Liite 1

Lisäkysymykset hajukaasujärjestelmään, Kirsi Hovikorpi, LUT

UNIVERSITY OF
TECHNOLOGY AND BUSINESS

”NCG järjestelmien prosessikonseptit”

Kirsi S. Hovikorpi

04.12.2018

Yliopisto Saimaan-rannalla

LAPPEENRANTA
UNIVERSITY OF TECHNOLOGY

”Best practice” soihdun operoinnissa ja polton aloituksessa?

- Tehtaat eivät halua pitää soihtua koko ajan tulilla ostopolttoaineella
- Skandinaavisissa olosuhteissa soihdun taajuusmuuntajatoiminen palamisilmapuhallin on hyvä pitää minimikierroksilla, koska
  - Soihdun palokammio on tällöin valmiiksi tuuletettu, käynnistyssekvenssi voi hypätä suoraan yli pitkäkestoisen tuuletusaskelman ja siirtyä sytytyspolttimen sytyttämiseen
  - Soihdun palokammio pysyy kuivana kesät talvet

”Best practice” soihdun operoinnissa ja polton aloituksessa?

- Nykypäivän uudet soihdut ovat valmiita ottamaan laitetoimittajasta riippuen CNCG kaasut polttoon 40 sekunnin … 5 minuutin viiveellä riippuen soihdun rakenteesta (pysty, vaaka) ja sisuskalujen materiaalista sekä käytettävästä tukipolttoaineesta.
- Yllä oleva 40 sekunnin kääntöaika edellyttää, että soihdun palamisilmapuhallin on ollut minimikierroksilla, tuuletussekvenssi voidaan hypätä käynnistyksessä yli, sytytyspolttimen ja tukipolttoaineen paineet ovat sulkuventtiileillä riittävät.

”Best practice” soihdun operoinnissa ja polton aloituksessa?

- Kun soihtu starttaa sytyttämällä sytytyspolttimen (yleensä propaania), syttyy ostotukipolttoaine soihdun pääpolttimessa ja kun pääpolttimen liekki on stabiloitunut antaa lupaehdot laitetoimittajista riippuen kääntää CNCG kaasut soihtuun vaikka riittäviä lämpöjä maksimi TRS-hapetukselle ei olisi vielä saavutettu.
- Maksimi hapetus 98 … 99.5% saavutetaan joillakin toimittajilla jo 180 sekunnin päästä CNCG kaasujen käännöstä.

”Best practice” soihdun operoinnissa ja polton aloituksessa?

- Maailmalla on tehtaita, joissa meesauuni toimii ns. väliaskelluksena CNCG kaasujen tripatessa pääpolttopaikassa esim. soodakattila- tai erillispolttokattilapoltossa, ja automaatio starttaa soihdun heti pääpolton tripatessa, ja operaattori tietoisesti kääntää CNCG kaasut soihdulle pois meesauunia häiritsemästä.
- Soihtu ainoastaan hapettaa TRS:t SO_2:ksi
- Jos halutaan minimoida SO_2-päästöjä, tulisi CNCG kaasut alkalipestä (NaOH) ennen soihdulle vientiä tai soihdusta poistuvista savukaasuista.

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

CNCG

- Suositeltavana lähtökohtana on, että olisi vähintään kolme (3) polttopaikkamahdollisuutta, joista yksi toimisi myös lyhyempiaikaisissa tehdasseisokeissa (esim. soihtu tai erillispolttokattila, joka tuottaa itse oman käyttöhöyryn)
- Järjestelmä tulee suunnitella kokonaisuudessaan mahdollisuudelle pantata kaasuja putkistoissa ja laitteissa useamman minuutin ajan pääpolttopaikan tripatessa vaihdettaessa varapolttopaikkaan, jonka käynnistys tarvitsee tietyn ajan

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

CNCG

- Maailmalla olevia eri variaatioita, joissa vähintään kolme (3) polttopaikkamahdollisuutta (riippuu onko kyseessä Green Field vaiko vanha tehdas, ja asiakkaan tarpeet rikin talteenotolle)
  - RB, Erillispolttokattila, Soihtu
  - RB, Meesauuni/t, Soihtu
  - RB, PB, Soihtu
  - Erillispolttokattila, PB, Soihtu
  - Kaksi erillispolttokattilaa, Soihtu
  - Kaksi soodakattilaa, Soihtu

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG

- Suositeltavana lähtökohtana, että kunkin osaston (kuitulinja, haihduttamo, kaustistamo) kaasut
  - Keräily omilla erillisillä taajuusmuuntajatoimisilla keskipakopuhaltimilla
  - Keräilyn kaasut omaan lauhdutus ja/tai pesurisysteemiin
  - Lauhtuneet lauhteet takaisin oman osaston prosesseihin
    - Kuitulinjan kuitupitoiset lauhteet kuitulinjalle
    - Kaustistamon meesapitoiset lauhteet kaustistamolle
    - Haihduttamon lipeäpitoiset lauhteet haihduttamolle

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Kuitulinjan DNCG hajukaasujen keräily ja käsittely
  - Esipesulla varustetulla lauhduttavalla pesurilla/pystytuubilauhduttimella
  - Jos on keräilykohteita, joissa vaahtoaa ja samalla mahdollisuus kuitujen ns. carry-over ilmiöön (esim. pesemön suodossäiliöiden keräily), jonkinlainen suorasuihkupesu vaahdon tappamiselle, ettei kulkeudu keräilylinjastoon
-

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Kuitulinjan Hakesiilon hönkien keräily ja käsittely
  - Hakesiiloon ainoastaan tuorehöyry, ei paisunnan TRS-pitoisia höyryjä (sisältää suuren määrän väkeviä, lauhtumattomia kaasuja).
  - Valtaosa maailmalla tapahtuvista DNCG-järjestelmien räjähdyksistä johtuu lipeän paisuntahöyryn suorasta käytöstä hakesiiloilla.

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Kuitulinjan Hakesiilon hönkien keräily ja käsittely
  - Koska hakesiilon höngät sisältävät yleensä aina hienoa puupölyä/kevyttä haketta, keräilyn höngät suositeltavaa mentävä aina hienoaine-erotuksen kautta omalle lauhduttimelle jonka jälkeen omalla puhaltimella kuitulinjan DNCG keräilyyn ja/tai taivaalle.
  - Etenkin havupuutehtailla lauhduttimella saadaan aikaiseksi tärpätin talteenottoa, vaikka kaasuja ei DNCG keräilyyn otettaisikaan

-

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Haihduttamon DNCG hajukaasujen keräily ja käsittely
    - Lauhduttava pesuri tai pystytuubilauhdutin omalla taajuusmuuntajatoimisella puhaltimella (itse suosisin pystytuubilauhdutinta)
    - Jos tarvetta pesukierron pH-säätöön, on pesurimalli suositeltavin
    - Haihduttamon lipeäsäiliöiden keräily toteutettava ns. suljetulla keräilyllä turhien hönkimisten ja keräilyn ilmavuotojen minimoimiseksi

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Haihduttamon DNCG hajukaasujen keräily ja käsittely
  - Lauhteet haihduttamon likaislauhdesäiliölle, ja jos johtokyky nousee, kääntö vuotolipeäsäiliöön
  - Mietityttänyt vahvamustalipeäsäiliöillä tapahtuva mahdollinen lipeän paisunta, jos haihdutinsarjojen paisunta tapahtuu väärässä paikassa, tulisiko olla keräilylinjassa omat HI-venttiilit

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Haihduttamon DNCG hajukaasujen keräily ja käsittely
  - Jos ns. neste-neste reboiler keittämöllä, mietiskelty, tuleeko etenkin havupuutehtailla tärpättijakeet lipeää pumpattavaan lipeäsäiliöön ja paisuuko lipeä säiliössä, jolloin suuri osa tärpätistä ja TRS-jakeita vapautuisi laimeiden hajukaasujen keräilyyn, tuoden mahdollisia vaaratekijöitä keräilyssä?

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG käsittelyt

- Kaustistamon DNCG hajukaasujen keräily ja käsittely
  - Itse suosisin pystytuubilauhdutinta (joillakin toimijoilla pesuri) omalla taajuusmuuntajatoimisella puhaltimella
  - Kaustistamon keräily toteutettava ns. suljetulla keräilyllä turhien hönkimisten ja keräilyn ilmavuotojen minimoimiseksi
  - Eniten päänvaivaa tukkeentumisilla ovat aiheuttaneet Sammuttajan ja Kaustisointisäiliöiden keräilyt.
  - Kalkin tuontiin ja kaasunkeräilykohdan sijaintiin ja mahdolliseen esipesuun kiinnitettävä sammuttajalla huomiota

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG

- Suositeltavana lähtökohtana on, että olisi kaksi (2) polttopaikkamahdollisuutta ja by-pass. Eli pääpolttopaikan lisäksi joku varapolttopaikka, mikä kykenee ottamaan laimeiden hajukaasujen suuren volyymin vastaan
- TUKES edellyttää tänä päivänä myös laimeiden systeemin suunnittelupaineeksi 50 kPa (ei ole siis vielä paineastia), taustalla tapahtuneet hajukaasuräjähdykset

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

DNCG

- Maailmalla olevia eri variaatioita, joissa vähintään kaksi (2) polttopaikkamahdollisuutta (riippuu onko kyseessä Green Field vaiko vanha tehdas)
  - RB, Erillispolttokattila (oltava riittävän iso), By-Pass
  - RB, PB, By-Pass
- Myös eri osastojen DNCG kaasujen jakoa eri polttopaikoille
  - Kuitulinjan ja haihduttamon DNCG kaasut RB:lle ja PB:lle, Kaustistamon DNCG kaasut meesauunille/neille
  - Enemmänkin on variaatioita

Eri tapoja kerätä ja käsitellä hajukaasut, kun tavoitteena on hajuton sellutehdas

Liuottajan ja Sekoitussäiliön höngät

- Maailmalla olevia eri variaatioita Liuottajan ja Sekoitussäiliön hönkien käsittelylle ja kytkemisille, joihin en ota tässä enempää kantaa.

Loppukevennys

LOPUKSI TAAS

”Kysymys: Miten keittämöoperaattorin asettaman CNCG keräilyn alipaineen-säädön asetusarvo voi koskaan tavoittaa haluttua -8 kPa, jos haihduttamon operaattorin ohjaama väkevien hajukaasujen keräilyn höyryejektorin alipaineen asetusarvo on -4 kPa?

Vastaus: Keskustelua enemmän osastojen välille ja ymmärrystä lukujen merkitykseen.”

\- Kirsi S. Hovikorpi –

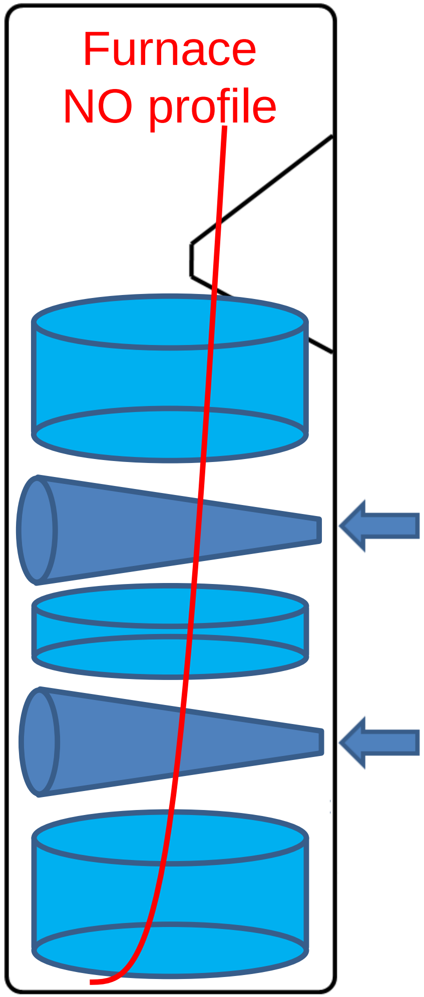
Liite 2

Projektin väliraportti: Evaluation of three different gas phase chemistry mechanisms for predicting NOx emission formation in recovery boilers, ÅA

Evaluation of three different gas phase chemistry mechnisms for predicting NOx emission formation in recovery boilers

