GREENHOUSE GAS AND RESOURCE CONSERVATION BENEFITS OF USING BLACK LIQUOR FOR ENERGY PRODUCTION

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Background

• In paper making, strong fiber bonding and brightness require
  – the separation of wood fibers
  – the removal of lignin from wood fiber
• This provided the impetus for the development of chemical pulping technologies
• Late 1800s and early 1900s pulping technologies
  – Sulfite pulping: Easily bleached pulp. Inexpensive pulping chemicals did not need to be recovered. Liquor discharged, often without treatment
  – Soda pulping: Worked only on hardwood. Modest pulp strength properties. Expensive make up chemicals
The Kraft process

• Soda process required additions of expensive NaOH/Na₂CO₃ to make up for lost chemicals

• In the late 1800s, German chemist C.F. Dahl discovered that when he used a less expensive chemical (Na₂SO₄) to supply the sodium, the introduction of sulfur was very beneficial
  – produced increased yield
  – gave a process that worked on a range of wood species
  – increased pulp strength (“kraft” is German for “strong”)

• 1930s – Tomlinson Recovery furnace was developed/deployed for recovering pulping chemicals and recovering energy from the organic matter in the spent Kraft pulping liquor (black liquor)

• By the 1950s, Kraft pulping was dominant

• Currently, about 99% of U.S. chemical pulp production is from Kraft mills (based on AF&PA statistics for 2006)
  – Even considering all wood pulp (chemical, semi-chemical and mechanical), Kraft pulp represents about 85% of the U.S. total
A bit more about Spent Pulping Liquor

• When pulp is produced from wood chips using a chemical process, such as the Kraft process, the fibers are separated from the remainder of the chip.
• The residual liquid is called spent pulping liquor. It contains the dissolved portions of the wood not needed for pulp and paper making as well as the spent cooking chemicals.
• Spent pulping liquor can be concentrated to produce a combustible material used as fuel in a recovery furnace (also called a recovery boiler).
  – The “recovery” consists of recovering pulping chemicals and energy from the spent pulping liquor.
• The most common form of spent pulping liquor is black liquor produced by the Kraft pulping process.
Black Liquor

Black liquor is separated from pulp in washing

Unwashed Pulp

Washing

Black Liquor

Washed Pulp
Recovery Furnace
Energy Products – Steam & Electricity Through CHP or Cogeneration

• Virtually all forest products facilities that produce high pressure steam and use it to generate electricity do so through a process called Combined Heat and Power (CHP) also known as Cogeneration

• With CHP or Cogeneration the high pressure steam turns a turbine to make electricity

• Useful thermal energy (low pressure steam) is also extracted from the turbine and used in the manufacturing process
Electricity in Typical Cogeneration System in Forest Products Industry

Recovery Furnace
Has an oxidative zone and a reductive zone

COGENERATION (Extraction/Condensing) TURBINE

High Pressure Steam

Electricity

To Grid

Low Pressure Steam

Electricity in Forest Products Industry

Black liquor

Smelt (Na₂S and Na₂CO₃)

Process
A Simplified Representation of the Chemistry in the Kraft Pulping and Chemical Recovery System

**The Sodium Loop**

Recovery Furnace + Smelt Dissolving Tank
Wood Organics + O₂ → biomass CO₂
Na and S Cpds. → Na₂S
Na Cpds + biomass CO₂ → Na₂CO₃

**The Calcium Loop**

Slaker
CaO + H₂O → Ca(OH)₂

Ca(OH)₂

Ca(OH)₂

CaO

CaCO₃

Lime Kiln
CaCO₃ → CaO + biomass CO₂↑
Fossil fuel + O₂ → CO₂↑

**Causticizing of Green Liquor to make White Liquor**

Na₂CO₃ + Ca(OH)₂ → 2NaOH + CaCO₃

**White liquor clarifier**

NaOH & Na₂S
stay in solution

CaCO₃
precipitates

**Pulping Digester**

NaOH + Na₂S + wood chips → Various Na and S Cpds, Pulp fibers, and Dissolved Wood Material.
A Simplified Representation of the Chemistry in the Kraft Pulping and Chemical Recovery System

- The Recovery Furnace produces energy in the oxidation zone of the furnace from dissolved organic matter.
- The energy drives the chemical reactions in the reduction zone of the furnace, converting the spent pulping chemicals into a form that they can be recovered ($\text{Na}_2\text{S} + \text{Na}_2\text{CO}_3$).
- The remaining energy is used throughout the mill and used to produce electricity, almost always via combined heat and power systems (CHP).

