NITROGEN IN WOOD AND ITS FATE AT KRAFT PULP MILLS

Klaus Niemelä, VTT Technical Research Centre of Finland Ltd

55th Anniversary International
Recovery Boiler Conference

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ABSTRACT

The first findings on the behaviour of wood-derived nitrogen in alkaline pulping of wood were made as early as in the 1870s. A few decades later, the first quantitative determinations on the formation of ammonia during kraft pulping were published. Despite its low overall yield, some ammonia could even be recovered as a valuable by-product in small-scale industrial operations for a short period in the 1910s.

After the invention of the Haber-Bosch method for the manufacture of ammonia (1909) and construction of the first industrial plant (1913) using that method, it became fully evident that wood cannot compete with the air as an economic source of nitrogen for the manufacture of ammonia. Therefore, the behaviour of wood nitrogen in the pulp mill processes attracted only marginal interest during the next 60–70 years.

The behaviour of wood-derived nitrogen and its different forms in different pulp mill operations became a topic of wider interest in the late 1980s and early 1990s when more detailed investigations on the NOx formation mechanisms in the recovery boilers were commenced. During the past decades it has been clearly established that practically taken all the recovery boiler NOx emissions are derived from the black liquor nitrogen. This nitrogen is, in turn, derived from the applied pulping raw materials where the nitrogen content is typically c. 0.05–0.2%.

This presentation will provide an overview of the nature of the typical nitrogen materials in wood and their reactions in the fibreline and recovery processes of kraft pulp mills, with some focus on the formation of various types of nitrogen compounds in pulping and their distribution into different process streams. The addressed topics will also include the nitrogen differences between hardwood and softwood species and needs for further studies, especially on the formation and control of black liquor nitrogen for the reduction of the NOx emissions.

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Nitrogen in wood and its fate at kraft pulp mills

Klaus Niemelä

June 6, 2019 55th Anniversary International Recovery Boiler Conference

Nitrogen in wood and its fate at kraft pulp mills – before the recovery boilers

- What is the content and nature of wood nitrogen?
- How does wood nitrogen react in pulping?
- How are the nitrogen compounds distributed into different streams?
- How could the amount or nature of nitrogen be controlled, before the recovery boilers?
- Any softwood – hardwood differences?

Proteins Nitrogen Evaporation Ammonia Amino acids Methanol Lignin Black liquor History Pulping By-products Condensates

Nitrogen in the Nature and pulping: a few historical notes

- 1766: Hydrogen as an element (Cavendish)
- 1772: Nitrogen as an element (Rutherford)
- 1785: Elemental composition of ammonia (Berthollet)
- 1838: Proteins named
- 1806–1935: Essential amino acids (20) found
- 1861–1883: The first studies on nitrogen in wood published

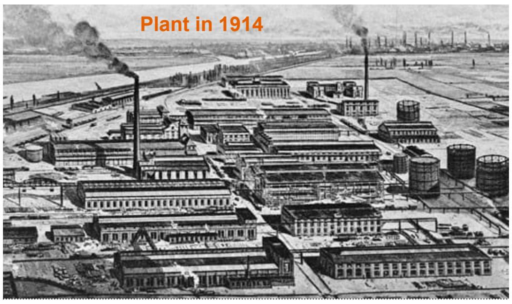
- 1840: Soda (NaOH) pulping for pine needles
- 1860s–1870s: Soda and kraft pulping for wood
- 1875: the first signs of ammonia formation in pulping
- 1876: the first organic nitrogen compound from pulping
- 1908: ammonia formation in pulping fully confirmed
- 1910s–1920s: ammonia recovered as a pulping by-product
- 1990s: the next organic nitrogen compounds from pulping
- 1990s–: detailed studies on nitrogen chemistry in black liquor combustion and white liquor preparation

The first ammonia plant (Oppau 1913)