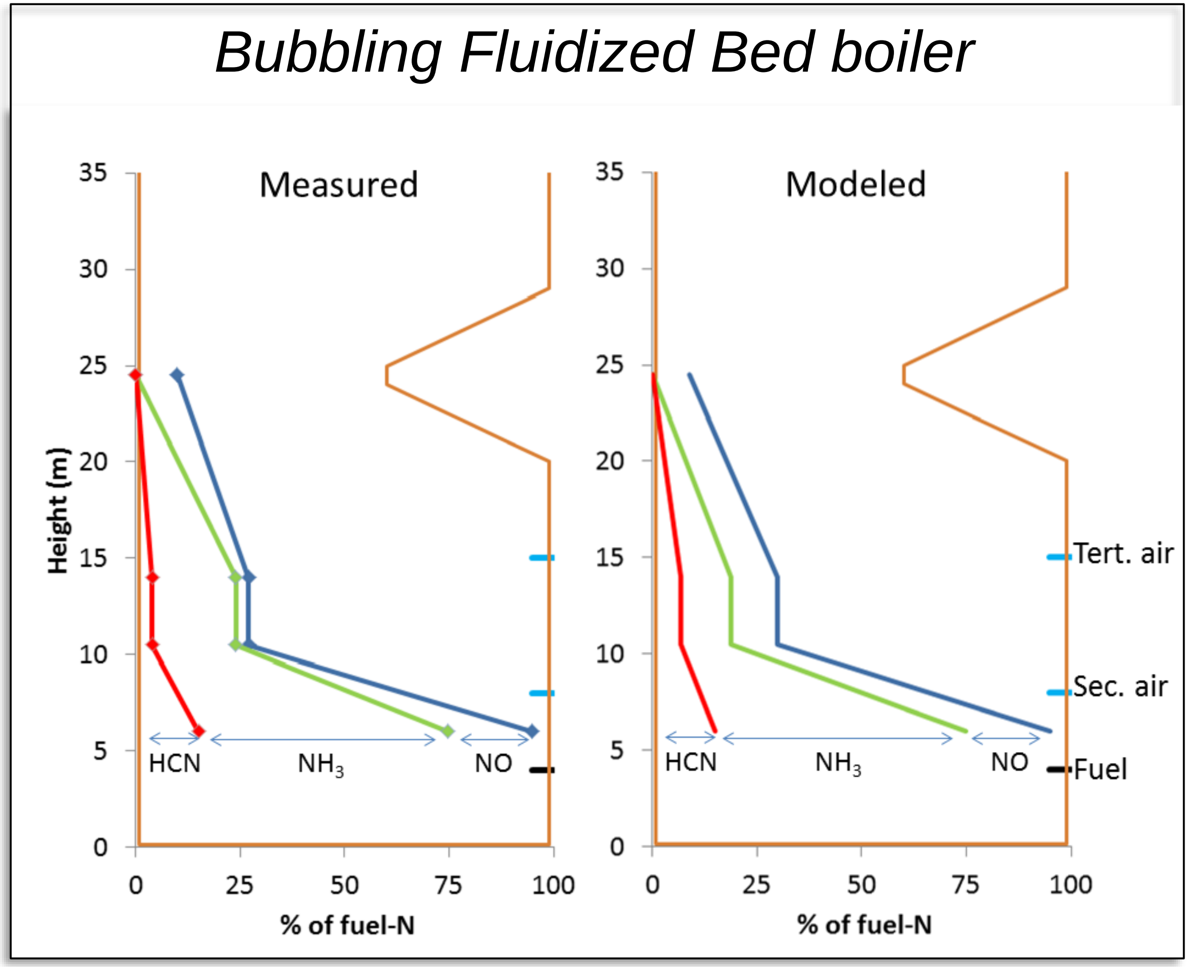
Markus Engblom
13.11.2018

”Jet-NOx” model

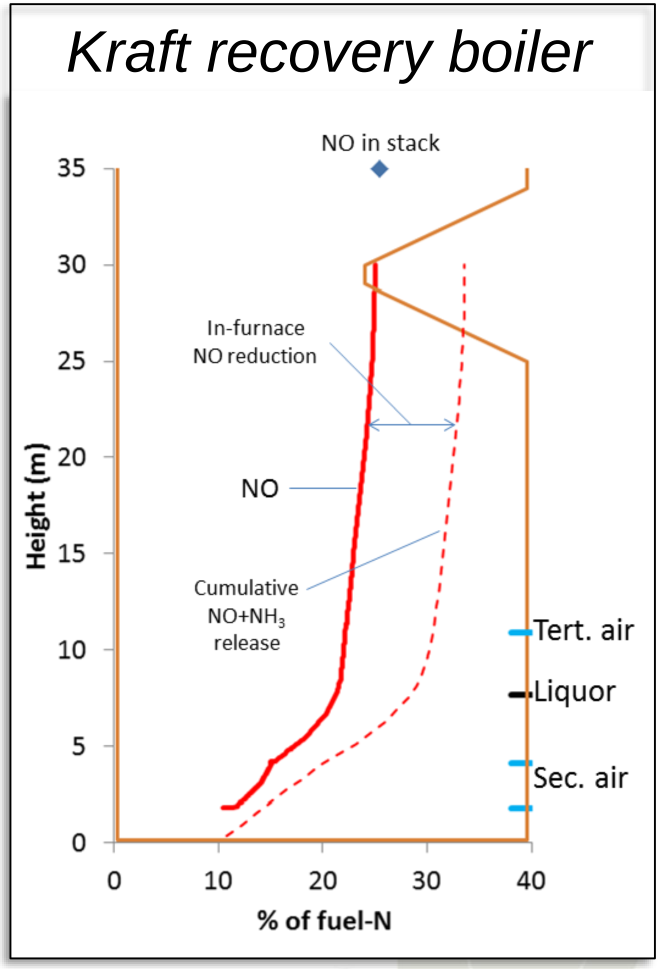


- Simplified fluid dynamics
  - Furnace sections and air jets
  - CFD for input
- Detailed kinetics
  - ÅA mechanism
  - CHEMKIN reactor network
  - ”Zwietering” reactors
- Prediction result is profiles of NO and other species as function of boiler height

”Jet-NOx” model



Bubbling Fluidized Bed boiler



Kraft recovery boiler

- Tool for understanding and predicting boiler NOx chemistry
  - Boiler NO in general well predicted

Objective

- Evaluate three different gas phase chemistry mechanisms in terms of NO formation predictions
  - 1) Detailed mechanism: reference. In terms of chemistry this type of mechanism is the most comprehensive. In some cases, this types of mechanisms have been combined with CFD, but mostly in simulation of laminar flames, not boiler simulations.

Objective

- Evaluate three different gas phase chemistry mechanisms in terms of NO formation predictions
  - 2) Skeletal mechanism: Based on a detailed mechnism, but with some reactions removed. Could be considered possible to be used in CFD boiler simulations. The key is to have a mechanism which still describes the chemisty well when compared to detailed mechanism. In practice this means that the relevant reactions have been retained, not removed

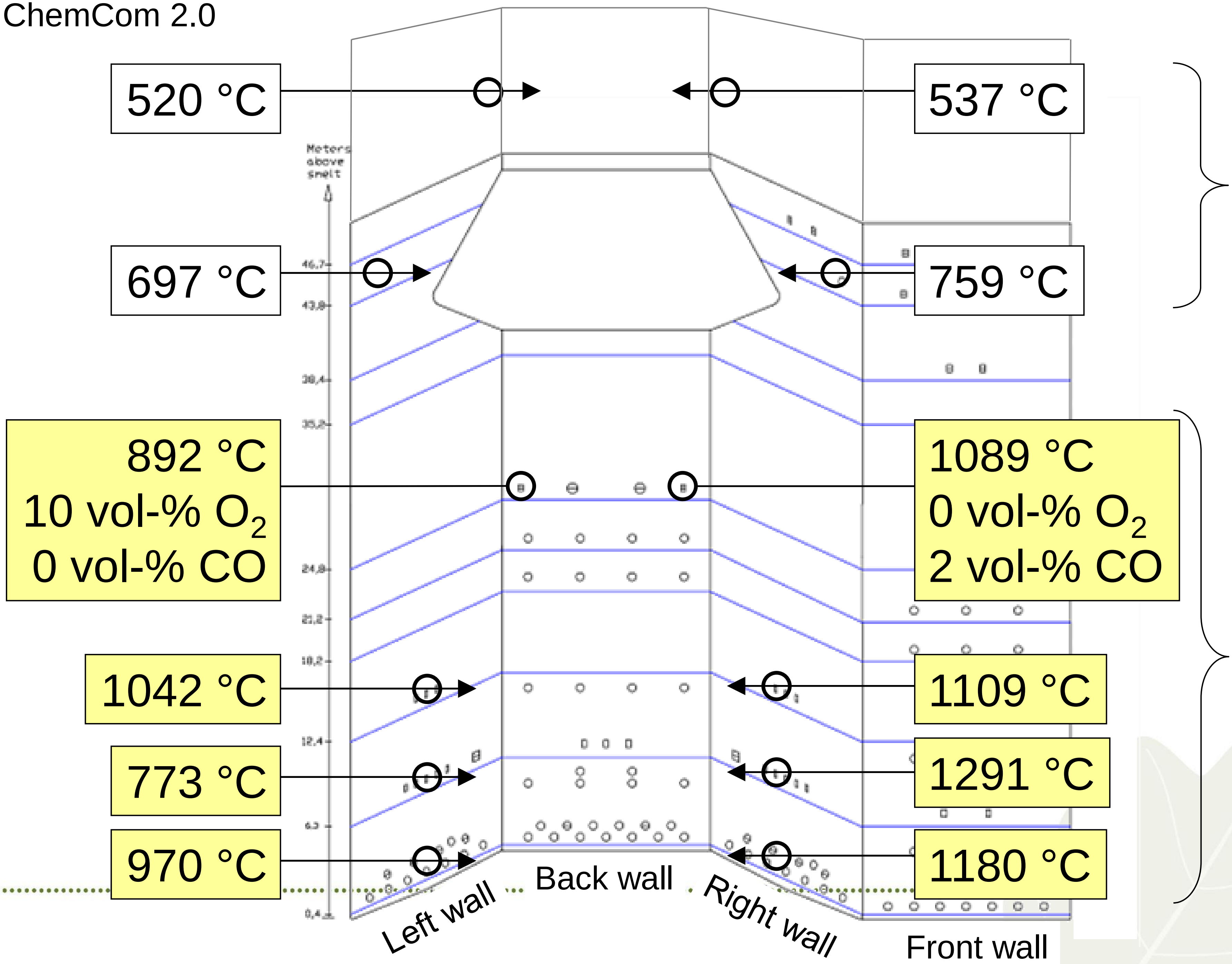
Objective

- Evaluate three different gas phase chemistry mechanisms in terms of NO formation predictions
  - 3) Global reaction mechansm, typically only two or a few reactions. Traditionally this type of mechanism has been used in CFD boiler simulations. Perhaps the most important objective of this work is to compare predictions using this type of simplified mechanism with predictions using detailed and skeletal mechanisms

Simulation cases

- Model an actual boiler operation situation, for which there is in-furnace data on nitrogen species (see slides below)
- The operational situation is characterized by asymmetric combustion
  - Righ side of boiler operating with high fuel/air ratio, reducing conditions, higher temperatures. The right side and locations where liquor hits walls, are characterized by higher NH_3 and HCN compared to NO
  - Left side having an excess of oxygen, operating under oxidizing conditions and lower temperatures. The left side is characterized by lower NH_3 and HCN, and higher NO compared to right side
- Simulation strategy: model right and left side of boiler separately, using three chemistry mechanisms

ChemCom 2.0



520 °C

537 °C

697 °C

759 °C

892 °C
10 vol-% O_2
0 vol-% CO

1089 °C
0 vol-% O_2
2 vol-% CO

1042 °C

1109 °C

773 °C

1291 °C

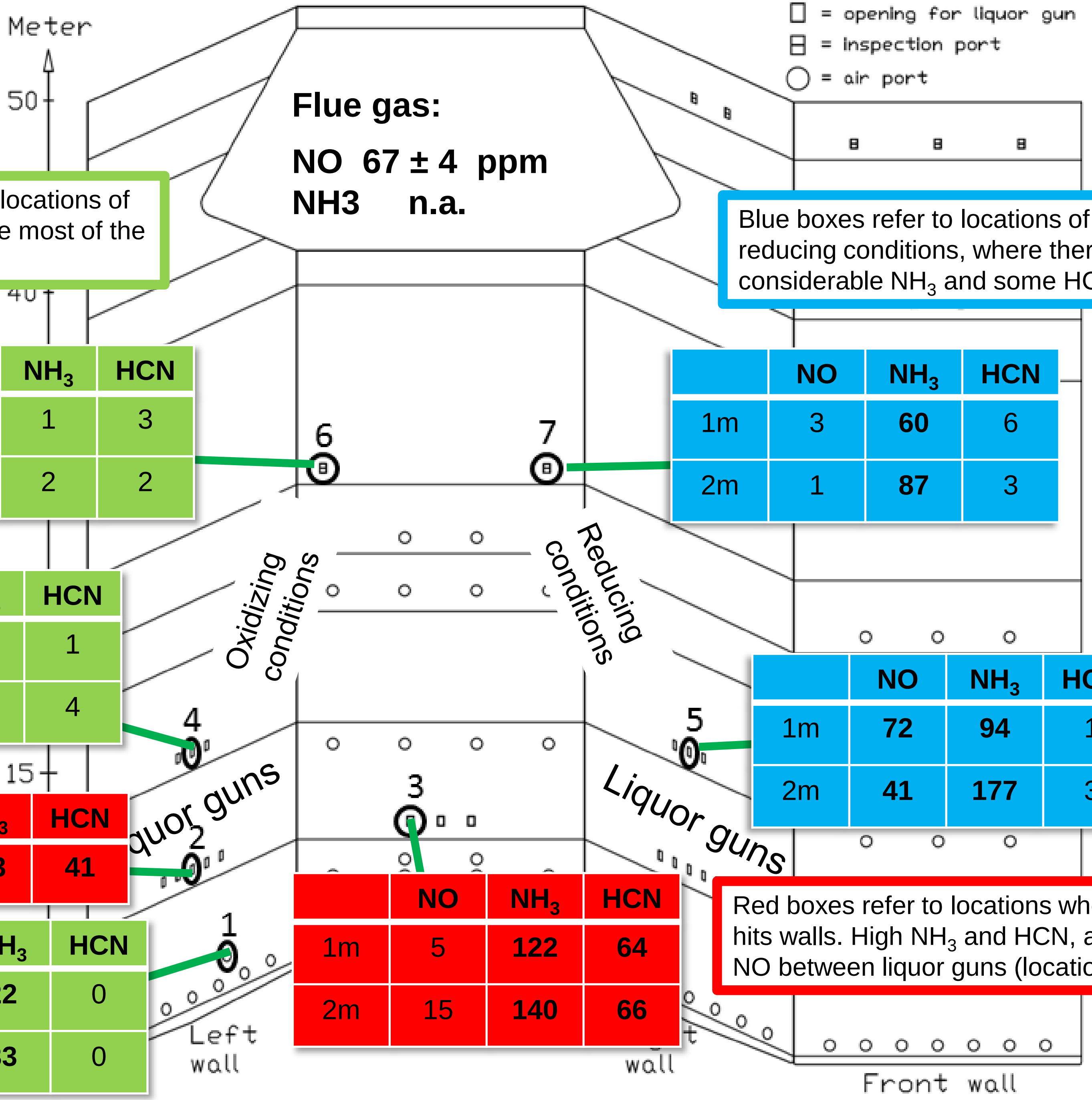
970 °C

1180 °C

Process data

Measurement campaign data

ChemCom 2.0
(Vainio et al.)



