Dissolving pulp and viscose staple fiber manufacturing
Puu-0.4110 Conventional and nonconventional pulping as a basis of biorefinery

Sirpa Välimaa Stora Enso Biomaterials
Contents

1. Dissolving pulp manufacturing
   – What is dissolving pulp
   – Market and demand
   – Textile market and viscose properties
   – Wood species
   – MWD and crystallinity
   – Pre-hydrolysis kraft process

2. Viscose staple fiber manufacturing
   – Viscose stable fiber production process
   – Controversial textile industry

3. Being an engineer in the changing forest industry
1. Dissolving pulp manufacturing
What is dissolving pulp?

- **Dissolving pulp**, also called **dissolving cellulose**, is a bleached wood pulp or cotton linters that has a high cellulose content (> 90%). It has special properties including a high level of brightness and uniform molecular-weight distribution.[1] This pulp is manufactured for uses that require a high chemical purity, and particularly low hemicellulose content, since the chemically similar hemicellulose can interfere with subsequent processes. Dissolving pulp is so named because it is not made into paper, but dissolved either in a solvent or by derivatization into a homogeneous solution, which makes it completely chemically accessible and removes any remaining fibrous structure. Once dissolved, it can be spun into textile fibers (viscose or Lyocell), or chemically reacted to produce derivatized cellulosics, such cellulose triacetate, a plastic-like material formed into fibers or films, or cellulose ethers such as methyl cellulose, used as a thickener.
Dissolving pulp is not only one grade

Dissolving Pulp Intermediate and End Products

- Raw materials
  - Softwood, hardwood, cotton linters

- Manufacturing process
  - Xanthation & regeneration
  - Acetylation
  - Etherification
  - Nitrification

- Product segment
  - Viscose
    - Viscose staple
    - Filament yarn
    - Cord
    - Industrial yarn
    - Cellophane
    - Sponge
    - Food casing
  - Acetates
    - Acetate tow
    - Acetate filament
    - Acetate mouldings
    - Acetate films
  - Ethers
    - Binders
    - Detergents
    - Glues
    - Food
    - Pharmacy
    - Oil drilling mud
  - Nitrates
    - Explosives
    - Lacquers
    - Celluloid

- Other processes
  - H$_2$SO$_4$
  - CuO$+N$
  - H$_2$OH

- Intermediate products
  - Parchment
  - Cuprammonium printing
  - Resins
    - Vulcan fiber
  - Laminating and impregnation paper
    - Filter paper
    - Speciality paper
Textile industry
Share of various fibers used for garment production

2006
- Synthetic fibers: 55%
- Wool: 2%
- Cotton: 38%
- Manmade cellulosic fibers: 6%

2012
- Synthetic fibers: 65.4%
- Wool and linen: 1.4%
- Cotton: 28%
- Manmade cellulosic fibers: 4.5%

Source: IVC 2007, RISI 2013

Figure 1
Chinese Textile Fiber Prices
US Dollars per Tonne

Source: CCFEI

Chinese dissolving wood pulp imports vs. Chinese viscose production (3 month moving average)

Million Tonnes

World Dissolving Pulp Demand

Source: Hawkins Wright, customs data
Viscose properties

- Easy to mix with other fibers
- Moisture absorption
- Touch & feel
- Drape
- Excellent reproduction of printing patterns
- Bright colors when printed
- Colors have excellent washing endurance
- Beautiful lustre
- Not electrifying
- Shrinking
- Wrinkling
Commodity dissolving pulp can be produced from many wood species.

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</tbody>
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Source: Hawkins Wright
The challenge is to preserve cellulose and remove hemicellulose, lignin and extractives.

**Wood fiber structure**

- W = warty layer
- S₂ = secondary wall inner layer (tertiary wall)
- S₂ = secondary wall middle layer
- S₁ = secondary wall outer layer
- P = primary wall
- M = middle lamella

**Chemical composition of wood fiber**

- CELLULOSE
- HEMICELLULOSES
- LIGNIN

**Fiber width ~ 30 µm**

Main variables

- **Raw material**
  - Wood pulp
    - HW
    - SW
  - Cotton linter
  - Bamboo

- **Production process**
  - Sulfite
  - Pre-hydrolysis
  - Alkaline extraction

- **Requirements per application**
  - Commodity – viscose
  - Acetate
  - Ether
  - Nitrocellulose
Crystalline and amorphous areas

- Fibre wall cellulose has high degree of crystallinity, 60-75%, due to which cellulose is relatively inert during chemical treatments.

- The chemical and thermal stability of hemicelluloses is generally lower that that of cellulose due to their lack of crystallinity and lower degree of polymerization.

- Hemicelluloses react more completely which is partly due to their location in the fibre walls.

Kuva 1. Osa selluloosan ketjumolekyyleja.


