## White liquor composition and calculations

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Concentration [g/l]</th>
<th>as NaOH</th>
<th>as compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>90.0</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>Na₂S</td>
<td>40.0</td>
<td>39.0</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>19.8</td>
<td>26.2</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>4.5</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td>Na₂S₂O₃</td>
<td>2.0</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₃</td>
<td>0.6</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Other compounds</td>
<td></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Total alkali (TA)</td>
<td>156.9</td>
<td>170.6</td>
<td></td>
</tr>
<tr>
<td>Total Sulfur (TS)</td>
<td>47.1</td>
<td>19.7</td>
<td></td>
</tr>
<tr>
<td>Effective alkali (EA)</td>
<td>110.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Active alkali (AA)</td>
<td>130.0</td>
<td></td>
<td></td>
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</tbody>
</table>

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Puu-0.4110: Conventional and Non-Conventional Pulping as a Basis for Biorefinery (7 cr)

Lecture 7:
Biomass fractionation. Part 3.
Batch and continuous digesters.
After this lecture the student

• is familiar with the concepts *batch digester* and *continuous digester* and can describe the technical principles, as well as the advantages and disadvantages, of each (e.g. in the case of kraft pulping)

• can describe what is meant with *modified cooking* concepts
Kraft cooking was invented 135 years ago!

- The main chemical cooking methods were invented between 1850–1900
  - 1850 Soda cooking (England, USA)
  - 1865 Sulfite cooking
  - 1879 Sulfate (kraft) cooking (Germany)
- Until 1950’s all cooking processes utilized batch digesters
  - Rotating spherical digesters
  - Conical bottom vertical digesters
At the beginning...and still today...used in small production pulp mills: Rotating spherical digesters

- Diameters 2–4 m allowed pulp amounts of 0.2–2 tons/batch
- Rotation for better contact between cooking liquid and chips
Papelera Mercedes (PAMER), Uruguay
Capacity 30 tons pulp/d
- Batch digesters can be heated either by direct steam or circulation equipped with a heat exchanger
- Having external circulation improved the uniformity of cooking considerably compared to rotating or direct steam heated digesters
Process steps of conventional batch cooking
Cooking conditions in conventional batch cooking
Typical features of conventional batch cooking

- Hot digester discharge ("hot blow") is mechanically very aggressive to fibers: major strength loss (30–35% measured as tear index at constant tensile)
- Although external circulation is performed, the uniformity of cooking is not acceptable (too much reject)
- Heat economy is bad (steam demand 4–5 GJ/ton pulp is 2–3 times that of continuous cooking)
Development of continuous digesters

• The development of continuous digesters was carried out in the 1940’s by the Norwegian-Swedish company Kamyr
• The first commercial Kamyr digester was started in 1952
• Since then, several steps of development have taken place…
Evolution of continuous digesters

- Joutseno -52
  - 100 ADt/day
  - 100 m³
  - Dia 2.500

- SW ca. 1000 ADt/day
  - 21 m

- SW 2140 ADt/day 3060 m³

- Euca 3000 ADt/day 3300 m³

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7. Fractionation: Part 3 – Batch and continuous digesters

Adopted from Kari Kovasin, 2008
The main driving forces for the further development of continuous digesters

- Hot digester discharge was very aggressive to fibers; the pulp quality was inferior to batch cooked pulp
  - Dilution of the bottom of the digester by wash filtrate (cooling effect)
  - Washing in counter-current before the cooling and digester discharge (“Hi-heat” washing)
  - Very long washing times made it necessary to carry out the impregnation stage in a separate vessel
Modern continuous digester
Process steps of conventional kraft cooking

Continuous cooking
- Chip steaming
- Feeding the chips into digester
- Impregnation of chips with cooking liquor
- Heating to cooking temperature
- Cooking phase
- Washing of chips in the digester
- Digester discharge

Batch cooking
- Feeding the chips into digester
- Chip steaming

• Conventional cooking means that the entire amount of the cooking liquor is charged at the beginning of the cooking cycle
• No profiling of chemical concentrations during the cook
Development of modern cooking technologies

• Modifying the chemistry
  – From conventional cooking to modified cooking
  – Cooking additives
  – Several commercial cooking processes and new trade / brand names

• Coping with the increasing production rate is a challenge for the digester design
Modified cooking – Why to do it?