Flue gas:

NO 67 ± 4 ppm
NH3 n.a.

Green boxes refer to locations of excess oxygen, where most of the nitrogen is NO

Blue boxes refer to locations of reducing conditions, where there is considerable NH_3 and some HCN

Red boxes refer to locations where liquor hits walls. High NH_3 and HCN, and also high NO between liquor guns (location 2)

	NO	**NH_3**	**HCN**
1m	**54**	1	3
2m	**59**	2	2

	NO	**NH_3**	**HCN**
1m	3	**60**	6
2m	1	**87**	3

	NO	**NH_3**	**HCN**
1m	**38**	6	1
2m	**39**	16	4

	NO	**NH_3**	**HCN**
1m	**72**	**94**	1
2m	**41**	**177**	3

	NO	**NH_3**	**HCN**
0.5m	**200**	**153**	**41**

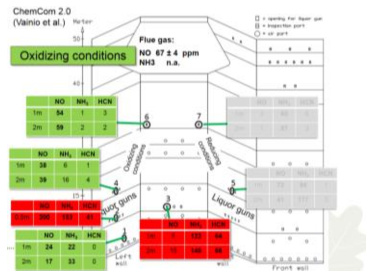
	NO	**NH_3**	**HCN**
1m	5	**122**	**64**
2m	15	**140**	**66**

	NO	**NH_3**	**HCN**
1m	**24**	**22**	0
2m	**17**	**33**	0

Results (1/2)

- Detailed chemistry mechanism
- Model correctly captures low NH_3 and low HCN on left side of boiler, most of the nitrogen is NO
- Final NO is also relatively well predicted

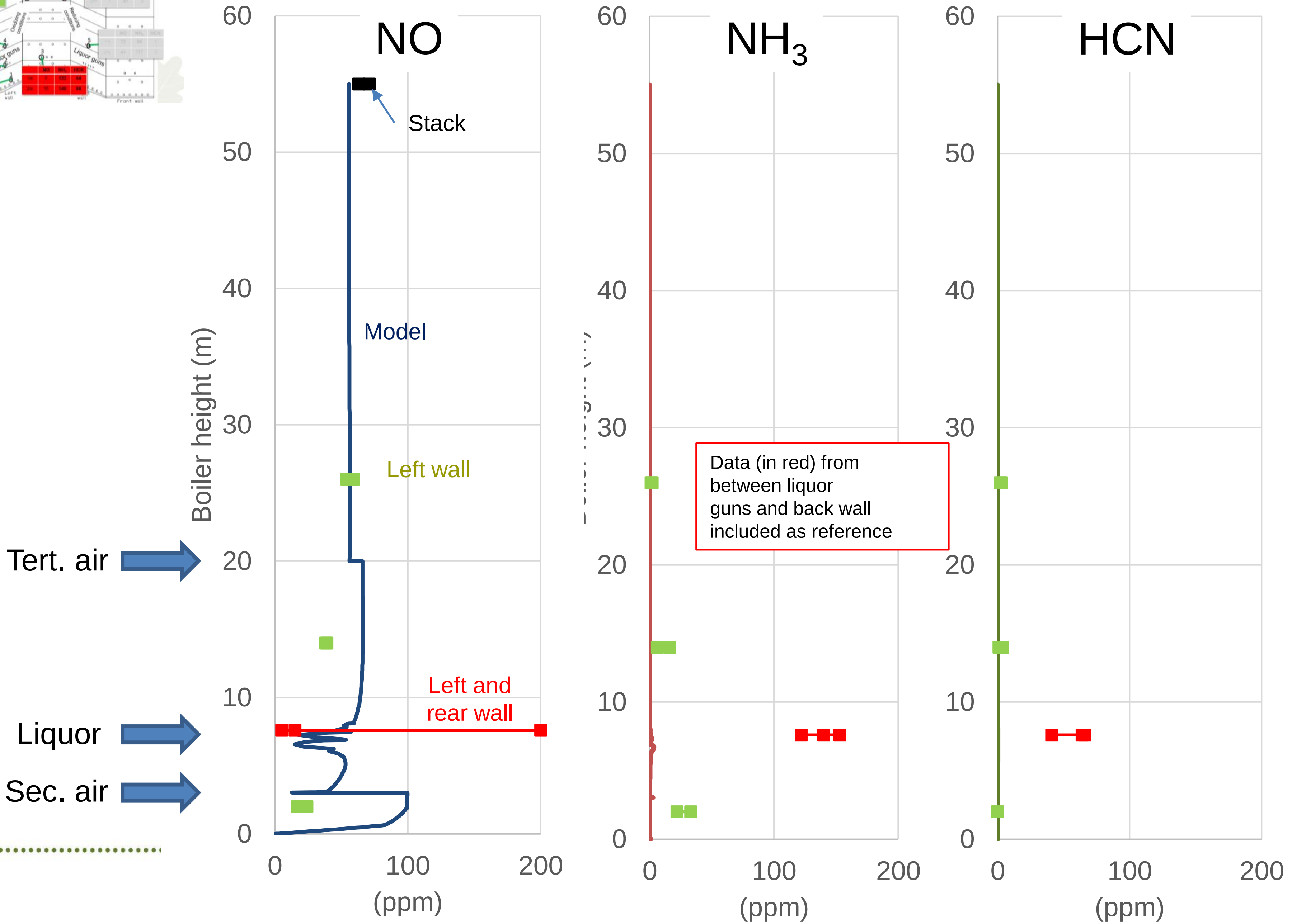
Modeled boiler left side - Oxidizing conditions



	NO	NH_3	HCN
1m	54	1	3
2m	59	2	2

	NO	NH_3	HCN
1m	38	6	1
2m	39	16	4

	NO	NH_3	HCN
1m	24	22	0
2m	17	33	0

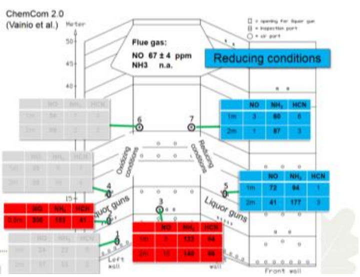


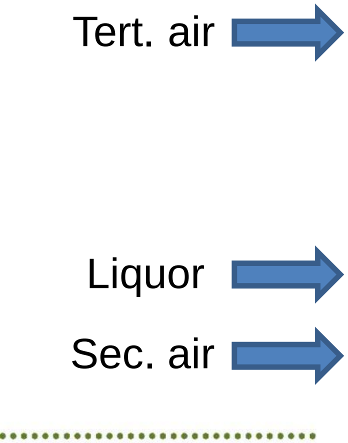
Data (in red) from between liquor guns and back wall included as reference

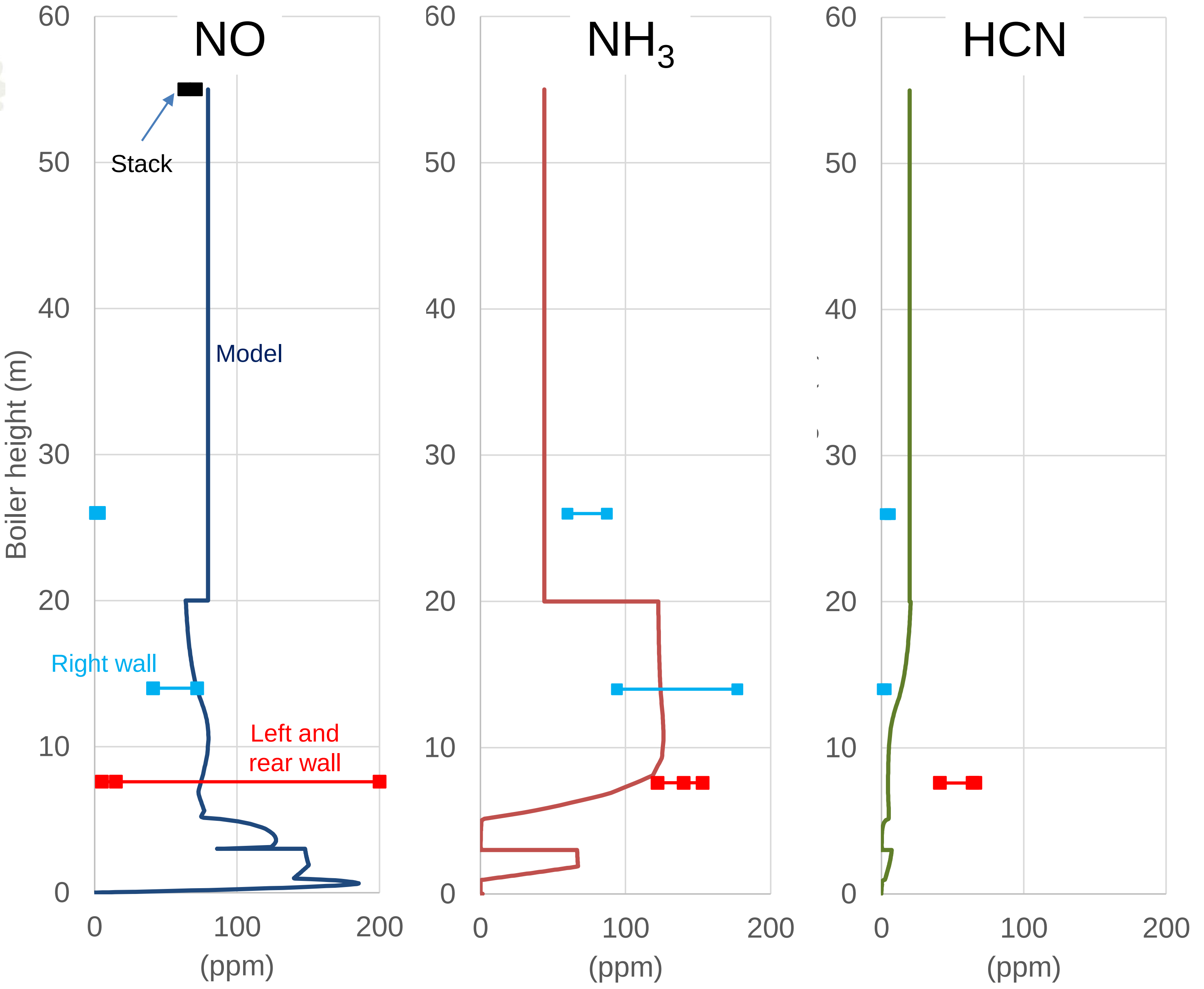
Results (2/2)

- Detailed chemistry mechanism
- Model correctly captures high NH_3 and existence of some HCN on right side of boiler
- NO level including final NO relatively well predicted

Modeled boiler right side - Reducing conditions





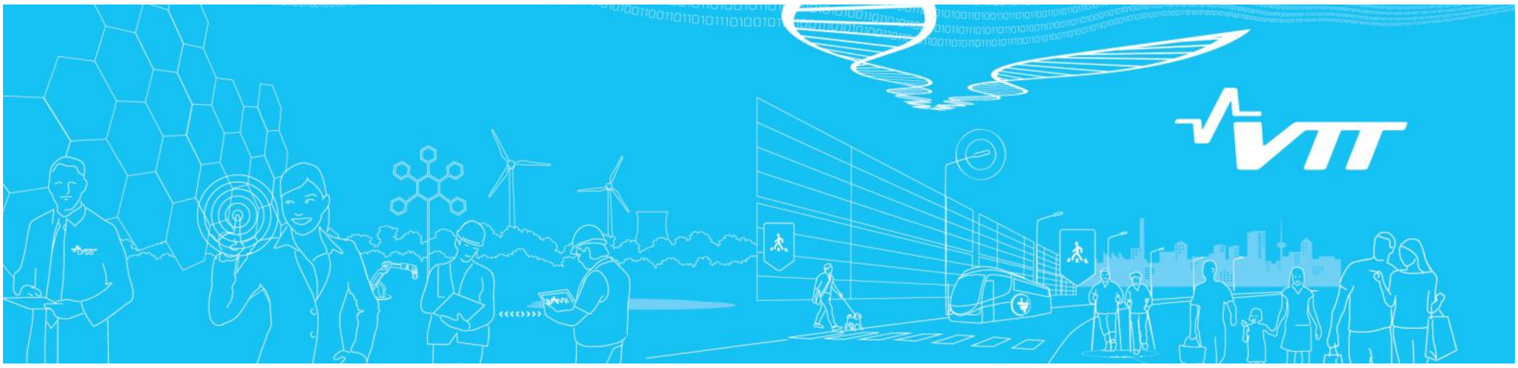


Summary

- Simulations using detailed chemistry done
  - Model correctly predicts trends when comparing left and right side of boiler
- Simulations using skeletal mechanism not done
  - However, with the simulation cases now set up, changing to skeletal mechanism straighforward
- Simplified chemistry simulations not done
  - Further work needed to implement simplified chemistry into Chemkin software. Requires adding own code
- Timeline: skeletal simulations will be completed during 2018, simplfied chemistry may require more time, until Q1 2019

Liite 3

Projektin loppuraportti: Soodakattilan NOx-päästön riippuvuus puuraaka-aineen typpipitoisuudesta, VTT



CUSTOMER REPORT

VTT-CR-XXXX-YY | 4.12.2018

Nitrogen in wood and its fate in kraft pulping – a review

Author: Klaus Niemelä

Confidentiality: Confidential vai public?