Fritz Haber

1868–1934

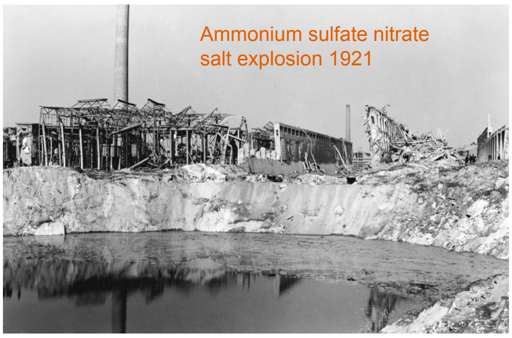
Nobel Prize 1918



Carl Bosch

1874–1940

Nobel Prize 1931



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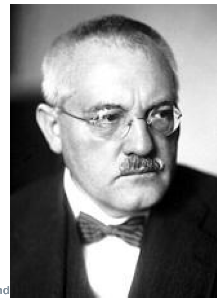
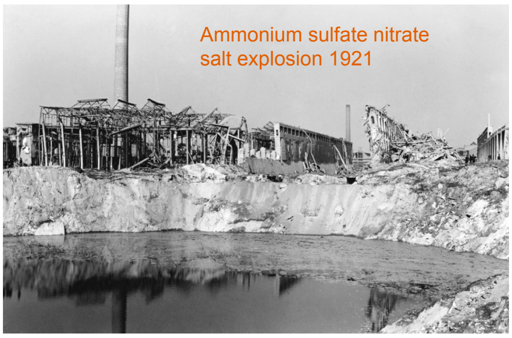
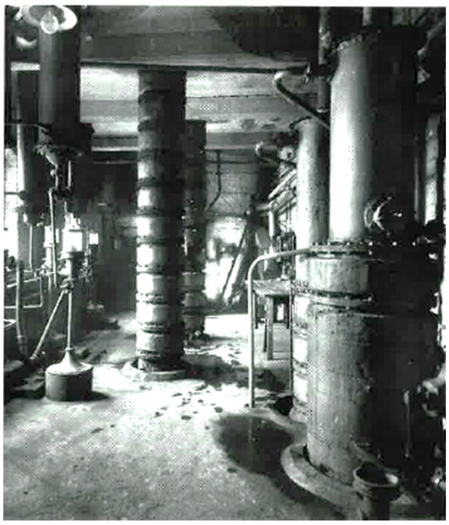




Ammonium sulfate nitrate salt explosion 1921

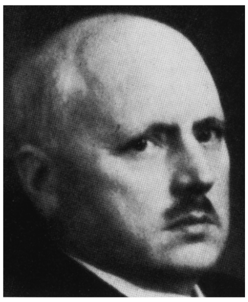
Ammonia as a pulping by-product

- Recovered as ammonium sulphate at Gutzeit pulp mill in Kotka, Finland, in 1916-1923.
- The process was developed by Alfons Hellström, the inventor of tall oil distillation process.
- The top production figure was 8180 kg, achieved in 1917.



Alfons Hellström

1877–1965



Nitrogen content of wood – overview

- Typical values vary from 0.05 to 0.2% (in bark from c. 0.2 to 1%)
- The first results on that level were published in 1883.
- The contents >0.3-0.4% are scarce (e.g. for some tropical trees).
- Data has been published dozens of different tree species.

- Review by Meerts (2002) addresses 47 hardwood and 9 softwood species, averages given below (%).

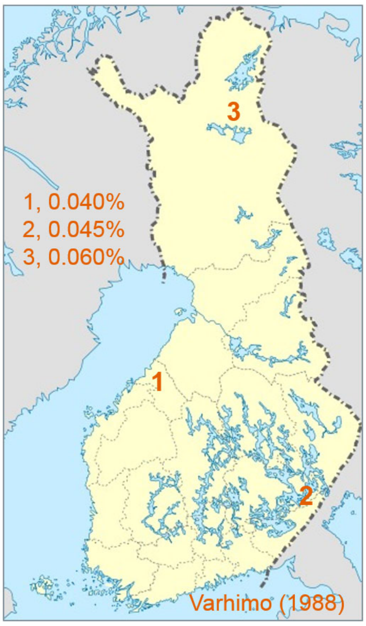
Tree type (n)	Heartwood	Sapwood
Angiosperms (47)	0.117 ± 0.050	0.174 ± 0.078
Gymnosperms (9)	0.080 ± 0.050	0.103 ± 0.042

Nitrogen contents & data variation

For a given tree species, varying data for the published nitrogen contents can typically be found, caused by (for example):

- different analytical methods
- sampling methods and tree parts
- age of the trees
- growth location (soil type, climate…)
  - example for Scots pine in Finland shown left
- use of fertilisation
- other factors
  - different stems form the same location may show different nitrogen contents

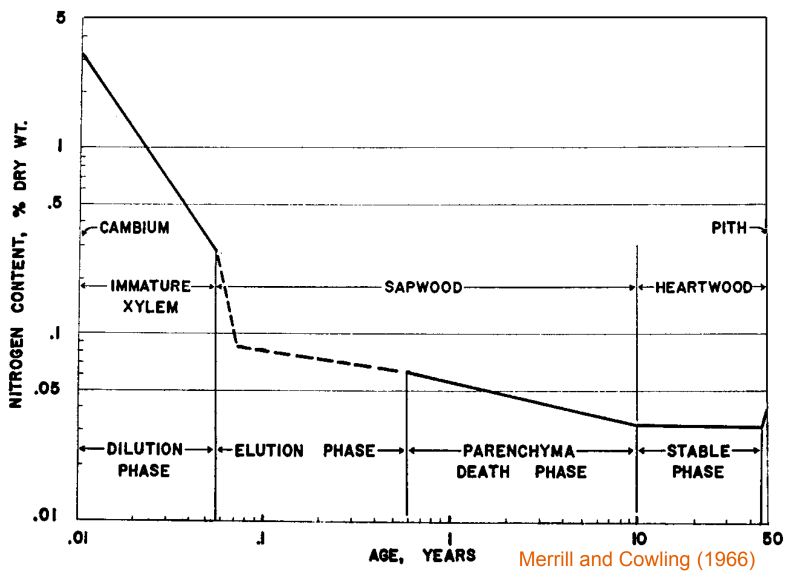
This type of factors hamper overall conclusions based on literature data from different sources.



