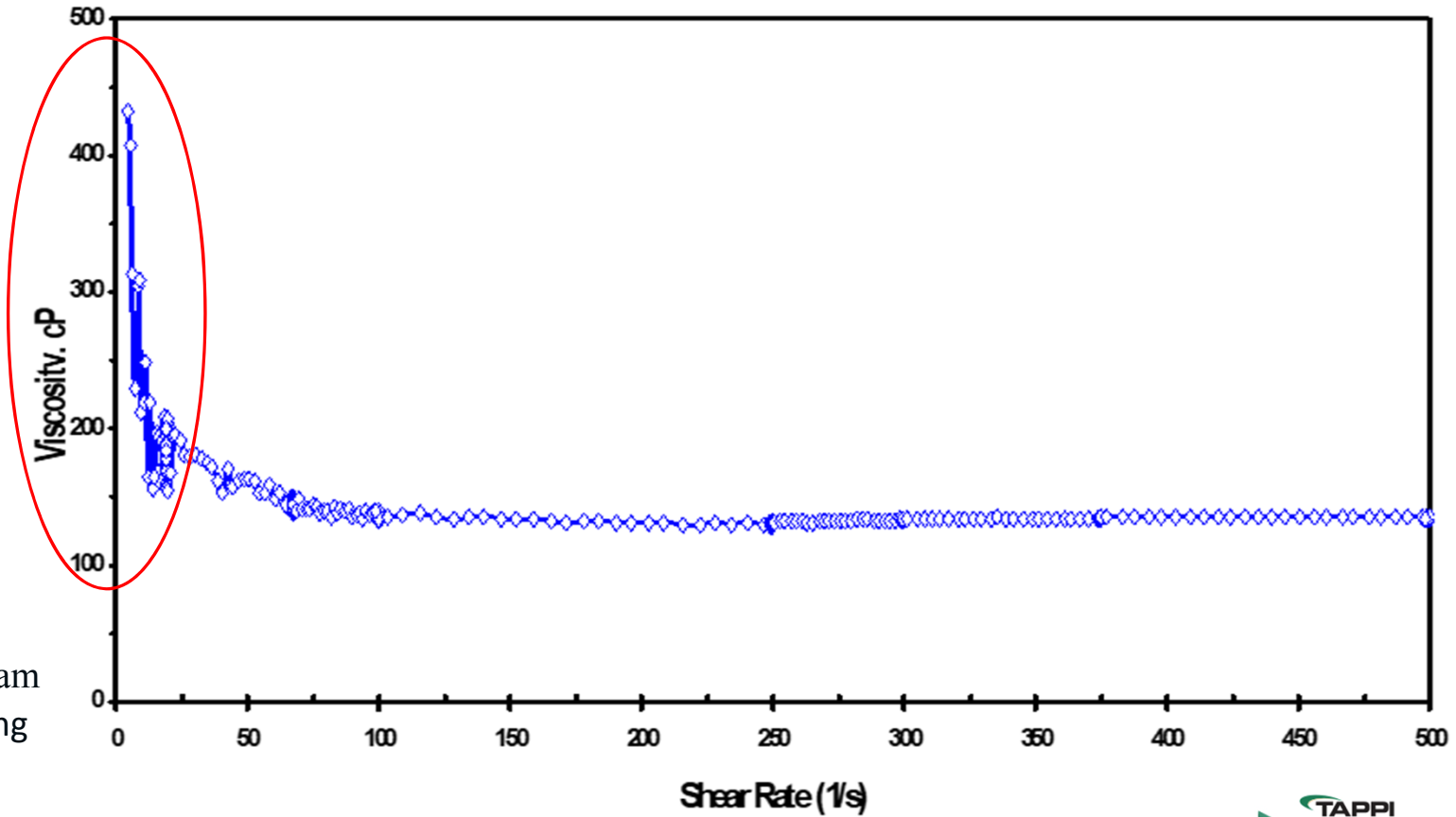
## Black Liquor Spray

- Prime determinant on carry over, bed formation, corrosion, fouling, and quality of smelt
- Difficult to control because of changing liquor properties
- High solids black liquor is a non-Newtonian fluid