Report’s title

Customer, contact person, address	**Order reference**
Project name	**Project number/Short name**

Summary

{Add city} 4.12.2018

Written by	**Reviewed by**	**Accepted by**
{Clarification of signature, position}	{Clarification of signature, position}	{Clarification of signature, position}

VTT’s contact address

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Contents

1. Introduction

During the past 20-30 years, the knowledge on the fate of wood-derived nitrogen at kraft pulp mills and on the factors affecting (and reducing) nitrogen oxide emissions has significantly increased. It still looks, however, that there is not yet sound reliable information available on all the correlations between the nitrogen contents in wood and black liquor, and the nitrogen oxide emissions. The creation of these correlations has apparently been hampered by varying data available (from literature and different laboratories) on the nitrogen contents, both in wood raw material and black liquors.

Therefore, the current review work was planned to cover the available literature and other potential information sources on the following questions: nitrogen contents in stemwood or pulp mill chips of the key Nordic wood raw materials (pine, spruce and birch), the chemical nature of the wood nitrogen, and the behaviour of nitrogen at the kraft pulp mills (covering both fibrelines and recovery lines).

The material for the current review was based on two different sets: 1) comprehensive collection of literature on wood nitrogen, collected at KCL during 2000–2002 as part of the Rempulp EU project, and 2) further literature searches that especially focused on the new material published during the past 15 years. For the searches, different databases and information sources available at VTT were used, strengthened by comprehensive searches with the help of Scopus and Google Scholar websites.

It can be mentioned here that the elemental composition of wood began to attract chemists during the second half of the 19th century. One of the first investigators was König, who in 1861 found that wood losses some of its nitrogen by copper sulphate treatment (but no exact figures were given). More precise data was later reported by Schroeder (1874), Gottlieb (1883), and Hartig (1888). According to Schroeder (1874), spruce and other woods always contain less than 0.3% of nitrogen. Slightly lower nitrogen figures were reported by Gottlieb (1883), whose numbers are in good agreement with the best current data. Today, there is a lot of wood nitrogen related information available, created for largely varying purposes. These have varied from industrial wood uses to environmental questions and numerous other needs. As a result, the data is also often heterogeneous and challenging to review and analyse; also different analytical methods easily make sound conclusions challenges.

2. NITROGEN IN WOOD – CONTENTS AND DISTRIBUTION

2.1 Nitrogen in softwood

During the comprehensive literature searches it became evident that there is a huge amount of information available on nitrogen contents in dozens of different softwood species covering numerous industrially important genera, including pines, spruces, firs, larches, hemlocks, cypresses and many others. It also became clear that the studies cover all different tree parts, including twigs and branches, bark, roots, and needles. Furthermore, it is evident that practically taken all the main softwood species contain equally low amounts of nitrogen in mature stemwood, as the figures above >0.2–0.3% have only seldom been reported. As will be shown later by selected examples, the highest nitrogen contents are typically found only in the outer layers of sapwood.

Due to the availability of the vast amount of published data, the present Section will mainly focus on the main Nordic softwood species, Scots pine (Pinus sylvestris) and Norway spruce (Picea abies). For comparison, however, selected data on other pine and spruce species will also be provided, strengthened by examples on other types of softwood species. The currently available information on wood nitrogen does not focus only on the total nitrogen contents. In addition, there is detailed information available on the distribution of nitrogen in different parts of stemwood. This type of variation will also be demonstrated below, with the help of selected examples.

For the nitrogen contents of Scots pine (Table 1) and Norway spruce (Table 2), most of the figures reported during the past 100 years have remained below 0.15%. In only a few cases any figures on the levels of >0.15% have been published. The highest figures for both pine (0.24%) and spruce (0.25%) are derived from the Swedish Ecocyclic pulp mill project (Anon. 1999) and may be explained by systematically different analytical approach.

Table 1. Nitrogen contents (%) of Scots pine, according to different sources.

Nordic studies		Other European studies	
Contents (%)	Reference	Contents (%)	Reference
0,07-0,13	Magnusson et al. 1979	0,13	Schwalbe & Becker 1919
0,04	Paavilainen 1980	0,05-0,09	Nickel 1960
c. 0,05-0,1	Siltala 1988, Helmisaari 1989	0,08-0,11	Becker 1962
0,06-0,07	Finér 1989	0,03-0,08	Popović 1966
0,05-0,08	Häsänen & Huttunen 1989	0,06	Keller & Nussbaumer 1993
0,04-0,08	Boutelje et al. 1990	0,07	Marutsky & Roffael 1977
0,09-0,11	Terziev et al. 1997	0,05-0,08	Adelsberger & Petrowitz 1976
0,06	Terziev 1995	0,13	Allsop & Misra 1940
0,04-0,06	Varhimo 1988	0,07	Ovington 1957
0,05	Telkkinen 1996, 1999	0,08-0,1	Wright and Will 1958
0,05-0,08	Hedenberg 1996	0,06-0,09	Laidlaw & Smith 1965
0,12-0,24	Anon. 1999	c. 0,04-0,1	King et al. 1974
0,07	Nurmi 1997		
0,04	Niemelä & Ulmgren 2002		
c. 0,05	Palvianen et al. 2010		

Table 2. Nitrogen contents (%) of Norway spruce, according to different sources.

Nordic studies		Other European studies	
Contents (%)	Reference	Contents (%)	Reference
0,07-0,17	Magnusson 1979	0,07	Marutsky & Roffael 1977
0,06	Finér 1989	0,04	Gottlieb 1883
0,05	Boutelje et al. 1990	0,11	Schwalbe & Becker 1919
0,03	Westernark et al. 1986	0,18	König & Becker 1919
0,04-0,05	Varhimo 1988	0,04-0,08	Becker 1962
0,05	Telkkinen 1996, 1999	0,07	Keller & Nussbaumer 1993
0,04-0,05	Hedenberg 1996	0,07-0,10	Ovington 1957
0,12-0,25	Anon. 1999	0,17	Ovington 1957
0,04	Nurmi 1997	0,07	Merrill and Cowling 1966a
0,09-0,13	Ingersleve 1999	c. 0,04-0,08	King et al. 1974
0,06-0,11	Anttonen et al. 2002		
0,08-0,15	Kaakinen et al. 2007		
0,14-0,16	Kaakinen et al. 2009		
c. 0,07	Palviainen et al. 2010		

There is an interesting difference between the above data reported for pine and spruce. Namely, nearly all the figures for pine are below 0.1%, whereas for spruce two different data sets can be recognised: those around from c. 0,04 to 0,08%, and those going clearly above 0.1% (up to 0.16-0.18%). No unambiguous explanation for that can now be given, and for example, no apparent differences could be recognised in the applied analytical methods to readily explain the differences.

For many of the above nitrogen contents figures there are ranges given, for a number of reasons. For example, Magnusson (1979), Varhimo (1988), Häsänen & Huttunen (1989) and Hedenberg (1996) have studied wood samples from several geographical areas. On the other hand, Nickel (1960), Siltala (1988), Boutelje et al. (1990) and many others have provided figures from different parts of the logs. There is also variation in the nitrogen contents caused by the use of different levels of fertilisation, e.g. those by Ingerslev (1999), Anttonen et al. (2002) and Kaakinen et al. (2007, 2009). Selected examples are given below to further demonstrate the extent of this type of variations.

Nickel (1960) investigated nitrogen and protein contents in a 100-year-old Scots pine wood and found a steep decrease from the utmost sapwood towards the heartwood, followed by a small rise in the inner heartwood zone towards the centre (Fig. 2). Orman and Will (1960) found a similar distribution pattern in a 26-year-old radiata pine. Becker (1962) investigated in detail nitrogen contents (expressed as proteins by multiplying with 6.25) in Scots pine and other softwoods (Fig. 2). His results support (and widen) those from the earlier investigations.

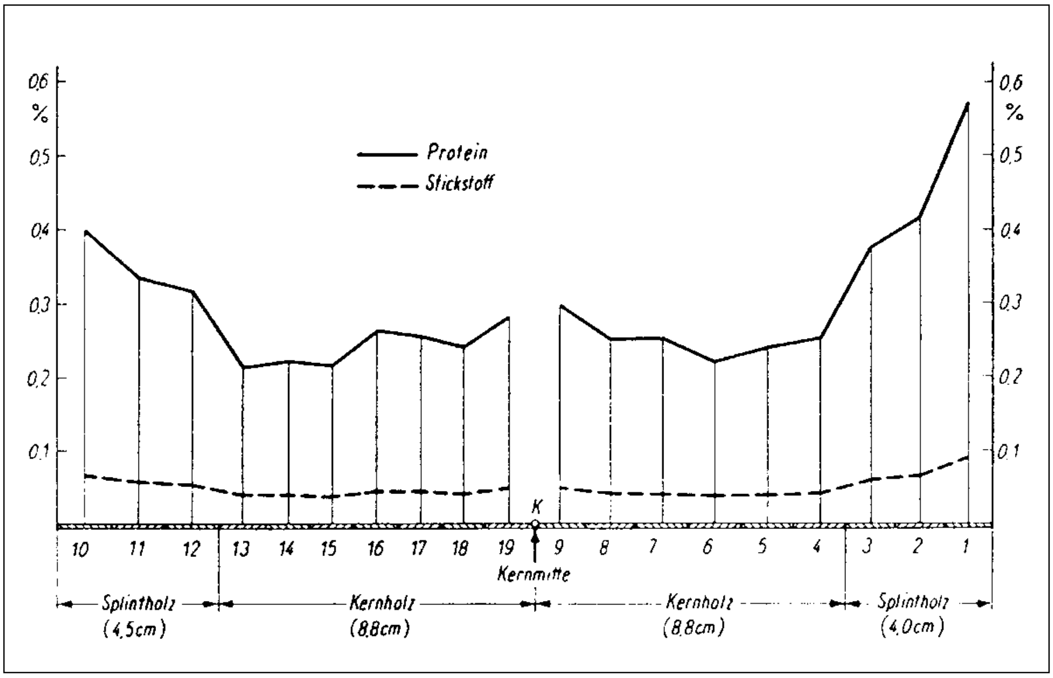


Fig. 1. Nitrogen and protein concentrations in a 100-year-old Scots pine (Nickel 1960).