Nitrogen in Scots pine – published data

Nordic studies		
Content (%)	Topic addressed, comments	Reference
0,07-0,13	Stemwood samples with bark, several Norwegian sites	Gislerud & Tveite 1973
0,05	Softwood chips from a Swedish mill	Magnusson et al. 1979, 1980
0,04	Effect of fertilisation on peatland	Paavilainen 1980
0,04-0,06	Pulp wood composition, samples from five regions	Varhimo 1988
c. 0,05-0,1	Distribution of nutrients in different tree parts	Siltala 1988
c. 0,05-0,1	English paper based on Siltala's M.Sc. thesis	Helmisaari and Siltala 1989
0,06-0,07	Effect on fertilisation on two Finnish regions	Finér 1989
0,05-0,08	Samples from five different Finnish regions	Häsänen & Huttunen 1989
0,04-0,08	N distribution in several Swedish planks, effect of drying	Boutelje 1990
0,04-0,19	Extension of Boutelje's (1990) work with planks	Theander et al. 1993
0,06	Fate of N in wood drying	Terziev 1995
0,05-0,08	Samples from three Swedish pulp mills	Hedenberg 1996
0,09-0,11	Samples from three Swedish locations	Terziev et al. 1997
0,05	Fate of nitrogen at pulp mills	Telkkinen 1996, 1999
0,07	Heating values of mature trees	Nurmi 1997
0,12-0,24	Swedish Ecocylic pulp mill project (1990s)	Anon. 1999
0,04	Fate of nitrogen in pulping	Niemelä & Ulmgren 2002
0,11	Softwood chips from a Swedish mill	Niemelä et al. 2003
c. 0,05	N content in stump wood (change during decay)	Palvianen et al. 2010

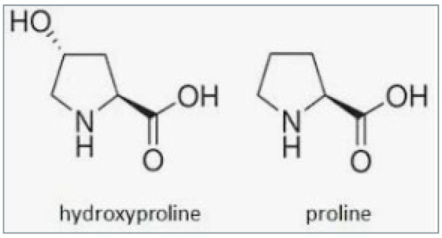
Indicative nitrogen distribution across the stem



Merrill and Cowling (1966)

Nitrogen in wood: proteins and amino acids

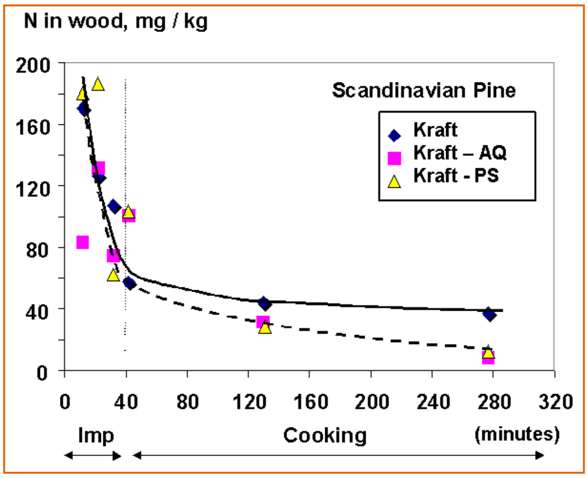
- Typical amount in wood c. 0.3 to 1.5% (as 0.05-0.2% N).
- The share of free amino acids varies for many reasons
- More detailed data available for hardwood than softwood proteins
- Important proteins include proline- and hydroxyproline-rich cell wall proteins (important structural roles)
- Several hundred different proteins known to exist
- Evidence is available on the covalent links between proteins and lignin
- Amino acid composition for many trees and several proteins have been reported



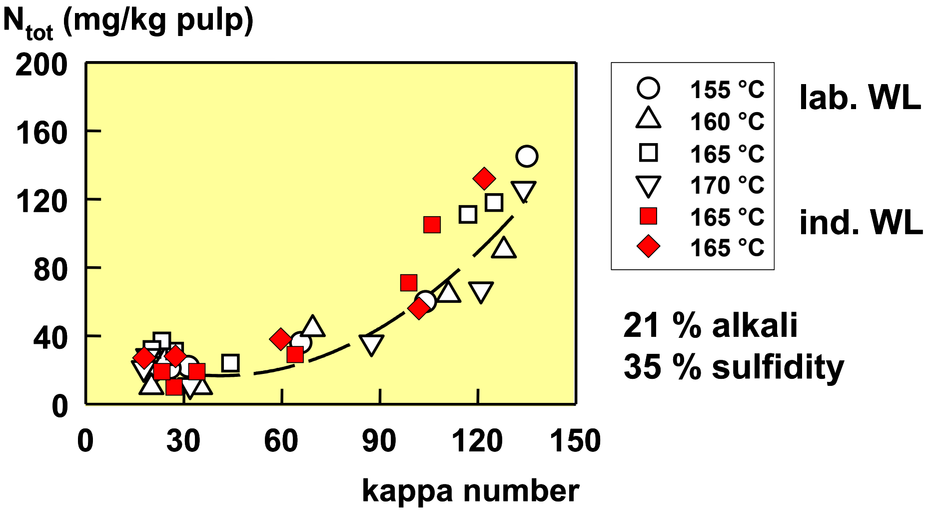
Behaviour of wood nitrogen in pulping

- Up to 95% of nitrogen is dissolved in black liquor, mainly in the early pulping stage.
- Veverka et al. (1993) reported 70-90% releases.
- The different pulping conditions have only minor (if any) effects.