Pre-Hydrolysis Kraft Process Description

Sirpa Välimaa
The pulp production process

1. **Wood**
2. **Wood room**
3. **Cooking**
4. **Oxygen treatment**
5. **Bleaching**
6. **Drying**
7. **Pulp**

**Lime kiln**

- **Weak liquor**
- **Causticizing**
- **Green liquor**

**Bark**

- **Soda recovery plant**
- **Concentrated waste liquor**

**Evaporation plant**

**Bark boiler**

**Energy production for the process**
Pre-hydrolysis kraft process description

- Pre-hydrolysis
- Neutralization
- Hot filling
- Cooking
- Displacement
- Unbleached pulp
Pre-hydrolysis

- Pre-hydrolysis is carried out by dosing steam both from the top and from the bottom of the digester.
- The process variables are hardwood source, liquor-to-solid ratio, acidity as well as temperature and time (which are creating a P factor together). Steam pressure is constant.
- As fibres are steamed acetic acid is released from labile acetyl groups present in the hemicellulose.
- Pre-hydrolysis degrades the major part of the hemicelluloses which then become solubilized in the subsequent alkaline process steps.
- Purification selectivity (the ratio of xylan-to-hemicellulose removal) is the highest during pre-hydrolysis and neutralization.
- Reactive hydrolysis products must be immediately neutralized, extracted and displaced prior to cooking.
Neutralization

• In the neutralization
  1. the organic acids in the pulp are neutralized with white liquor by pushing it through the chip bed in the digester
  2. Oligo- and monosaccharides are subjected to extensive fragmentation reactions and solubilized in the neutralization liquor
• The process variable is the white liquor amount. White liquor consistency is constant.
• The degradation of the hydrolytically cleaved hemicelluloses which started in the pre-hydrolysis still continues during the neutralization step
• Neutralization requires a sufficient supply of effective alkali to ensure the complete extraction of the polysaccharides and to prevent re-condensation and re-precipitation of both carbohydrates and lignin compounds
• Delignification starts immediately after introduction of the neutralization liquor
  • improved permeability of the cell wall due to increased pore volume
  • Improved penetration of the cooking liquor and the partial hydrolytic cleavage of lignin structures and lignin-carbohydrate bonds
• The neutralization step is immediately succeeded by a hot liquor filling

Hot liquor filling

- The neutralization liquor is displaced with hot white liquor and hot black liquor
- Hot displacement is efficient for both delignification as well as for final purification
- The highest delignification rate is achieved in the hot displacement
Cooking

- Cooking stage controls the final delignification bringing down the kappa number (lignin content of the pulp) to the needed level.
- The process variables are temperature and time (which create an H factor together).
- Cooking has the highest delignification selectivity but it also removes low-chain hemicelluloses.
- Cooking ensures a homogeneous pulp quality due to levelled-out alkali profile.
- Cooking process is important for viscosity and brightness control.

Displacement

• The purpose of the displacement is to terminate the cooking process
• The cook is terminated by cold displacement from the bottom of the digester to the top of the digester using washing filtrate
• Cold displacement means < 90 C temperature
• Displacement time has connection to pulp quality
• The pulp is displaced into a blow tank from where it continues to knot separation – wash presses – oxygen delignification- wash press – screening – wash precipitator – brown stock tank – bleaching (D₀-EoP-D₁-P) – drying machine

Good quality dissolving pulp means…

• Guaranteeing good reactivity of the pulp by skillful processing of pulp in
  – Pre-hydrolysis
  – Neutralization
  – Cooking
• And having optimal process
  – times
  – temperatures
  – alkali (concentration, residue and dosage)
  – pH
What is reactivity and why it is important?

- Cellulose chain consists of glucose-anhydride-units which bound together with β1,4 bonds.
- The solubility of the native cellulose (cellulose I) is low as it has a dense crystalline structure and a lot of hydrogen bonds.
- Solubility and reactivity can be increased through chemical handlings – modification can be carried out in the hydroxyl-units (cellulose I > cellulose II).
- Reactivity means the ability of the dissolving pulp to participate various chemical reactions in the production process of regenerated cellulose.
- Each glucose-anhydride-units has three hydroxyl-groups in three positions; 2, 3 and 6. The most impact on reactivity has the positions 2 and 3.
- Reactivity is connected with accessibility and substitution:
  - Accessibility = the ability of cellulose to react with NaOH in the mercerization and activate the pulp
  - Substitution = how many of the hydroxyl-groups is reacting
- Reactivity is both affected by the raw material used in the process as well as the dissolving pulp production process.