**Pulping Digester**

$\text{NaOH} + \text{Na}_2\text{S} + \text{wood chips} \rightarrow$ Various Na and S Cpds., Pulp fibers, and Dissolved Wood Material.

**Lime Mud**

$\text{CaCO}_3$
This study

• The question: What are the greenhouse gas and resource conservation benefits of using black liquor solids in the Kraft recovery system?
  – Relative to a comparable system relying on fossil fuels

• Use life cycle thinking to compare the GHGs emitted, and non-renewable energy required to produce one gigajoule of energy output and the chemicals required for pulping via;
  • the use of black liquor solids in the Kraft recovery process
  • various fossil fuel-based systems to produce the same quantities of energy output and pulping chemicals
  – where the amounts of wood used and pulp produced are equal in both systems
The system based on using black liquor solids in the Kraft recovery system
The system based on using black liquor solids in the Kraft recovery system

Small additions to make up for losses from the recovery system

Some fossil fuel required in lime kiln (not suited to burning black liquor)
The Kraft recovery process

• Has 2 functions
  – chemical production
  – energy production (almost always via combined heat and power, CHP)

• For comparison purposes, we need to consider an alternative fossil fuel-based system that provides the same functions
The system based on using fossil fuels to provide the same functions

Alternative purchased chemical production by fossil fuel-based systems

Alternative management of black liquor solids (to compare with the Kraft recovery system where black liquor solids are used in chemical and energy production).

Alternative fossil fuel scenarios
Since we are interested in the difference, we only need to model those aspects that are different.
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Also important to understand that the systems are equal with respect to the amounts of:

- Pulp produced
- Types and amounts of energy output
- Wood used
- Chemical application rates in pulping, etc.
Modeling of processes within the system boundaries

- No modeling needed for processes that are the same in both systems
- Model for Kraft recovery system
  - Modeled using representative industry conditions
  - Based on a recent industry LCA study and WinGEMS, a widely-used mass and energy balance model for pulp and paper mills
- Model for chemical production to supply chemicals if not produced from Kraft BLS
  - public LCI databases
- Model for fossil fuel production
  - public LCI databases
- Model black liquor solids management if not recovered
  - Too much uncertainty to model
  - Instead, the analysis ignores the emissions and non-renewable energy associated with any hypothetical alternative management, resulting in an understatement of the benefits of managing the material in the Kraft recovery system
Regarding biogenic CO$_2$ emissions...

- Alternative management methods for black liquor solids would result in the biogenic carbon in black liquor solids being returned to the atmosphere.
- So the flows of biogenic carbon to the atmosphere are the same for both systems, and can be ignored.
Scenarios analyzed

• All possible combinations of the following scenarios
  – Lime kiln fueled with natural gas, fuel oil, or petroleum coke
  – Kraft system equipped/not equipped with cogeneration (CHP)
  – Fossil fuel-based electricity produced by U.S. average grid, coal, combined cycle natural gas
  – Fossil fuel-based steam produced from coal or natural gas
Results – GHG emissions
(with CHP in the Kraft system: almost universally applied)

- Emissions \( \approx 16 \) to \( 19 \) kg CO\(_2\) eq./GJ energy output
- Emissions \( \approx 150 \) to \( 210 \) kg CO\(_2\) eq./GJ energy output

Average advantage for the black liquor solids-based system with CHP
\( \approx 160 \) kg CO\(_2\) eq./GJ energy output
GHG and Non-renewable energy results

Reductions accomplished relative to a comparable fossil fuel-based system*

* The ranges reflect the variation in the results of the different scenarios examined in the study.
Scenarios include systems with CHP and systems without CHP
Results: page 1 of 2

• The GHG emissions and non-renewable energy consumption for a system using black liquor solids in the Kraft recovery system are approximately 85% lower than those for a comparable fossil fuel-based system

• Use of black liquor solids in the Kraft recovery system avoids approximately 160 kg CO$_2$ eq. per GJ of energy output from the system

• Applying these results to the production of Kraft pulp in the U.S., the avoided emissions are approximately 80 million tonnes CO$_2$ equivalents per year
  – These avoided emissions are essentially equal to the total Scope 1 + Scope 2 emissions from the U.S. pulp and paper industry (all mills)
Results: page 2 of 2

• The results are robust
  – The benefits occur without affecting the amount of wood harvested or the amount of chemical pulp produced
  – The results do not depend on the accounting method for biogenic carbon
  – The findings are valid across a range of assumptions about the displaced fossil fuel, the GHG-intensity of the grid and the fossil fuels used in the lime kiln
  – Even without CHP, 80 to 90% of the benefits are retained
Thank you

Questions?