Lab scale pulping of pine wood at 165 °C



Effect of pulping conditions on the nitrogen removal from pine



The formation of ammonia in pulping

Lab scale pulping experiments, nitrogen in weak black liquor

Raw material	Kappa number	Total N, mg/L	Ammon. N, mg/L	Ammon. N, %
Birch	100	49.6	6.8	13.7
Birch	15	159.7	21.7	13.6
Eucalyptus	81	66.3	8.1	12.2
Eucalyptus	13	100.5	12.3	12.2
Pine	134	96	7.5	7.8
Pine	88	170	13	7.6
Pine	18	180	16	8.9

Lab scale pulping of the pine wood, nitrogen in weak black liquor

Compound (fraction)	Kappa 134	Kappa 88	Kappa 18
Total N, mg/L	96	170	180
Ammonium N, mg/L	7.5	13	16
Lignin, g/L	11.1	40.9	62
Nitrogen in lignin, %	0.26	0.058	0.045
Nitrogen in lignin, mg/L	29	24	28

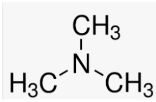
Organic compounds from proteins and amino acids during pulping

- Proteins are degraded (to an unknown extent) to lower fragments and simple amino acids.
- Limited information is available on these reactions under pulping conditions.
- The amino acids may be further composed to more simple amino acids and different cyclic and acyclic compounds.
- Some of these compounds can also be found in condensates, turpentine, and rectified methanol (limited data available).

Examples:

- Trimethylamine found in black liquor 1876 (Knösel). It was recognised by odour in spruce soda black liquor 1893 (Klason).
- The next organic compounds in black liquor were found 1990 (Niemelä), including pyrroles and pyridines.

Trimethylamine



Amino acids in black liquor (tentative)

Amino acids (mg/l) in two pine kraft black liquors.

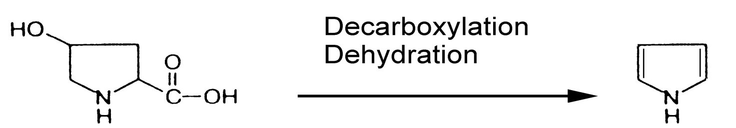
Amino acid	BL I	BL II
Aspartic acid	5.6	0.9
Glutamic acid	12.4	13.4
Serine	0.6	0.5
Glycine	13.7	6.9
Arginine	21.9	16.6
Alanine	9	6
Tyrosine	6.4	4.6
Cystine	51.5	10.4
Valine	4.7	2.2
Methionine	6.8	6.8
Isoleucine	2.4	1.1
Leucine	9.8	9.4
Total (mg/l)	135.8	78.8

Extent of ammonia formation from selected amino acids

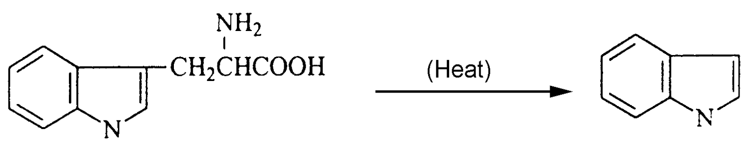
Percent of ammonia (of total nitrogen) after alkali treatment of selected amino acids at 170 °C

Glycine	$CH_2(NH_2)COOH$	1.2
Valine	$(CH_3)_2CHCH(NH_2)COOH$	1.6
Lysine	$H_2NCH_2(CH_2)_3CH(NH_2)COOH$	1.5
Serine	$HOCH_2CH(NH_2)COOH$	22.0
Aspartic acid	$HOOCCH_2CH(NH_2)COOH$	7.4

Cyclic compounds from amino acids



Hydroxyproline Pyrrole



Tryptophane Indole

Indicative nitrogen balance from lab scale pulping studies

▪ Ammonia	10-15%
▪ Amino acids	10-15%
▪ Cyclic compounds	2-5%
▪ Lignin-bound*	15-20%**
▪ Other (proteins?)	40-50%

*The nature of the nitrogen groups is unknown.
**Typical N content of kraft lignins is 0.05-0.1%.

Nitrogen contents in industrial softwood and hardwood kraft black liquors

- Lab scale studies suggested the liberation of more nitrogen from softwood than hardwood pulping.
- These figures are not fully in line with the average data collected by Labtium Eurofins (FI) during the past few years (courtesy of Jorma Tornianen).

Black liquor origin	N (%), average	N (%), range
Pine/spruce (n = 10)	0.075	0.066–0.095
Birch (n = 10)	0.096	0.085–0.106

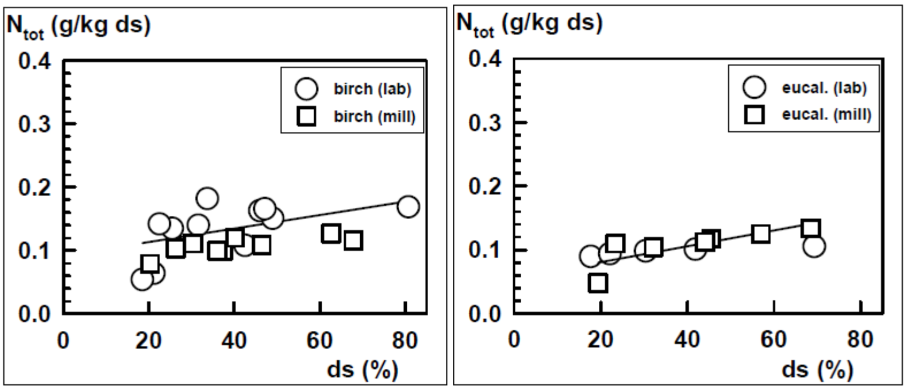
Method developed for black liquor nitrogen: K. Niemelä and M. Tuominen, Determination of total nitrogen content in kraft black liquors, 13th International Symposium on Wood, Fibre, and Pulping Chemistry, Auckland, New Zealand, May 16–19, 2005, 341–344.