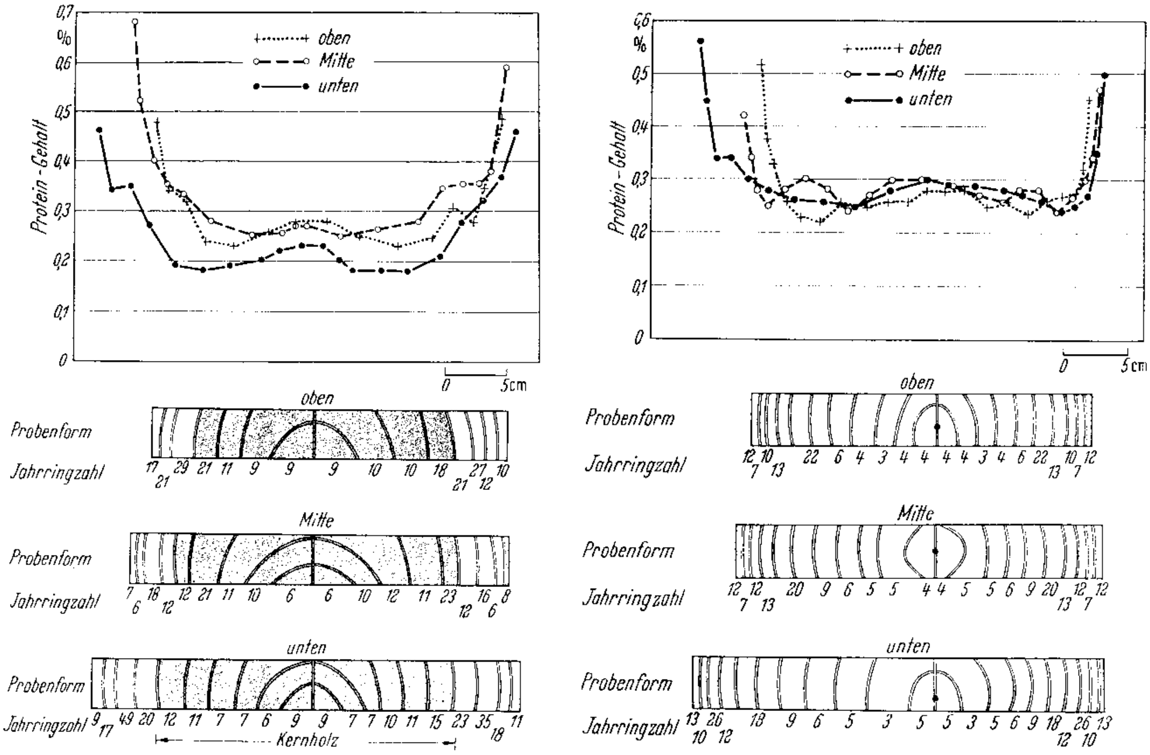


Fig. 2. Protein concentrations over cross sections in Scots pine (left) and Italian spruce (*Picea excelsa*, right) at three different heights (oben, Mitte, unten) corresponding to 2.5, 5, and 7.5 metres (Becker 1962). Similar distribution was also found (figure not reproduced) for a noble fir (*Abies pectinata*).

Apparently one of the most comprehensive of the above-mentioned distribution-related studies is that by Siltala (1988). In his M.Sc. Thesis, he investigated distribution of nitrogen in pine seedlings, young trees, and mature trees, paying attention to xylem, inner bark, outer bark, seasonal changes, and soil fertilisation (Figs. 3–8). The major results from the Siltala's Thesis are also published in a scientific paper by Helmisaari and Siltala (1989).

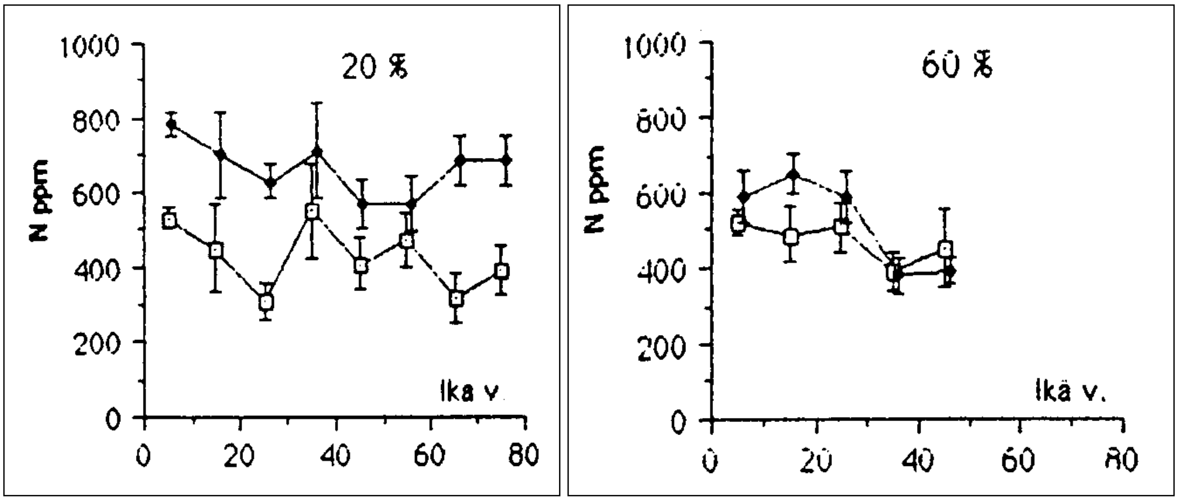


Fig. 3. Horizontal distribution of nitrogen in pine wood (xylem) at relative heights of 20% and 60%, according to Siltala (1988). *Ikä* refers to number of growth rings; • indicates pine grown in a fertilised area; and ☐ refers to pine grown in a non-fertilised area.

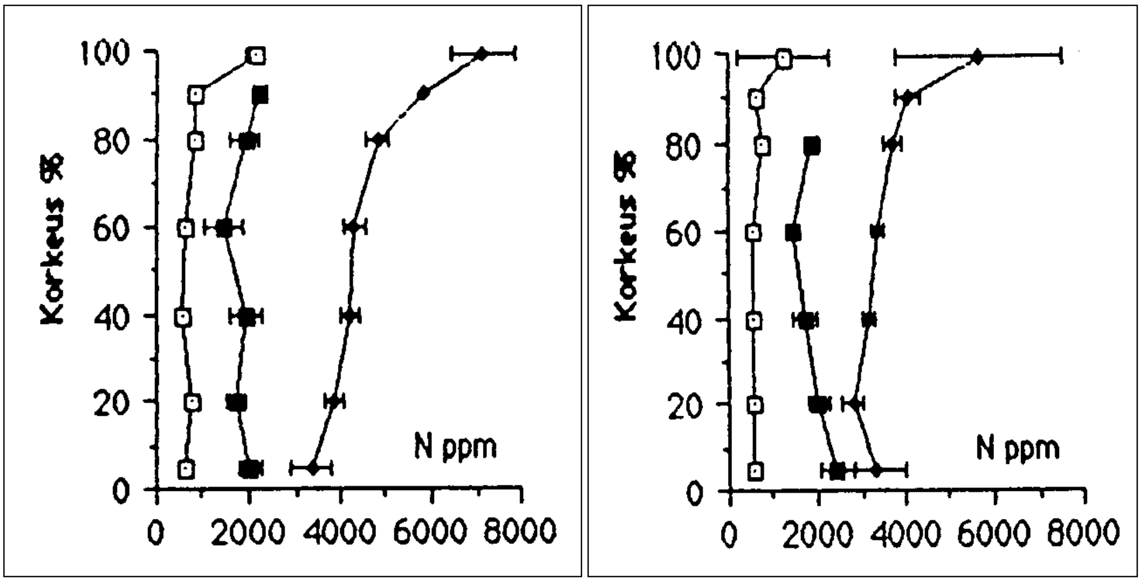


Fig. 4. Vertical distribution of nitrogen in pine wood grown in a fertilised (left) and non-fertilised (right) area, according to Siltala (1988). *Korkeus* refers to relative tree height; ☐ indicates xylem; ■ indicates inner bark, and • indicates outer bark.

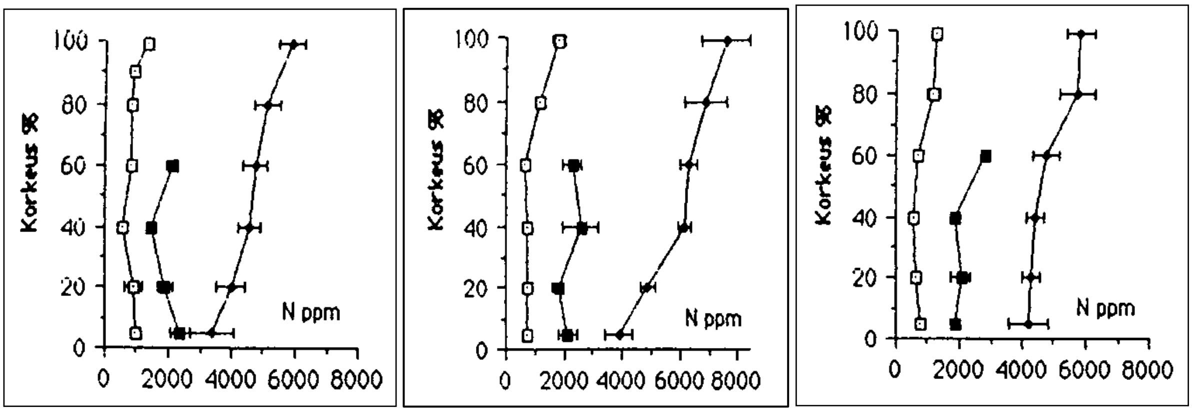


Fig. 5. Vertical distribution of nitrogen in pine wood grown in different localities, according to Siltala (1988). Symbols as in Fig. 3.

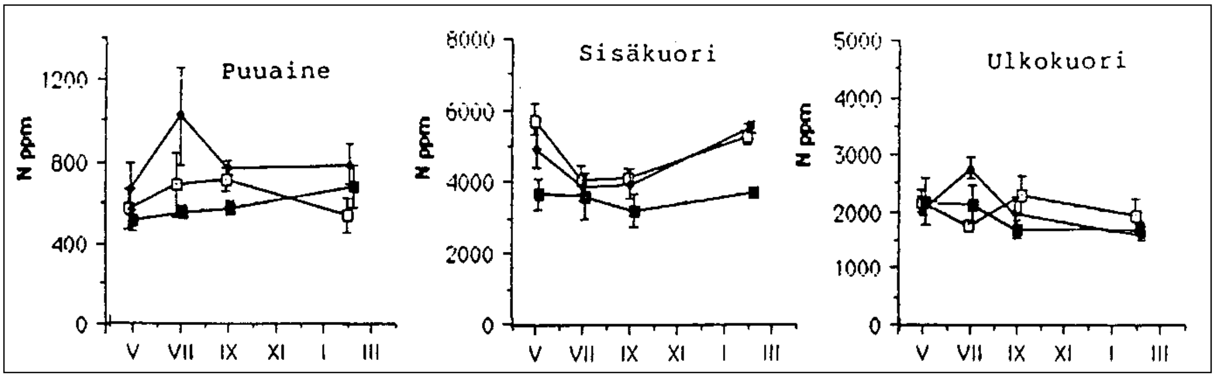


Fig. 6. Seasonal variation of nitrogen content in pine wood xylem (left), inner bark (middle), and outer bark (right), according to Siltala (1988). ☐ indicates seedlings; ■ indicates young forest, and • indicates mature trees.

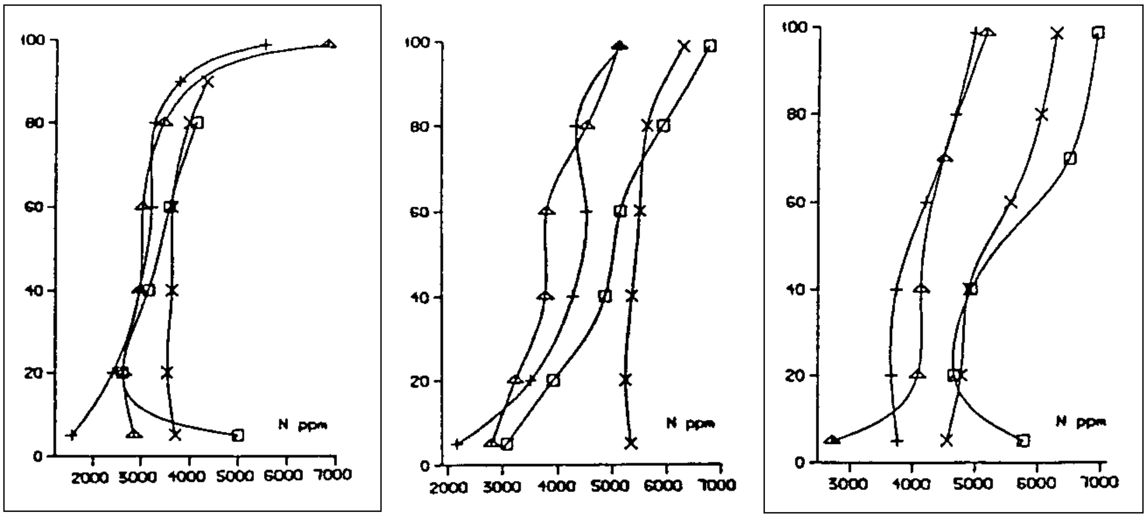


Fig. 7. Seasonal variation in vertical nitrogen content in inner bark of pine: mature trees (left), young trees (middle), and seedlings (right), according to Siltala (1988). Sampling in February (□), May (☐), July (⊗), and September (+).