2. Viscose staple fiber manufacturing
Viscose process

Description of the viscose process
- **Mercerization**
  - Cellulose is absorbed with approx. 18% NaOH to create alkali cellulose
  - After proper swelling, the excess NaOH is removed by pressing to create the wanted dry-matter content

- **Shredding**
  - The purpose of the shredding is to create more reacting surface to alkali cellulose

- **Pre-aging**
  - Alkali cellulose is reacting with air and the average molecular chain length decreases
  - For example, 45°C and 5 h; the viscosity is adjusted with temperature
  - Catalysts can be used to speed up the reaction, for example Fe, Mn, and Co compounds

- **Xanthation and dissolving**
  - Alkali cellulose reacts with CS2 and creates cellulose xanthogenate
  - Reaction time in closed reactor for example 1 h in 23°C
  - Cellulose xanthogenate is dissolved in a mixer in weak NaOH to create viscose
Ripening
- viscose is ripened in 20 C for 5 to 24 h
- in this connection the viscose is filtered from 2 to 3 times to remove the unreacted cellulosic fibers as well as other impurities

Air removal
- the air and gas bubbles in the viscose are removed in a vacuum

A typical viscose is syrup like liquid that contains 5-7% sodium and 7-10% cellulose
Spinning viscose is pumped into spinning nozzles. A common amount of holes in the nozzles is 1500-14000 pcs (sometimes even 54000 pcs). The size of the holes is 45-200 μm. The spinnerettes are in the spinning bath consisting in Na₂SO₄ (10-30%), H₂SO₄ (6-10%) and ZnSO₄ (1-4%). The temperature of the spinning bath is 40-60 C. Typical VSF spinning machine can have 150-400 nozzles and spinning speed of 40 to 80 m/min.
Stretching the fibers after spinning to create strength

First washing before leading the continuous fiber into cutter

Finishing of fibers after cutting (fibers forming a mat on a wire):
- washing with water and NaOH solution to remove the carbon
- some hypochlorite bleach the fibers but brightness mainly from pulp fibers
- acidification with acetic acid to neutralize the fibers
- surface friction decreasing
- drying, opening up and baling of fibers
Chemistry of creating viscose fibers from dissolving pulp

\[
\text{Dissolving pulp} \xrightarrow{\text{NaOH}} \text{Mercerization} \xrightarrow{\text{O}_2 (\text{Co})} \text{Pre-ripening} \xrightarrow{\text{Xanthation}} \text{CS}_2 \xrightarrow{\text{Dissolving}} \text{Viscose fibers}
\]
Few puzzles to be solved in the textile industry…

- Recovery of the chemicals from the viscose process
- Production conditions
- Occupational health and safety
- Alternative processes to CS₂
- Fashion industry and brand owners
- Fast fashion
- Consumer readiness to pay from sustainable fashion
What is sustainable fashion?

- Polyester vs. viscose
- Cotton vs. viscose
- R-PET
- High quality material vs. fast fashion
- Domestic vs. exported
- Recycling of clothes
- Sewing and having the clothes sewed

IT IS YOUR LEGACY!
3. Being an engineer in the changing forest industry
CONGRATULATIONS TO WINNERS OF STORA ENSO AWARDS!

06 May 2015 18:00 GMT
News Group

Awards winners, nominees and the Awards Committee on stage with the CEO.

The winners of the 2015 Stora Enso Awards were announced in Helsinki on 6 May. Cheering and applause filled the room when all nominees were presented, and the winners were celebrated by everyone.

The Awards have been nominated and selected by us employees. Nominations were submitted from all over Stora Enso. The nominations were then shortlisted by an Awards Committee to three per category, and employees were able to vote their favourites among these final nominations. Winners were selected based on the number of votes they received.

"The Awards are important because we need to recognise achievements, and people like to be recognised for good things", said CEO Kalle Sundström in the Awards ceremony.

"This has truly been a fantastic year for the Awards. We have seen over 120 nominations. All of the final nominees received several hundred votes in the final voting", said Per Lyrvall, who chaired the Awards Committee.

Rethink Award
Sirpa Välimaa – for her proactive desire and passion to find new ways to add real value for Stora Enso
Love your job and it loves you back!

- Grab the opportunities
- Be the game changer
- Multitasking
- Ability to work in global organization – language and cultural learning
- Project leading skills
- Do not be afraid to learn new – challenge yourself
- Ability to make decisions with insufficient information
- Bringing new products to market is not easy – not inside your company nor the actual sales work and convincing customers
- Lead and keep up the spirit
- Ability to convince others if you know the way
Finland’s Future - scientific TV series on MTV3 starting on January 2016

- Stay tuned for many opportunities for wood to help to solve the challenges caused by the world megatrends
- Pilot episode available in

http://suomentulevaisuus.com/#esittely
Meet me in Design Factory on Friday 4th Dec 9:00-13:00 at Stora Enso stand to discuss more!

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Rethink. Everything.