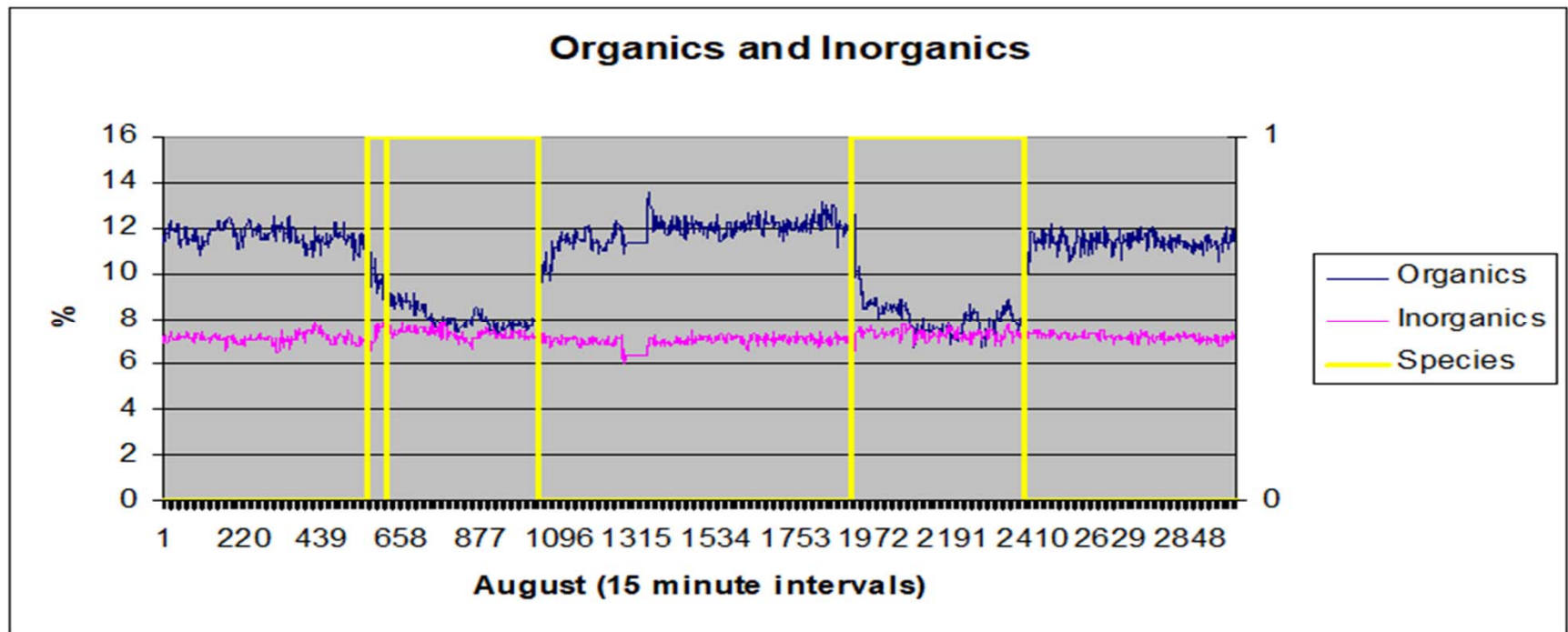
# When Shear is Reduced Viscosity Increases