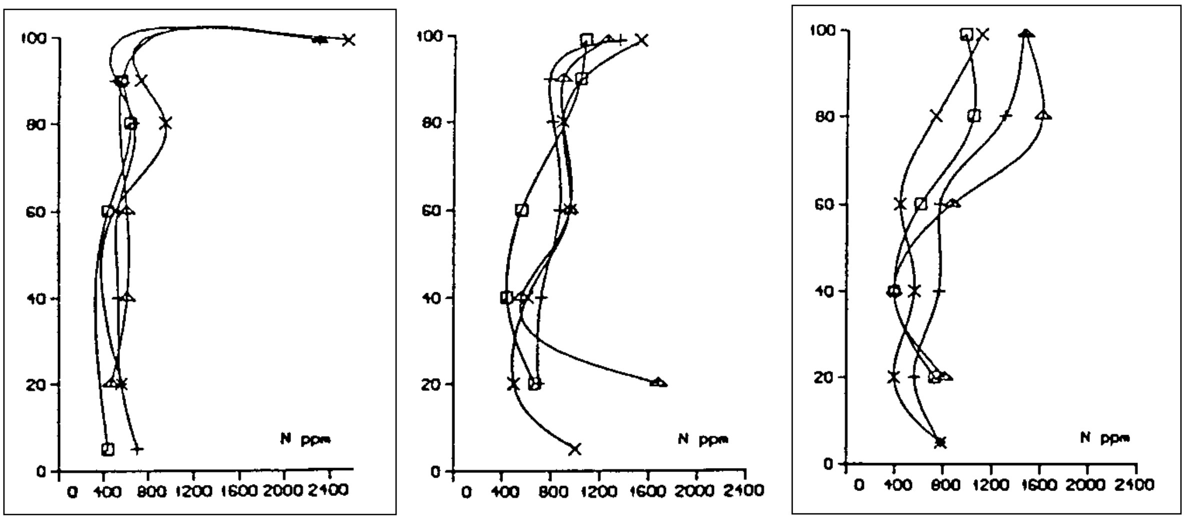


Fig. 8. Seasonal variation in vertical nitrogen content in outer sapwood of pine: mature trees (left), young trees (middle), and seedlings (right), according to Siltala (1988). Sampling in February (□), May (☐), July (⊗), and September (+).

The above Siltala's (1988) figures for Scots pine clearly confirm earlier findings on higher nitrogen content in wood bark, and also reveal some seasonal variation. This type of variation is, however, much more typical for hardwood (Section 2.2).

Results from a highly interesting study were published by Kaakinen et al (2007) some years ago, including measurements on the effects of nitrogen-fertilisation on the nitrogen contents of Norway spruce on two locations in Finland. They studied "the effect of long-term nitrogen fertilisation on wood chemistry at two boreal sites in Finland: the northern site (Kemijärvi) and the southern site (Heinola). N-fertilisation was repeated in five-year intervals from the 1960s. The trees that had been planted in 1938 and 1954, in the northern and the southern site, respectively, were harvested in October 2002. Altogether 20 trees, in five different size classes, either unfertilised or fertilised, were felled. Wood sections at breast height, consisting of five consecutive annual rings, from six (Kemijärvi) or five (Heinola) points with different distances from the pith were examined. Differences in growth between the northern and southern sites were marked in favour of the southern site. In the northern site fertilisation had clearly increased the diameter growth, while in the southern site fertilisation had no effect. Nitrogen fertilisation resulted in slight changes in wood chemistry that included increased nitrogen concentrations in the northern site and extractives in the southern site (Table 3). Stem wood had higher concentrations of extractives, starch, and uronic acids, and lower concentration of cellulose, in the northern than in the southern site".

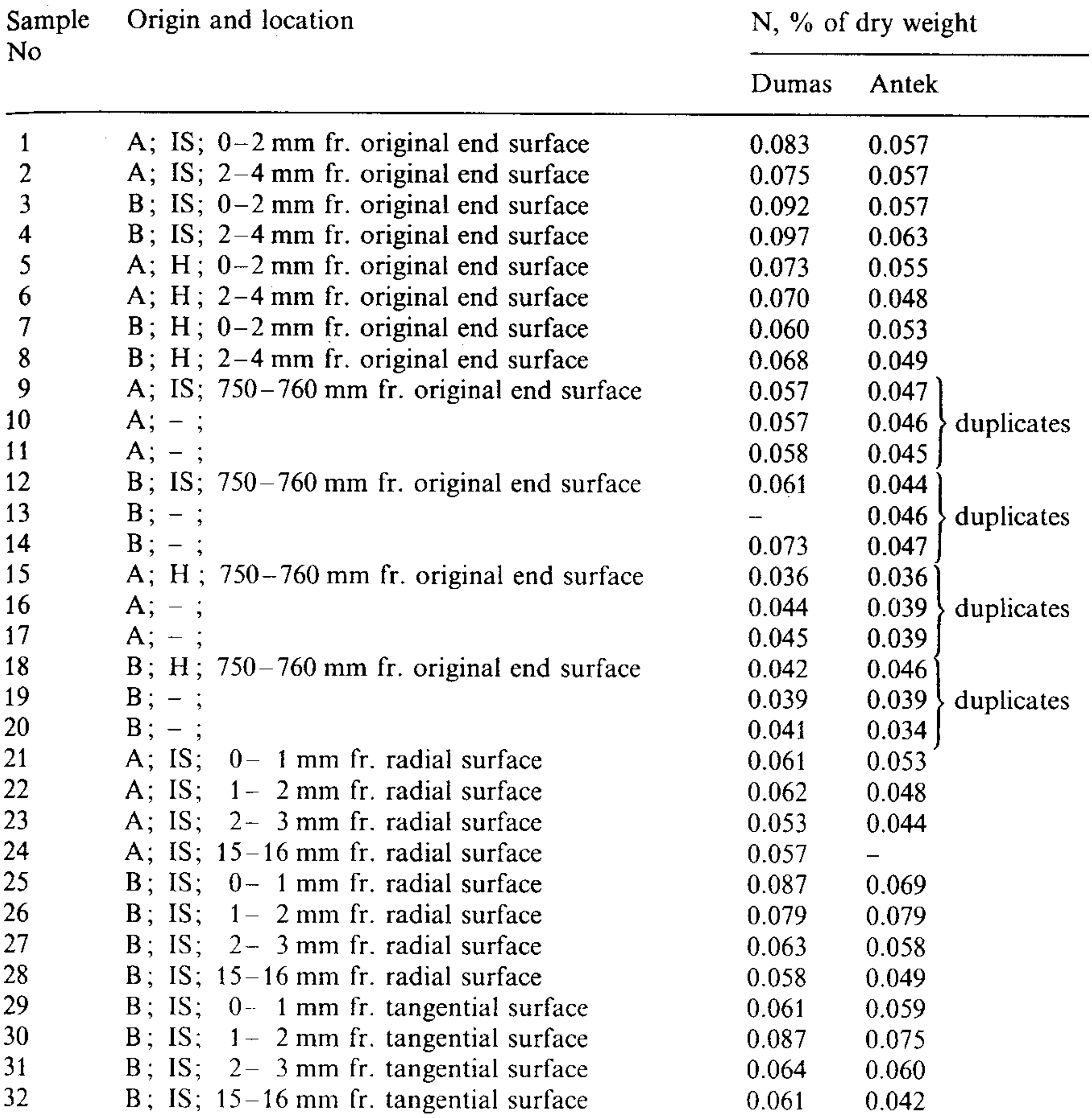
Table 3. Wood component concentrations (% DM) and ratios from the pith to the bark in the northern site (Kemijärvi) and in the southern site (Heinola) in Finland (Kaakinen et al. 2007). U, unfertilised; F, nitrogen-fertilised.

Annual ring sections	Carbon		Nitrogen		Carbon/nitrogen		Total lignin/nitrogen	
	U	F	U	F	U	F	U	F
The northern site								
1958–1962	49.92 ± 0.05	50.00 ± 0.24	0.112 ± 0.008	0.098 ± 0.013	455 ± 33	542 ± 73	277 ± 17	316 ± 44
1965–1969	49.66 ± 0.09	49.93 ± 0.07	0.110 ± 0.004	0.108 ± 0.009	455 ± 19	481 ± 42	263 ± 10	281 ± 24
1975–1979	49.76 ± 0.05	49.95 ± 0.10	0.120 ± 0.004	0.112 ± 0.007	417 ± 16	452 ± 25	242 ± 11	259 ± 13
1985–1989	49.52 ± 0.17	49.63 ± 0.20	0.102 ± 0.016	0.136 ± 0.007	553 ± 113	365 ± 17	317 ± 62	213 ± 8
1993–1997	49.66 ± 0.04	49.65 ± 0.13	0.130 ± 0.000	0.143 ± 0.008	382 ± 0	351 ± 18	222 ± 4	204 ± 13
1998–2002	49.83 ± 0.17	49.35 ± 0.22	0.133 ± 0.009	0.148 ± 0.003	381 ± 26	335 ± 7	221 ± 18	190 ± 7
The southern site								
1963–1967	50.70 ± 0.24	50.64 ± 0.08	0.088 ± 0.008	0.094 ± 0.005	596 ± 54	544 ± 29	345 ± 32	317 ± 17
1973–1977	50.76 ± 0.15	50.78 ± 0.10	0.076 ± 0.007	0.100 ± 0.007	693 ± 65	518 ± 38	403 ± 40	299 ± 20
1983–1987	50.60 ± 0.09	50.76 ± 0.06	0.106 ± 0.011	0.102 ± 0.008	503 ± 62	510 ± 41	291 ± 38	288 ± 26
1993–1997	50.42 ± 0.10	50.56 ± 0.08	0.108 ± 0.004	0.118 ± 0.012	469 ± 17	457 ± 67	265 ± 7	258 ± 39
1998–2002	50.28 ± 0.07	50.24 ± 0.08	0.150 ± 0.012	0.140 ± 0.004	343 ± 26	360 ± 12	193 ± 14	201 ± 6

Kaakinen et al. (2009) also compared the properties and composition of control and nutrient optimised Norway spruce stems, grown in Sweden. The reported nitrogen contents were 0.14 and 0.16% for the control and nutrient optimised samples, respectively. Anttonen et al. (2002) also studied in Sweden the impacts of optimal fertilization of chemistry of spruce and found the wood nitrogen increase from 0.06 to 1.1%

Other type of data on concentrations and distribution of nitrogen in pines comes from several studies on the effect of drying on nitrogen compounds. For example, Boutelje (1990) analysed a large number of pine plank samples (at different locations) with both Antek and Dumas methods (Table 4). The latter method always gave somewhat higher nitrogen figures. The results are also discussed by Theander et al. (1993).

Table 4. Nitrogen content in 32 samples taken from two Scots pine planks (A and B), according to Boutelje et al. (1990). IS, inner sapwood; H, heartwood. See the original work for the sampling details and for the effects of drying on the nitrogen content. The original work also gives some nitrogen concentrations for Norway spruce.



Sample No	Origin and location	N, % of dry weight		
		Dumas	Antek	
1	A; IS; 0–2 mm fr. original end surface	0.083	0.057	
2	A; IS; 2–4 mm fr. original end surface	0.075	0.057	
3	B; IS; 0–2 mm fr. original end surface	0.092	0.057	
4	B; IS; 2–4 mm fr. original end surface	0.097	0.063	
5	A; H; 0–2 mm fr. original end surface	0.073	0.055	
6	A; H; 2–4 mm fr. original end surface	0.070	0.048	
7	B; H; 0–2 mm fr. original end surface	0.060	0.053	
8	B; H; 2–4 mm fr. original end surface	0.068	0.049	
9	A; IS; 750–760 mm fr. original end surface	0.057	0.047	duplicates
10	A; – ;	0.057	0.046	
11	A; – ;	0.058	0.045	
12	B; IS; 750–760 mm fr. original end surface	0.061	0.044	duplicates
13	B; – ;	–	0.046	
14	B; – ;	0.073	0.047	
15	A; H ; 750–760 mm fr. original end surface	0.036	0.036	duplicates
16	A; – ;	0.044	0.039	
17	A; – ;	0.045	0.039	
18	B; H ; 750–760 mm fr. original end surface	0.042	0.046	duplicates
19	B; – ;	0.039	0.039	
20	B; – ;	0.041	0.034	
21	A; IS; 0– 1 mm fr. radial surface	0.061	0.053	
22	A; IS; 1– 2 mm fr. radial surface	0.062	0.048	
23	A; IS; 2– 3 mm fr. radial surface	0.053	0.044	
24	A; IS; 15–16 mm fr. radial surface	0.057	–	
25	B; IS; 0– 1 mm fr. radial surface	0.087	0.069	
26	B; IS; 1– 2 mm fr. radial surface	0.079	0.079	
27	B; IS; 2– 3 mm fr. radial surface	0.063	0.058	
28	B; IS; 15–16 mm fr. radial surface	0.058	0.049	
29	B; IS; 0– 1 mm fr. tangential surface	0.061	0.059	
30	B; IS; 1– 2 mm fr. tangential surface	0.087	0.075	
31	B; IS; 2– 3 mm fr. tangential surface	0.064	0.060	
32	B; IS; 15–16 mm fr. tangential surface	0.061	0.042	

The above studies, substantiated by that of King et al. (1974), also reveal some re-distribution of nitrogen during drying. This was studied in more detail by Terziev (1995) and Kreber et al. (1998). Selected examples shown in Figs. 9–10 show the tendencies of (soluble) nitrogen to migrate from deeper layers towards the surface, particularly during kiln drying. There is also some stain formation, believed to be caused by Maillard-type reactions between amino acids and carbohydrates. This has also been evidenced in a more detailed study of the nitrogen compounds (Donald et al. 2000).