• Lower steam consumption
• Environmental reasons
  → extended cooking to lower lignin content
  → lower bleaching chemical consumption
• Pulp quality
• Efficient use of alkali
• Often essential due to higher production rates
Important steps of development in modern cooking technology took place at the beginning of 1980’s

- Hartler and Teder (Sweden) introduced the ”four rules of cooking modification”
  - modified continuous cooking (MCC of Kamy AB)
- Displacement batch cooking was developed:
  - The main driving force was improved heat economy
  - Also features of the modified cooking chemistry
  - First commercial process was the RDH-process of Rader (Rapid Displacement Heating)
Cooking modification "rules"

1. Alkali concentration must be leveled out
   – Decreased in the beginning
   – Increased at the end

2. The concentration of hydrogen sulfide ions should be as high as possible
   – Especially at the beginning of the bulk delignification phase

3. The concentration of dissolved lignin and sodium ions in the liquor should be as low as possible
   – Especially in the final cooking phase

4. Temperature should be low
   – Especially at the beginning and at the end of the cook
Modified Continuous Cooking
Continuous flows in continuous cooking

- Inlet and outlet streams steady
  - Chip feed
  - Liquor feed
  - Pulp discharge
  - Black liquor extraction
- Chip flow downward
- Liquor flow co-current or countercurrent (e.g. Hi-Heat washing zone)
Conventional Continuous Cooking
One-vessel digester (hydraulic)
The effect of alkali profiling ("Rule 1")

- First trials of Continuous Cooking Modification 1983 at Varkaus mill
- White liquor was added at three points in the digester
  - Impregnation
  - Transfer circulation
  - Countercurrent cooking
- A recirculation line for liquor around impregnation vessel was installed
- The final stage of the cook was carried out in countercurrent mode
The effect of black liquor HS⁻ ("Rule 2")

- A high HS⁻ ion concentration in the early stage of cooking has turned effective particularly in cooking of softwood (faster cooking, better fiber quality)
- Practical implementation to increase HS⁻ ion concentration at the beginning of cooking → black liquor re-circulation
The effect of dissolved solids ("Rule 3")

- Flow-through type laboratory pulping simulations have shown:
  - High dissolved solids have a detrimental impact on pulp strength and on bleaching response
  - Dissolved wood solids consume alkali in secondary reactions during pulping especially during initial part of bulk delignification
Continuous cooking processes

Ahlstrom/Kamy AB splits at the beginning of 1990’s

Kamy AB splits at the beginning of 1990’s

Kvaerner Pulping -> Metso Paper (currently)

Conventional Continuous Cooking -> MCC

EMCC -> Lo-Solids -> Lo-Solids EAPC -> Downflow Lo-Solids

ITC -> BLI -> Concurrent Compact Cooking

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Lo-Solids™ cooking (Andritz)
Compact cooking (Kvaerner)
Alkali profiles of continuous cooking

![Graph showing alkali profiles with time (min) on the x-axis and EA (g/l) on the y-axis. The graph includes lines for Impregnation, Cooking 1, Cooking 2, Hi-Heat, Extraction MCC, Transfer circulation, and Extraction conventional. The graph also shows different cooking methods: Conv., MCC, and EMCC/ITC.](image-url)
Alkali profiles of continuous cooking

- Conv.
- Lo-Solids

EA (g/l)

0 30 60 90 120 150 180 210 240 270 300 330

Time (min)

0 30 60 90 120 150 180 210 240 270 300 330
From countercurrent to downflow cooking

- Problems of countercurrent stages:
  - Non-uniformity of flows and temperature
  - Unstable runnability

- Benefits of concurrent / downflow cooking:
  - Smoother movement of the chip column
  - Increased total capacity of the digester
Development of continuous cooking flow direction