Nitrogen in softwood turpentine

- The ammonia smell was known to the pioneering mill staff recovering soda turpentine as early as 1875 in Germany.
- The modern studies are very limited.
- Total nitrogen contents found: 60-160 mg/L
- Ammonia nitrogen found: 5-15 mg/L
- Main organic nitrogen compounds include pyrroles and other cyclic compounds

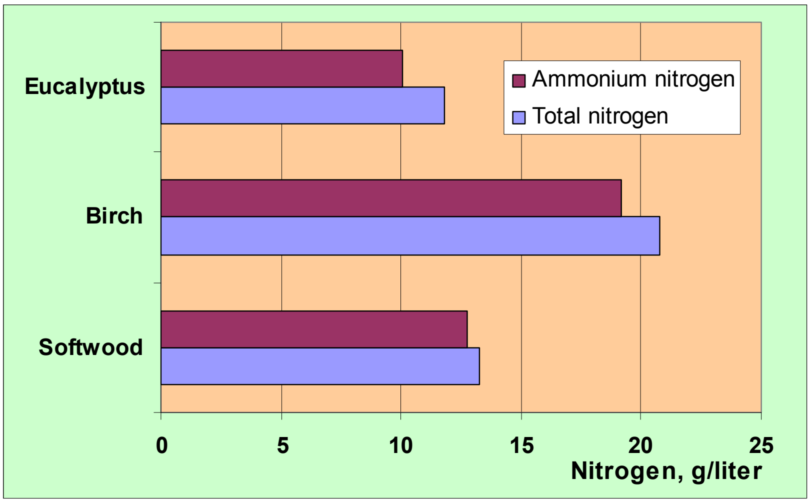
Nitrogen release during black liquor evaporation

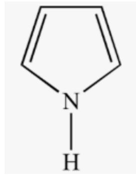
- The lab scale experiments have confirmed that most of nitrogen is released before 30% d.s. contents.
- The main nitrogen compound is ammonia.
- The organic compounds include pyrrole and other amino acid degradation products