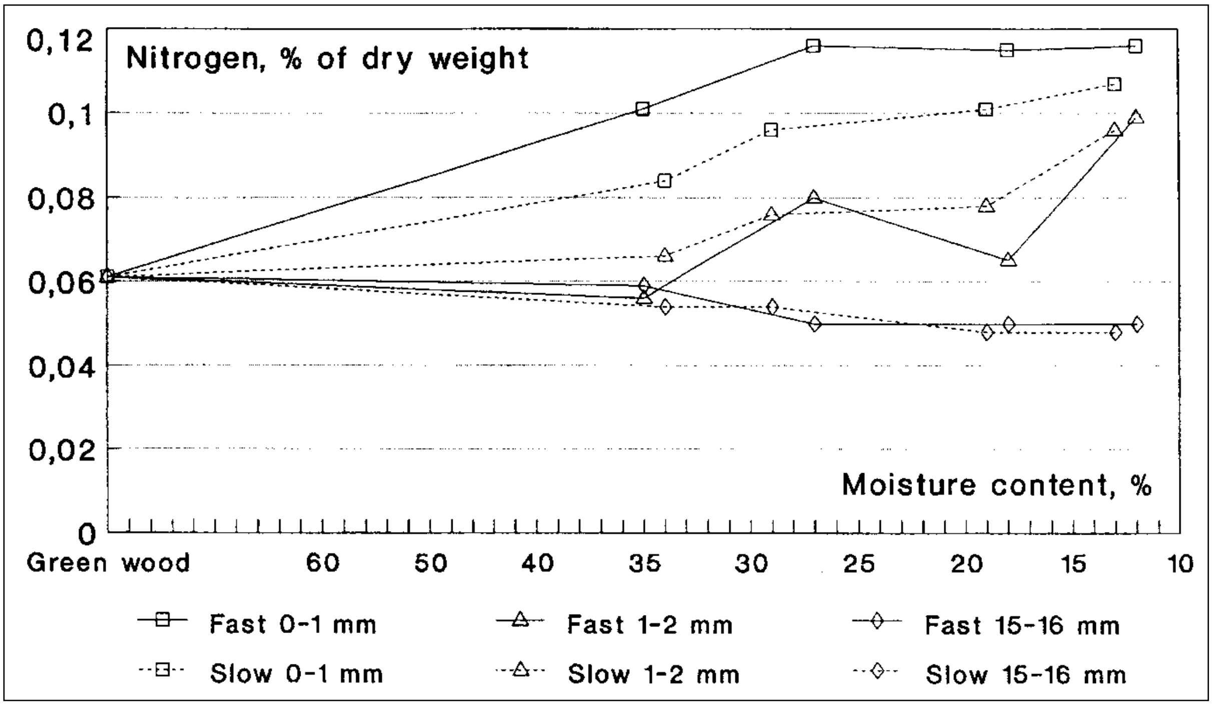


Fig. 9. Concentration of nitrogen in unedged planks of Scots pine during kiln drying at 80 C, as a function of moisture content. (Terziev 1995). Note the increase of nitrogen content in the surface layers, as a result of nitrogen migration from deeper layers. Similar tend was not found during air drying (see the original publication for that).

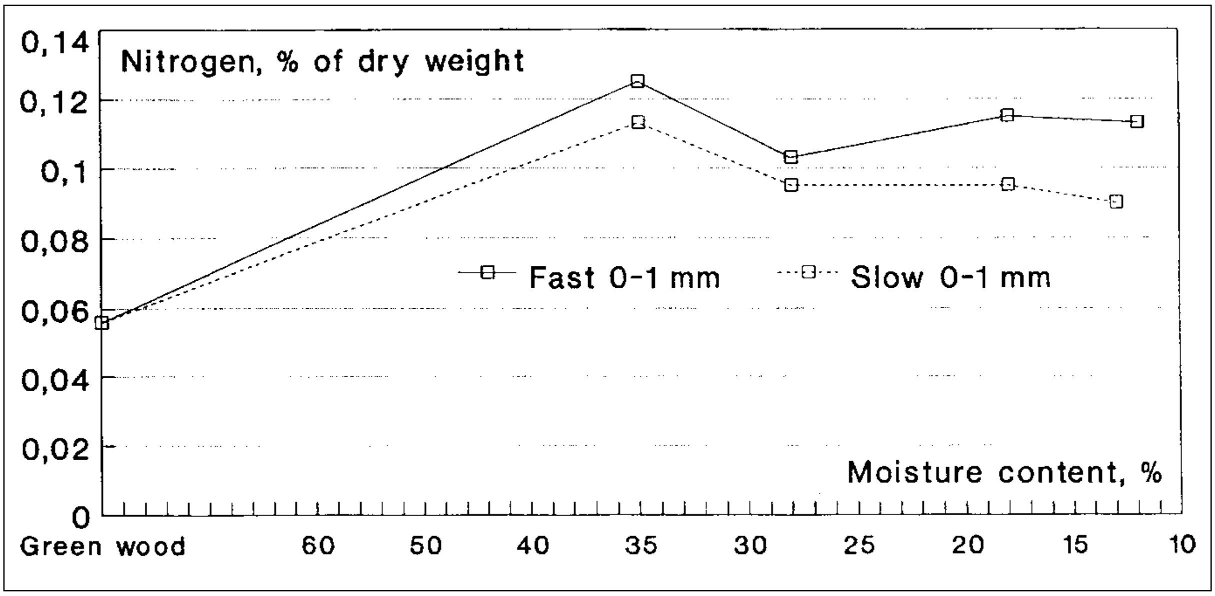


Fig. 10. Concentration of nitrogen in edged planks of Scots pine during kiln drying (Terziev 1995).

As already pointed out in the beginning of this Section, other pine and spruce species (as well as softwoods from other genera) all seem to have very similar or even equal nitrogen contents. In this context it is not justified to provide detailed summaries on such investigations. For the potential need of further information on this question, the following references can be recommended as representative examples:

- Meerts (2002) has summarised contents of nitrogen and other nutrients for nearly 100 different wood species, including >20 softwoods. For comparison, the summary tables from this study are provided in Appendix 1.
- A large number of papers report the nitrogen contents of c. 0.04-0.12% for several foreign pine species, such as contorta, echinata, elliottii, nigra, lambertiana, monticola, palustris, ponderosa, taeda, radiata and strobus (e.g. Allison et al. 1963, Ovington 1957, Wright and Will 1958, Orman and Will 1960, Young and Guinn 1964, Merill and Cowling 1966a, Ziegler 1968, Haas and Kremer 1964, Young 1971, Birk and Vitousek 1986, Wong and Wilkes 1988, Martin et al. 2015).
- Similar (usually c. 0.05–0.15%) nitrogen contents have been reported for numerous foreign spruce, fir, larch and hemlock species (for example by Allison et al. 1963, Ovington 1957, Young and Guinn 1964, Ziegler 1968, Haas and Kremer 1964, Young 1971, and Martin et al. 2015).

2.2 Nitrogen in hardwood

For the contents of nitrogen in the Nordic birch wood, there is clearly less information available than for softwood (Table 5). The scattered data reveals the concentration ranges very similar than those in softwood, covering a few examples showing values below 0.1%, and several examples with somewhat higher figures. The highest reported figures seem to be just under 0.2%. The figure of 0.18% by Palviainen et al. refers to birch stumpwood.

Data collected by Meerts (2002) for dozens of different hardwood species includes only a few examples of any species with the nitrogen contents of c. 0.2-0.25%, more typical ranges being around 0.05–0.17%. It thus looks that the Nordic birch species represent typical nitrogen contents among many other hardwood genera. In the total dataset by Meerts, the average values for nitrogen were 0.08% and 0.11% in all softwood and hardwood (heartwood) materials, respectively. It may be added here that the typical Eucalyptus wood nitrogen contents were around 0.1–0.15%.

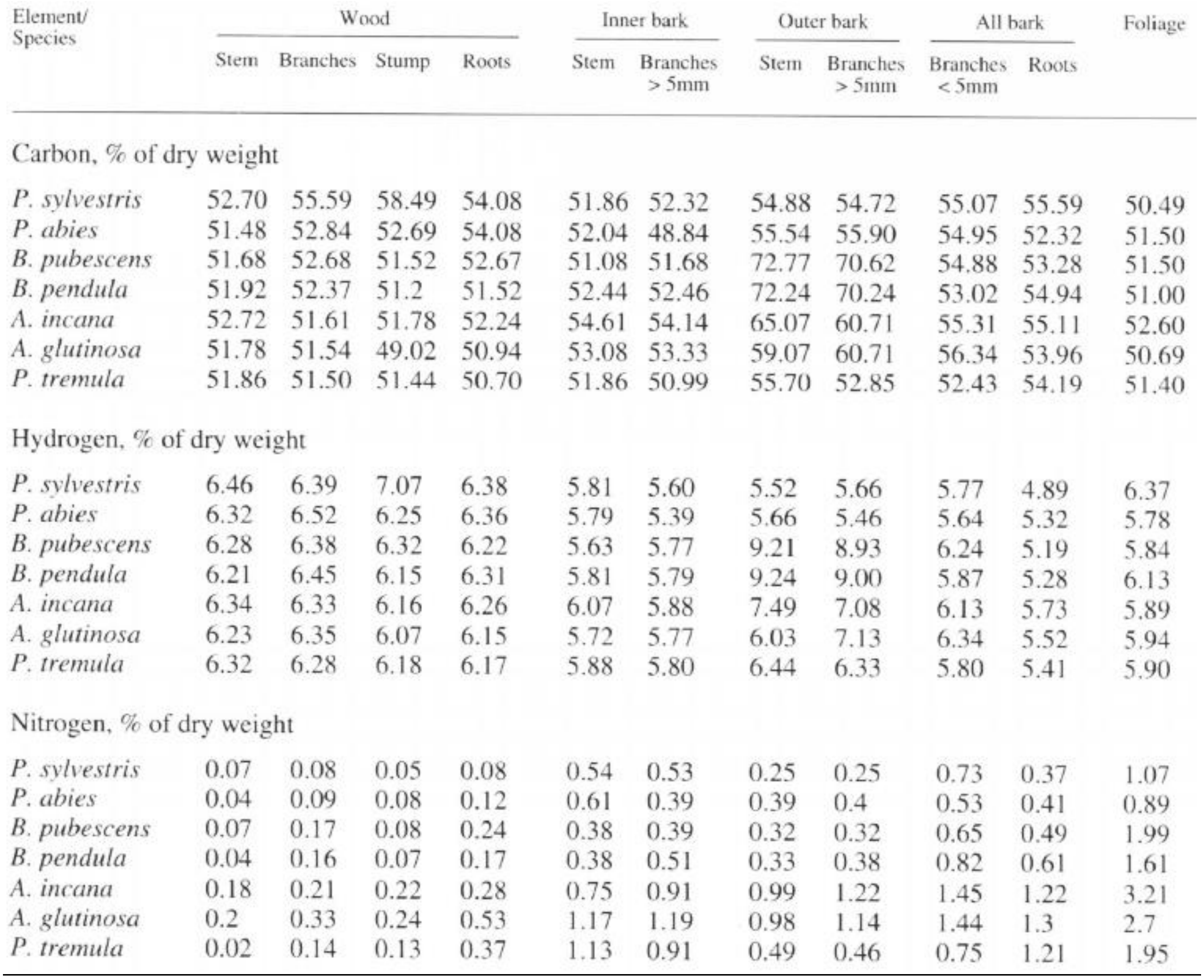
Table 5. Nitrogen contents (%) in birch (Betula pendula/verrucosa), according to the selected Nordic and European studies.

Nordic studies		Other European studies	
Contents (%)	Reference	Contents (%)	Reference
0,06-0,15	Magnusson et al. 1979	0,1	Gottlieb 1883
0,11-0,19	Mälkönen & Saarsalmi 1982	0,12	Schwalbe & Becker 1919
0,08-0,11	Varhimo 1988	0,19	König & Becker 1919
0,08-0,1	Telkkinen 1996, 1999	0,14	Marutzky & Raffael 1977
0,07-0,08	Hedenberg 1996	0,14-0,15	Ovington 1957
0,04-0,07	Nurmi 1997		
0,06	Niemelä and Ulmgren 2002		
0,13	Niemelä et al. 2003		
c. 0,18	Palviainen et al. 2010		

2.3 Nitrogen in wood bark

It has already been mentioned that sapwood and especially bark contains more nitrogen than heartwood. As a good representative example on the nitrogen contents in the main Nordic (Finnish) bark, a summary table from Nurmi (1997) is reproduced (Table 6).

Table 6 Content of carbon, hydrogen and nitrogen in different parts of the main Finnish softwood and hardwood species (Nurmi 1997).