Lo-Solids

110°C

150°C

150°C

150°C

Downflow Lo-Solids

110°C

150°C

150°C

150°C
Downflow Lo-Solids® Cooking, two-vessel system
Liquor travels from the screens, through the circulation pump, heat exchanger, to the centerpipe where it travels radially through the chip mass, heating the chips as it passes through them, returning to the screens to be recirculated. (source: www.metso.com)
Summary of continuous cooking

- Continuous cooking is the leading cooking technology today
- The latest major installations for cooking eucalyptus and/or acacia in South America and Asia are based on continuous digesters
- Introducing the Four Rules of modified cooking chemistry has brought a sequence of new continuous cooking technologies
Batch cooking modifications
Features of batch cooking

- “Primitive but effective”
- Easy to maintain
- Production is very safe:
  - easy to take one digester out at a time for maintenance
Features of batch cooking

- Digester house is an assembly of individually loaded digesters
  - 4 minimum to maintain reasonable sequencing and steam loading
  - 6 - 8 maximum to use same header pipe lines
  - Several lines can use same tank farm
- Less sensitive to chip quality (than continuous cooking)
- Possibility to produce different grades of pulp in the same cooking plant
Modern batch cooking processes

- Based on liquor displacement technology
- Pressurized liquor accumulators
- Improved heat economy
- Low temperature impregnation possible
- Liquor concentration profiling during impregnation and cooking
- Gentle pump discharge
- So far, the highest measured pulp strength delivery with softwood… pulp equals laboratory made pulp
Batch digester house

Kraft pulping (Super Batch)

Batch cooking plant with four digesters

- Impregnation liquor tank
- Displacement liquor tank
- Chips
- Discharge tank

- Black liquor tank
- HWL tank
- HBL tank 1
- HBL tank 2

(HWL=hot white liquor
HBL=hot black liquor)

KnowPulp 7.0, 2008
SuperBatch digester 400 m$^3$

- Chip feed screw
- Direct steam
- Circulation screens

Kyösti Ruuttunen
The main cooking modification rules in displacement cooking (SuperBatch)

1. Alkali concentration must be leveled out
   - Very low $\text{HO}^-$ at the beginning
   - High residual EA at the residual phase, back-end of cooking

2. The concentration of hydrogen sulfide ions should be as high as possible
   - Very much $\text{HS}^-$ at the beginning of bulk delignification phase
Displacement Batch Processes
RDH and SB: Black liquor started displacement batch
WLI: White liquor started displacement batch

Conventional Batch Cooking
- RDH
- SuperBatch
- EKONO
- WLI
- EnerBatch

SuperBatch-K

CBC

Continuous Batch

Lenzing Technology
SuperBatch cooking process

- Pump Discharge
- SuperBatch Displacement Technology
- Chip Fill and Impregnation
- Hot Liquor Fill
- Displacement
- Heating and Cooking
SuperBatch references

- Wisaforest 1320
- Metsä-Botnia 1700
- Kernjärvi 700
- Frövi 650
- Stendal 1850
- Steti 560
- Valdivia 2390
- Enocell 1770
- Kaukas 2070
- Phoenix 370
- Advance Agro 560
- Riau 1 + Riau 2 2680 + 3300

SuperBatch references

- SW mills
- SW/HW mills
- HW mills
- Campaign mills

Design Capacity

Mill ADT/d
Summary of modern batch cooking processes

- Main references from softwood cooking from the 90’s (better pulp quality; nowadays no major difference with continuous cooking)
- Varying and ”bad” quality chips can be processed
- Not competitive in very large installations (complicated, need of very good control systems)
Additional material
Digesters for other raw material, such as cereal straws, annual grasses and bagasse
Flow diagram for wheat straw pulping using the Pandia continuous digester system

Source: Kocurek 1983
Pandia continuous digester system

- Main references at pulp mills utilizing non wood fibers, such as bagasse and cereal straw
- Installed in over 200 pulp mills
PANDIA digester systems
AGRO’s Continuous Digester CD-600