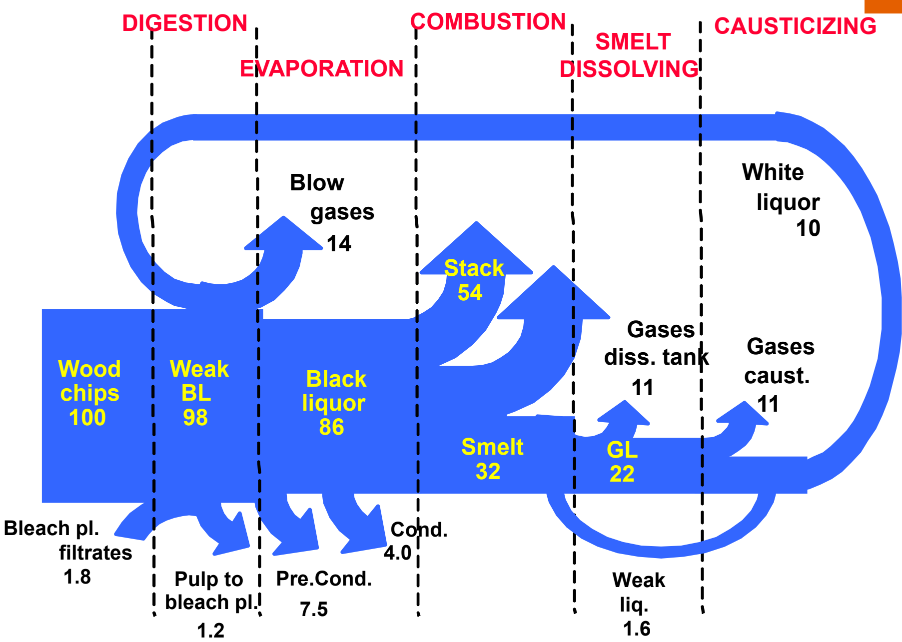
Nitrogen in rectified methanol

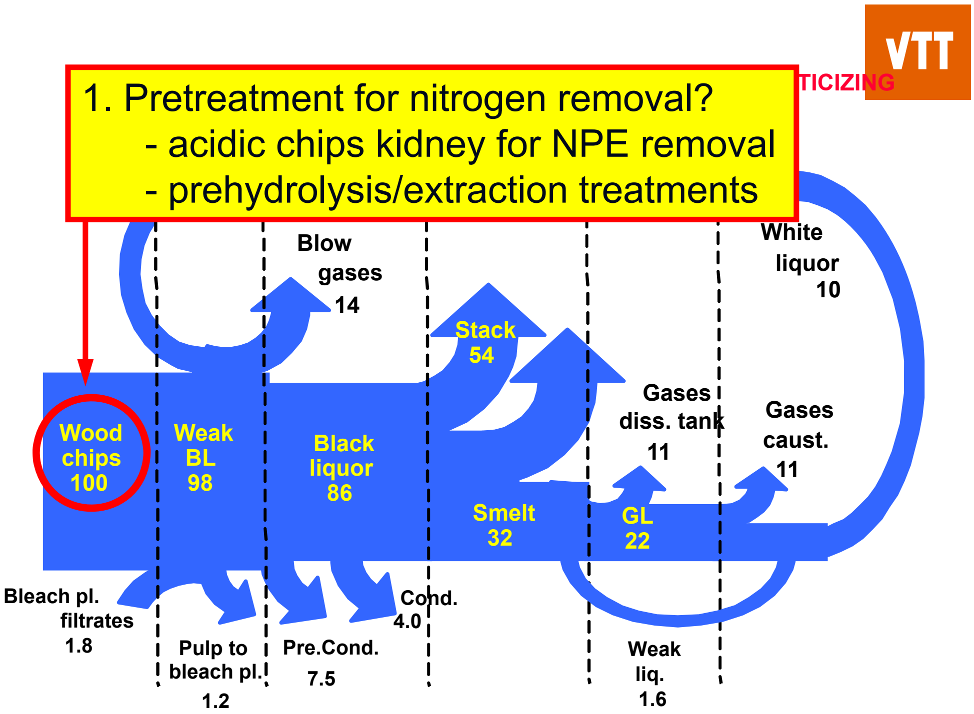
- The main organic nitrogen compound is pyrrole
- Novel amine-type compounds have been tentatively identified