Pak Wong Steam  
Power Meeting  
2007

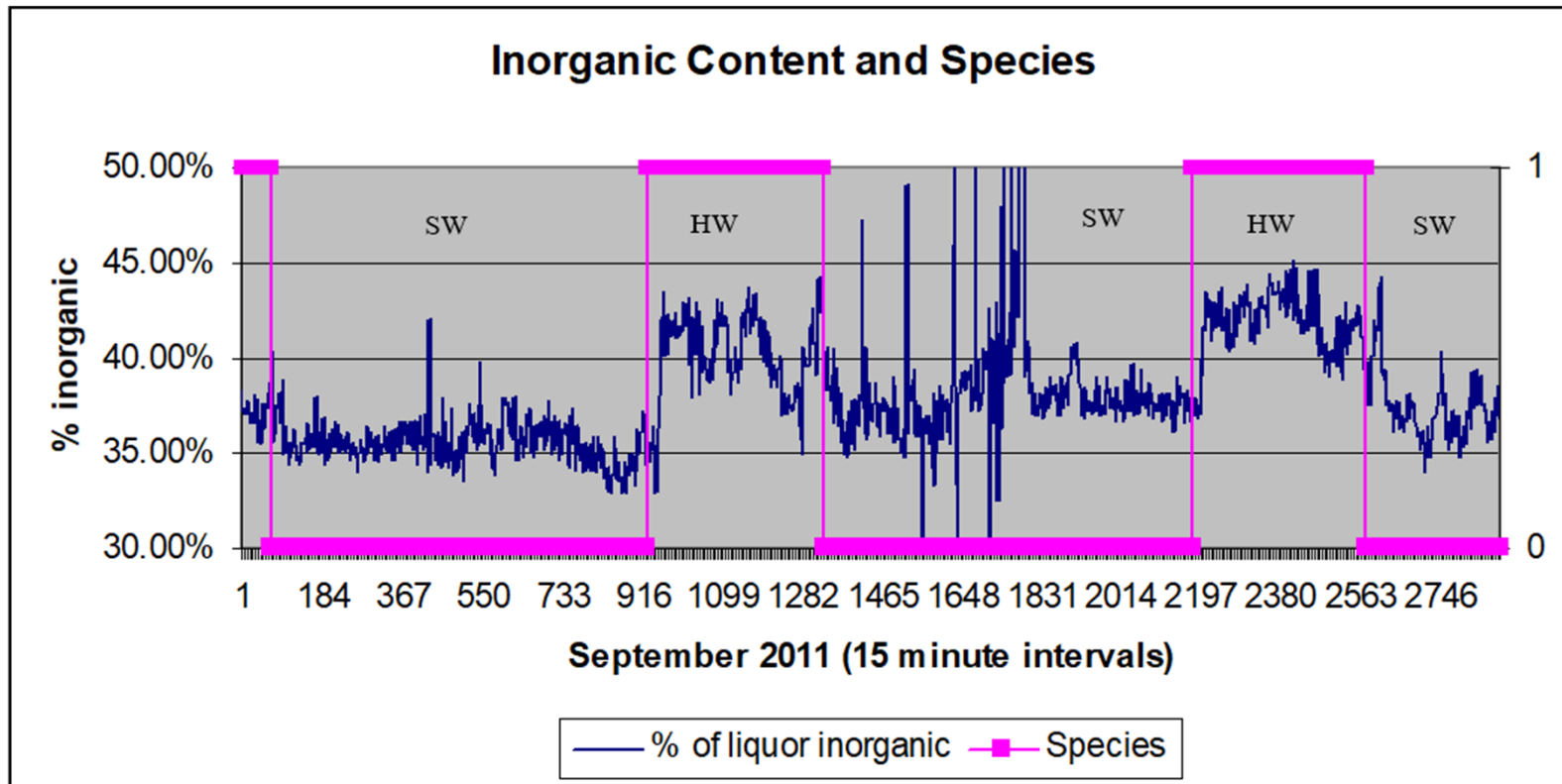


# The Organics Change with Species



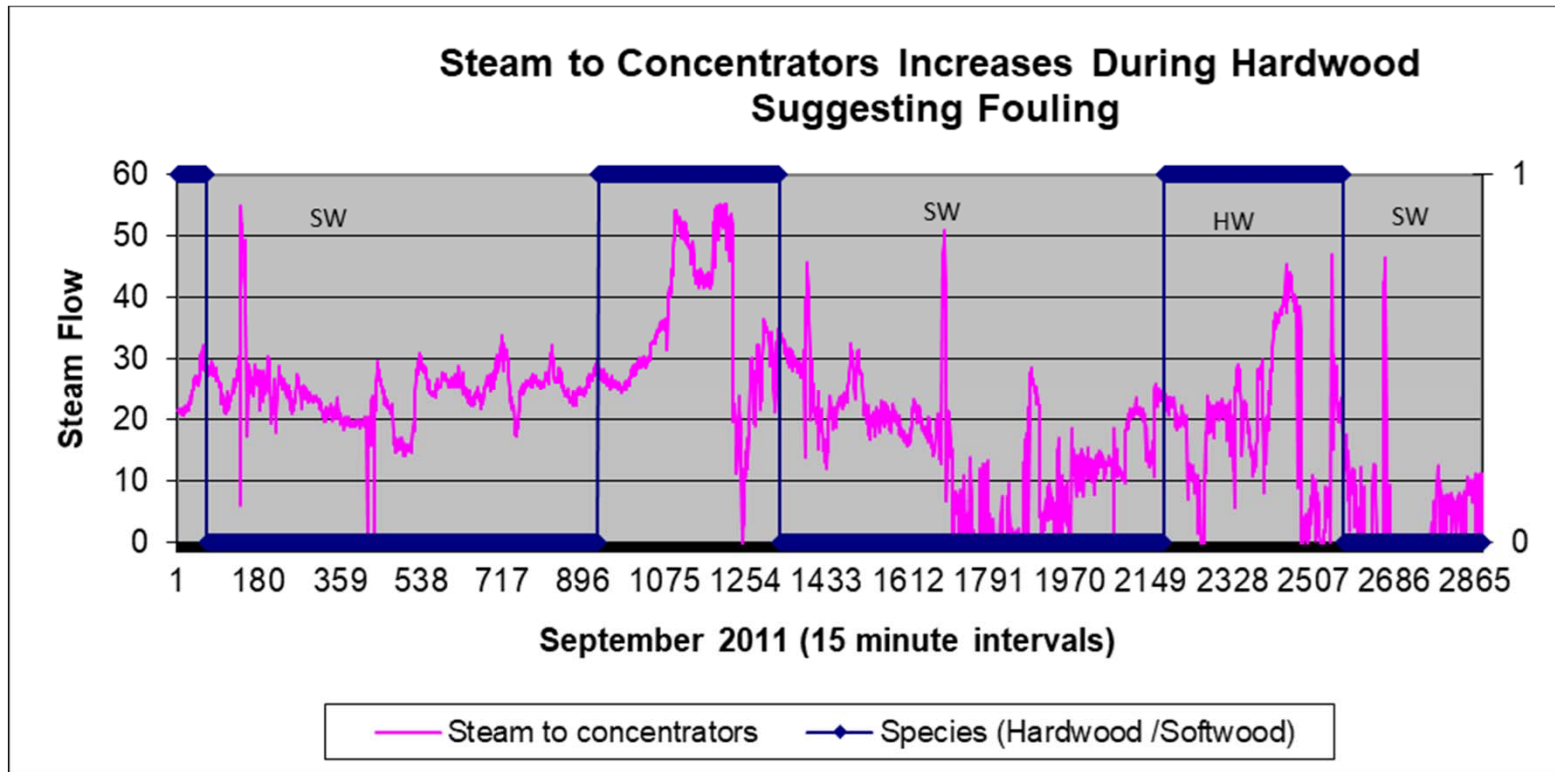


# Inorganics are Higher on HW



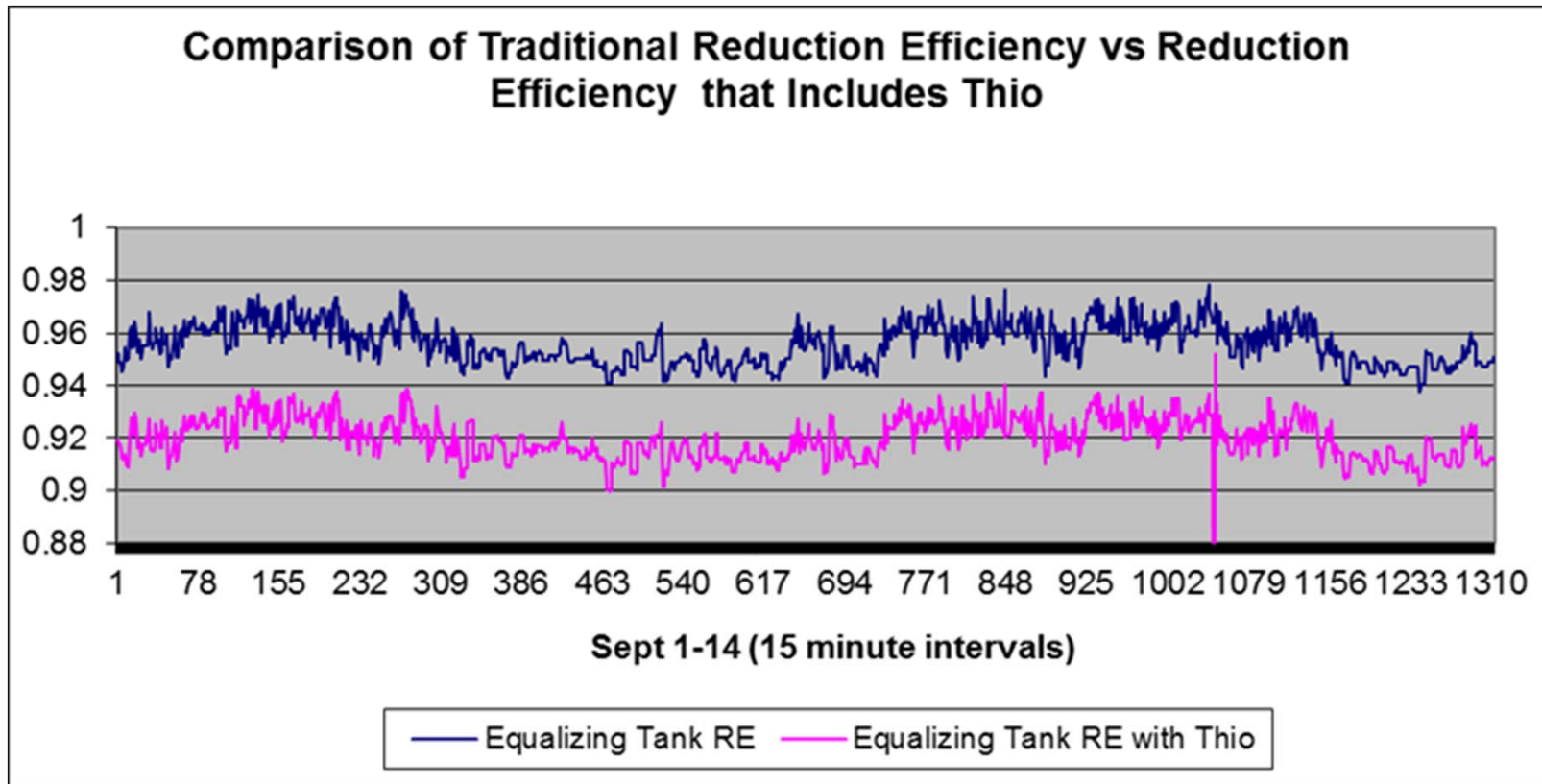


# Critical Solids Determinations Need an Online Inorganic/Organic Ratio





# Reduction Efficiencies Should Include Thiosulphate –both are deadloads





## Summary

- Boiler vendors have done a remarkable job in making new boilers more efficient in every way
- However, the majority of the recovery boilers in the world are old and small with numerous operating concerns
- An increased knowledge of the properties of black liquor has the potential to reduce variability and improve operating conditions
- The use of FT-NIR spectroscopy, has been shown through online mill data, to have a significant potential to provide this increase in understanding
- It uses no chemicals, it is fast, it needs no sample preparation, and it can analyze more than one property at a time



*“If you want to find the secrets of the Universe, think in terms of energy, frequency and vibration.”*

Nicolai Tesla

Questions?