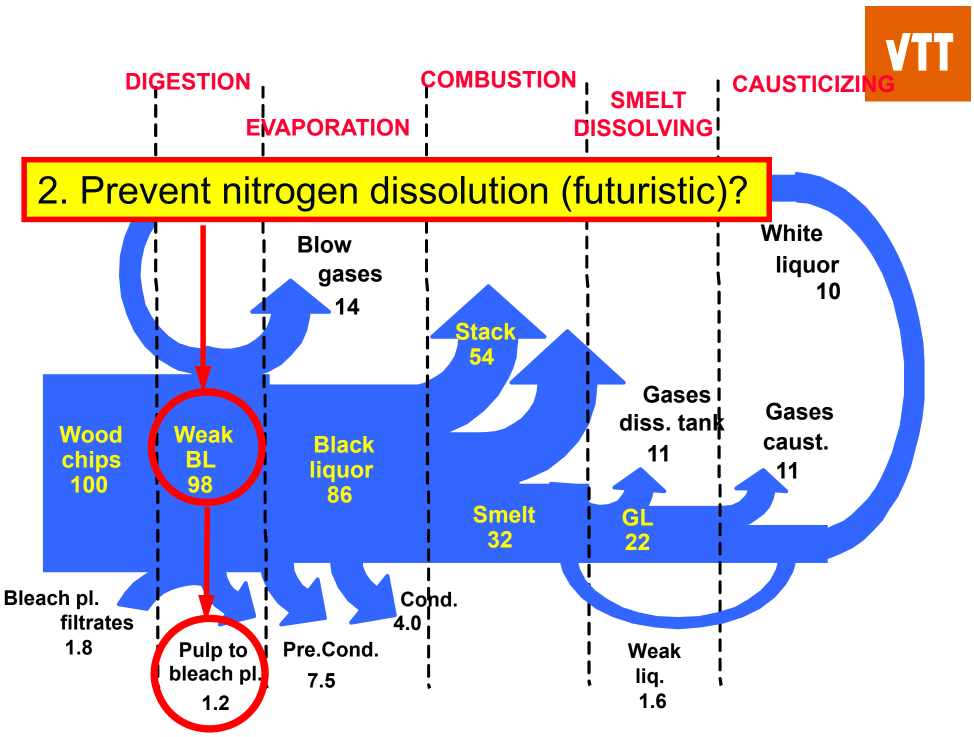


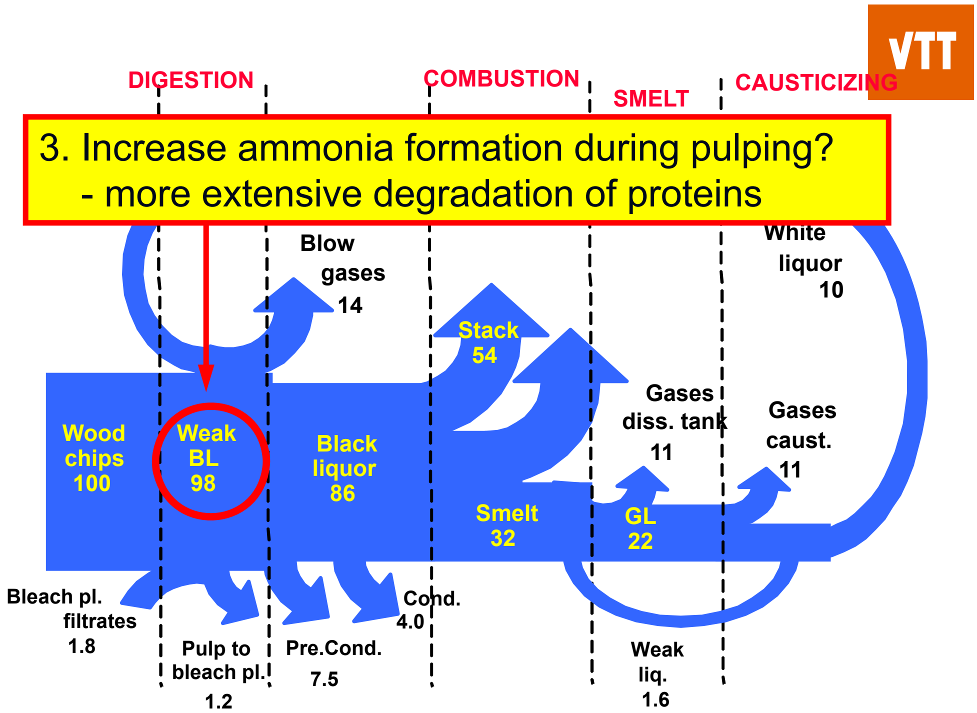


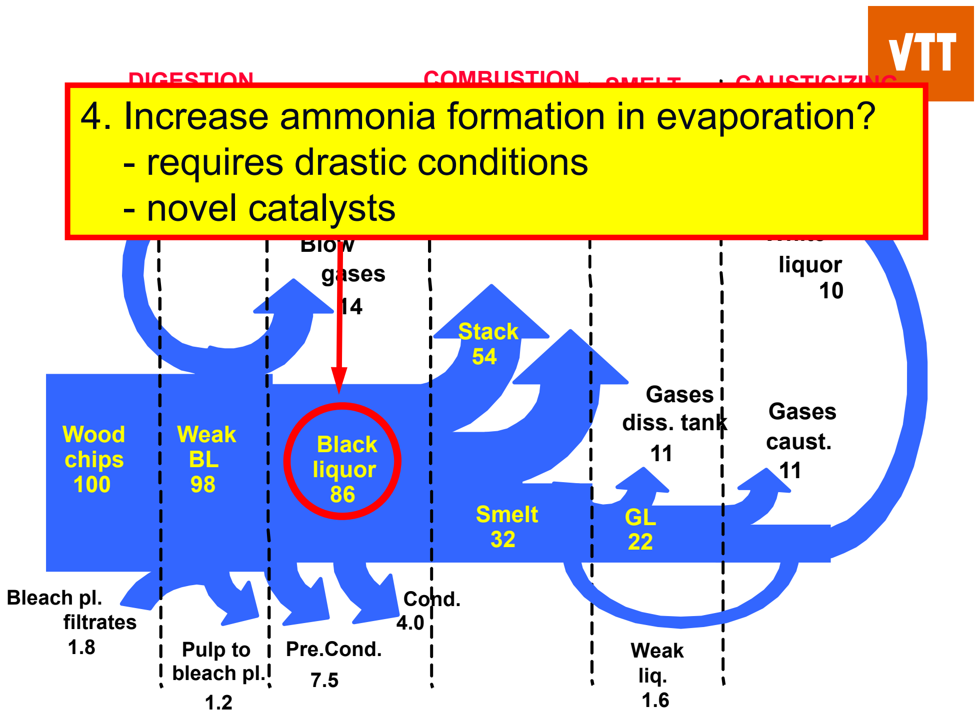
Example of nitrogen balance




1. Pretreatment for nitrogen removal?
- acidic chips kidney for NPE removal
- prehydrolysis/extraction treatments
TICIZING
Wood chips 100
Weak BL 98
Black liquor 86
Blow gases 14
Stack 54
Smelt 32
GL 22
Gases diss. tank 11
Gases caust. 11
White liquor 10
Bleach pl. filtrates 1.8
Pulp to bleach pl. 1.2
Pre.Cond. 7.5
Cond. 4.0
Weak liq. 1.6

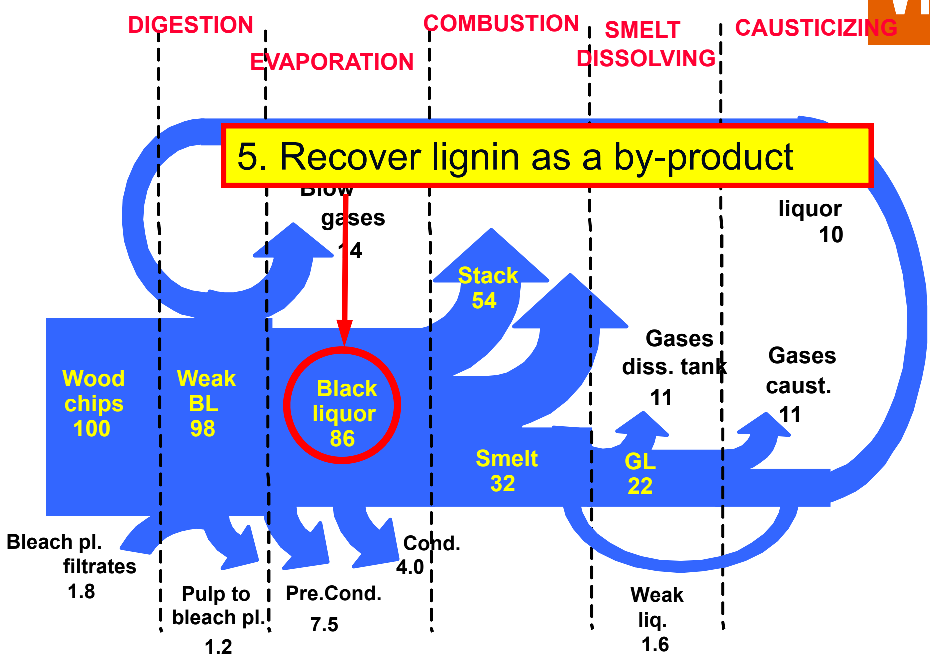

DIGESTION
EVAPORATION
COMBUSTION
SMELT DISSOLVING
CAUSTICIZING
2. Prevent nitrogen dissolution (futuristic)?
Wood chips 100
Weak BL 98
Black liquor 86
Blow gases 14
Stack 54
Smelt 32
GL 22
Gases diss. tank 11
Gases caust. 11
White liquor 10
Bleach pl. filtrates 1.8
Pulp to bleach pl. 1.2
Pre.Cond. 7.5
Cond. 4.0
Weak liq. 1.6


VTT
DIGESTION
COMBUSTION
SMELT
CAUSTICIZING
3. Increase ammonia formation during pulping?
- more extensive degradation of proteins
Blow gases 14
White liquor 10
Stack 54
Gases diss. tank 11
Gases caust. 11
Wood chips 100
Weak BL 98
Black liquor 86
Smelt 32
GL 22
Bleach pl. filtrates 1.8
Pulp to bleach pl. 1.2
Pre.Cond. 7.5
Cond. 4.0
Weak liq. 1.6

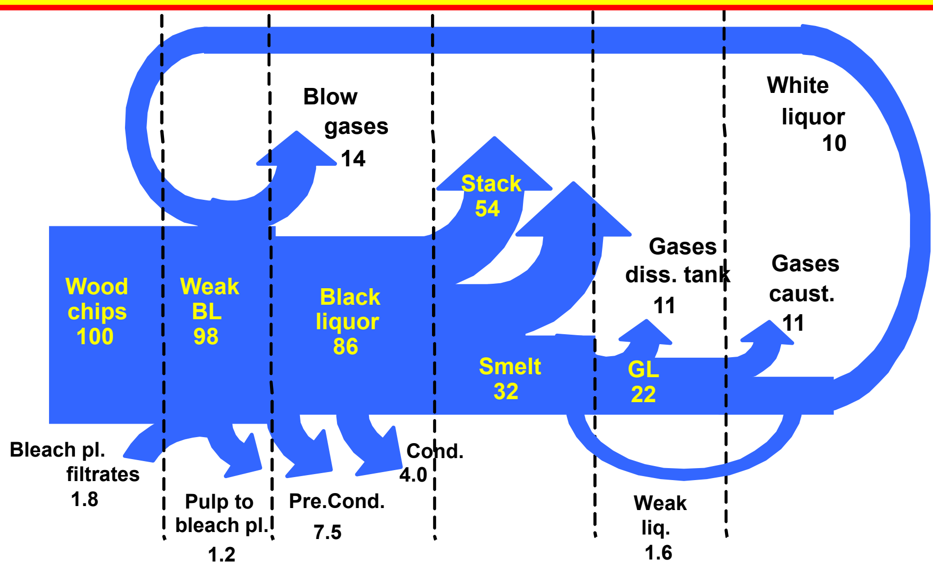

VTT
DIGESTION
COMBUSTION
SMELT
CAUSTICIZING
4. Increase ammonia formation in evaporation?
- requires drastic conditions
- novel catalysts
Blow gases 14
liquor 10
Stack 54
Gases diss. tank 11
Gases caust. 11
Wood chips 100
Weak BL 98
Black liquor 86
Smelt 32
GL 22
Bleach pl. filtrates 1.8
Pulp to bleach pl. 1.2
Pre.Cond. 7.5
Cond. 4.0
Weak liq. 1.6

Effect of heat treatment of black liquors on nitrogen release

Black liquor	N_{tot} in BL, g/kg ds	Released, no HT	Released, with HT at 200 °C, 3 h	Released, with HT at 200 °C, 16 h	Released, with HT at 300 °C, 2 h
Pine lab	0.59	0.21 (35%)	0.25 (42%)	0.30 (51%)	–
Softw. mill	0.57	0.10 (18%)	0.25 (44%)	0.30 (53%)	–
Birch lab	0.71	0.17 (24%)	0.45 (63%)	–	–
Birch mill*	1.27	–	–	–	0.94 (74%)
Birch mill	0.83	0.14 (17%)	0.30 (36%)	–	–
Eucal. lab	0.51	0.10 (20%)	0.30 (59%)	–	–
Eucal. mill	0.86	0.13 (15%)	0.45 (52%)	–	–



Learn more about the formation, nature and reactivities of black liquor nitrogen



Waldwolle process and products

- Invented by Joseph Weiss (1787-1868), Austria, in 1840
- Chemical and mechanical separation process, based on alkaline boiling of needles (dissolves extractives etc). Yields up to 50%.
- Cellulosic fibers – strong and elastic – recovered and could be spun, felted or woven
- Carpets, matting, mattresses, upholstering, different textiles…
- Also antiseptic materials (today: oxycellulose)

- Operated 1840s-1910/1920s? in Austria, Germany, Sweden, Holland, France, Brazil, USA, elsewhere…? In 1896, 29 looms in the USA used this fiber.
- Waldwolle process by-product: essential oil or turpentine oil. Also briquettes from the resinous residue (high fuel value).
- Fibres may be almost as long as needles (extreme >20 cm fibers)