Element/ Species	Wood				Inner bark		Outer bark		All bark		Foliage
	Stem	Branches	Stump	Roots	Stem	Branches > 5mm	Stem	Branches > 5mm	Branches < 5mm	Roots	
Carbon, % of dry weight											
P. sylvestris	52.70	55.59	58.49	54.08	51.86	52.32	54.88	54.72	55.07	55.59	50.49
P. abies	51.48	52.84	52.69	54.08	52.04	48.84	55.54	55.90	54.95	52.32	51.50
B. pubescens	51.68	52.68	51.52	52.67	51.08	51.68	72.77	70.62	54.88	53.28	51.50
B. pendula	51.92	52.37	51.2	51.52	52.44	52.46	72.24	70.24	53.02	54.94	51.00
A. incana	52.72	51.61	51.78	52.24	54.61	54.14	65.07	60.71	55.31	55.11	52.60
A. glutinosa	51.78	51.54	49.02	50.94	53.08	53.33	59.07	60.71	56.34	53.96	50.69
P. tremula	51.86	51.50	51.44	50.70	51.86	50.99	55.70	52.85	52.43	54.19	51.40
Hydrogen, % of dry weight											
P. sylvestris	6.46	6.39	7.07	6.38	5.81	5.60	5.52	5.66	5.77	4.89	6.37
P. abies	6.32	6.52	6.25	6.36	5.79	5.39	5.66	5.46	5.64	5.32	5.78
B. pubescens	6.28	6.38	6.32	6.22	5.63	5.77	9.21	8.93	6.24	5.19	5.84
B. pendula	6.21	6.45	6.15	6.31	5.81	5.79	9.24	9.00	5.87	5.28	6.13
A. incana	6.34	6.33	6.16	6.26	6.07	5.88	7.49	7.08	6.13	5.73	5.89
A. glutinosa	6.23	6.35	6.07	6.15	5.72	5.77	6.03	7.13	6.34	5.52	5.94
P. tremula	6.32	6.28	6.18	6.17	5.88	5.80	6.44	6.33	5.80	5.41	5.90
Nitrogen, % of dry weight											
P. sylvestris	0.07	0.08	0.05	0.08	0.54	0.53	0.25	0.25	0.73	0.37	1.07
P. abies	0.04	0.09	0.08	0.12	0.61	0.39	0.39	0.4	0.53	0.41	0.89
B. pubescens	0.07	0.17	0.08	0.24	0.38	0.39	0.32	0.32	0.65	0.49	1.99
B. pendula	0.04	0.16	0.07	0.17	0.38	0.51	0.33	0.38	0.82	0.61	1.61
A. incana	0.18	0.21	0.22	0.28	0.75	0.91	0.99	1.22	1.45	1.22	3.21
A. glutinosa	0.2	0.33	0.24	0.53	1.17	1.19	0.98	1.14	1.44	1.3	2.7
P. tremula	0.02	0.14	0.13	0.37	1.13	0.91	0.49	0.46	0.75	1.21	1.95

Similar data for pine, spruce and birch bark nitrogen has also been reported by Hedenberg (1996), using material from several Swedish pulp mills. Otherwise, it is especially noteworthy that the highest nitrogen contents always seem to be present in inner bark, demonstrating the role of good debarking as one of the means to control pulp mill's NOx emissions.

2.4 Nature of nitrogen compounds in wood

There should be no doubt that majority of wood nitrogen is bound to proteins, although free amino acids are apparently also always present. Lower amounts of miscellaneous organic nitrogen compounds have also been reported, and in addition, some inorganic compounds (ammonia and nitrate) can be found. The existing literature on wood amino acids and proteins is relatively extensive (Lists 1-2), indicating that typical major plant amino acids also play key roles in trees.

List 1. Studies on characterisation conifer proteins and free amino acids.

Holmes and Kurth (1961), Barnes (1963), Fukuda (1963), Laidlaw and Smith (1965), Durzan and Steward (1967), Hodges et al. (1968), Ziegler (1968), Clark and Mills (1970), Adelsberger and Petrowitz (1976), Butcher and Fountain (1987), Fukuda et al. (1988), Wetzel and Greenwood (1989), Harms and Sauter (1991), Roberts et al. (1991), Pietiläinen and Lähdesmäki (1995), Lähdesmäki and Pietiläinen (1996), Donald et al. (2000), Sudachkova et al. (2000), Hafrén (2007).

List 2. Examples of studies on characterisation of hardwood proteins and amino acids.

Mittler (1953), Reuter and Wolffgang (1954), Bollard (1957), Mugg (1959), Lamport and Northcote (1960), Barnes (1963), Dickson (1989), Dietrchs and Funke (1967), Sauter (1981), Titus et al. (1982), Cleve et al. (1988), Putman et al. (1989, 1991), Wetzel and Greenwood (1991a, 1991b), Harms and Sauter (1992), Sauter and van Cleve (1994), Stepien et al. (1992, 1994), Close (1996), Sauter and Wellenkamp (1998), Sauter et al. (1989, 1999).

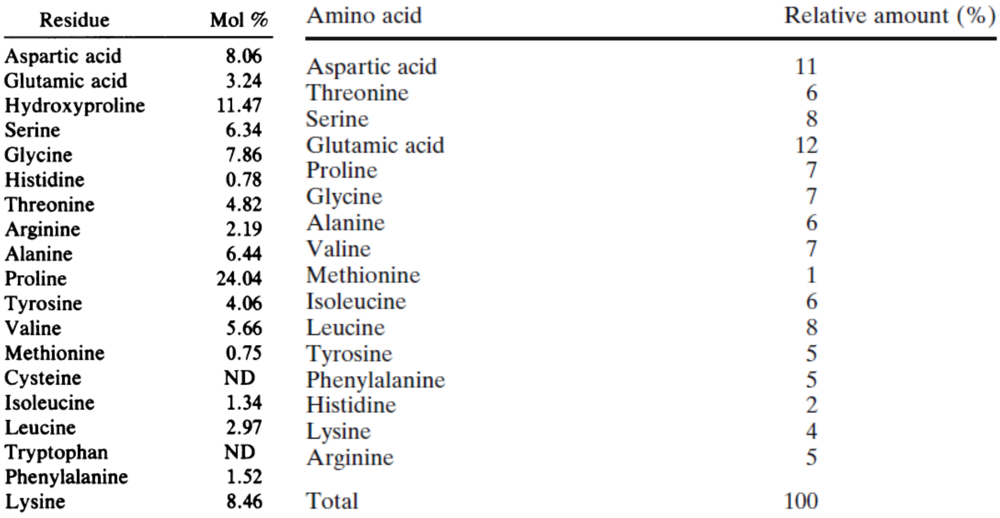
During the past years and, more and more attention has been paid to the roles and characterisation of different cell wall proteins in wood (List 3), as more advanced isolation and analysis techniques have been developed. For example, Gion et al. (2005) identified 175 proteins in a wood forming tissue of maritima pine and found them play a role in either defence (19.4%), carbohydrates (16.6%) and amino acid (14.9%) metabolisms, genes and proteins expression (13.1%), cytoskeleton (8%), cell wall biosynthesis (5.7%), secondary (5.1%) and primary (4%) metabolisms.

List 3. Studies on protein-lignin complexes, protein-polysaccharide complexes and cell wall proteins in wood.

Heath et al. (1971), Whitmore (1982), Dill et al. (1984), Fukuda et al. (1988), Bao et al. (1992), Karácsonyi et al. (1996, 1998), Gion et al. (2005), Makarova et al. (2015), Costa et al. (2016), Fleming et al. (2016).

Examples of amino acid compositions in Nordic softwood raw materials are given in Tables 7-8. Of these amino acids, hydroxyproline produces a specific compound during kraft pulping that can be found in black liquors, condensates, and rectified methanol. Another example (Table 9) refers to a study by Adelsberger and Petrowitz (1976) who analysed total nitrogen and protein in different parts of pine wood stem, and confirmed the dominating role of proteins compared to total nitrogen.

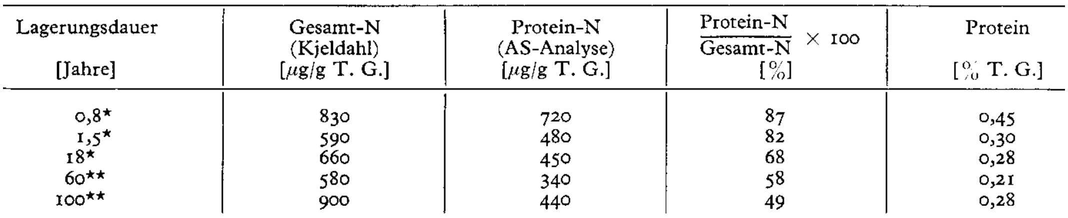
Tables 7-8. Amino acid composition in Scots pine (left, Bao et al. 1992) and Norway spruce TMP pulp proteins (Hafrén 2007).



Residue	Mol %
Aspartic acid	8.06
Glutamic acid	3.24
Hydroxyproline	11.47
Serine	6.34
Glycine	7.86
Histidine	0.78
Threonine	4.82
Arginine	2.19
Alanine	6.44
Proline	24.04
Tyrosine	4.06
Valine	5.66
Methionine	0.75
Cysteine	ND
Isoleucine	1.34
Leucine	2.97
Tryptophan	ND
Phenylalanine	1.52
Lysine	8.46

Amino acid	Relative amount (%)
Aspartic acid	11
Threonine	6
Serine	8
Glutamic acid	12
Proline	7
Glycine	7
Alanine	6
Valine	7
Methionine	1
Isoleucine	6
Leucine	8
Tyrosine	5
Phenylalanine	5
Histidine	2
Lysine	4
Arginine	5
Total	100

Table 3.21. Concentrations of total nitrogen and protein-nitrogen in different annual growth rings of a pine wood stem (Adelsberger and Petrowitz 1976).



Lagerungsdauer [Jahre]	Gesamt-N (Kjeldahl) [μg/g T. G.]	Protein-N (AS-Analyse) [μg/g T. G.]	$\frac{\text{Protein-N}}{\text{Gesamt-N}} \times 100$ [%]	Protein [% T. G.]
0,8*	830	720	87	0,45
1,5*	590	480	82	0,30
18*	660	450	68	0,28
60**	580	340	58	0,21
100**	900	440	49	0,28

3. Fate of wood nitrogen at kraft pulp mills

During the past decades, more and more attention has been paid to the fate of wood nitrogen and its reaction products, both in the fibreline and recovery line processes. Important recent sources of information include extensive studies at Åbo Akademi (Kymäläinen, DeMartini, Vähä-Savo et al.) and EU funded project Rempulp (Reduction of air emissions at kraft pulp mills) (Niemelä et al. 2003). The Rempulp project included the creation of nitrogen balances at three pulp mills, using hardwood (birch and eucalyptus) and softwood as raw materials. In this Chapter, short summary on the key steps is given, supported by selected results mainly from the above studies.

According to the current understanding, nitrogen fate in the pulping stage includes:

- The nitrogen content of the wood raw material is typically 0.05–0.15% (by weight).
- A substantial part of the nitrogen is dissolved from the wood chips into the cooking liquor at early pulping stages; there are no raw material-specific differences. The pulps going to bleaching contain only traces of nitrogen.
- Kjeldahl method was optimised and calibrated for the determination of total nitrogen in black liquors.
- The cooking conditions have only marginal effects on the release of nitrogen from chips.
- Approximately 10–15% of wood nitrogen is converted into ammonia during pulping. Model compound experiments have shown that different amino acids produce ammonia in different yield levels (e.g. 5–20%)
- Most of proteins are apparently linked to kraft lignin that always contains some nitrogen.
- Small amounts of amino acids can also be found in black liquors. Also, there is a number of other (cyclic) compounds formed from different amino acids. Some of the products are specific for certain amino acids, such as the formation of pyrrole from hydroxyproline.

During black liquor evaporation:

- Ammonia and other volatile nitrogen compounds are readily transferred to the condensates at early evaporation stages. There is only some additional ammonia formation during later evaporation stages.
- The extent of nitrogen removal during evaporation can be increased by high-temperature black liquor treatments. The required conditions are, however, probably too drastic for full mill-scale applications. The increased formation of volatile sulphur compounds in such treatments also needs to be taken into account.
- Ammonia and other volatile nitrogen compounds are stripped off from foul condensates, and are thus also found in rectified methanol. Ammonia is always the dominating nitrogen compound in rectified methanol. Some amide-type compounds have not yet been fully identified.
- Ammonia can also be separated as a by-product (from different streams), as happened in Kotka in the 1910s.

In black liquor combustion and white liquor preparation:

- Nitrogen entering the recovery boiler with the black liquor is converted during combustion to gaseous N_2, NO, and cyanate (OCN^-) in the smelt. The combustion conditions can be controlled to increase nitrogen incorporation into smelt which offers certain opportunities to force more nitrogen as ammonia to different gaseous streams (for separate handling or combustion).
- During combustion, carefully designed air staging conditions and novel vertical air systems have strong potential for minimising the NOx emissions.

- Cyanate originating from the smelt is slowly converted into ammonia during green liquor handling and white liquor preparation. The kinetics shows significant mill-to-mill differences.
- Some ammonia is removed from the green and white liquors with the vent gases, but most of it returns to cooking with the white liquor. Ammonia emissions from the causticisation lines may correspond to one third of all nitrogen emissions from the recovery cycles.
- Proper handling of all non-condensable gases (NCGs), stripper off-gases or rectified methanol, and causticisation vent gases is of great importance for controlling the millwide NOx balances. The experience has shown that the recovery boilers offer the best option for the low NOx combustion of these ammonia-containing streams.
- If necessary, it is also possible to remove ammonia from stripper off-gases, methanol or vent gases before combustion. The removed ammonia could be used, for example, in selective catalytic reduction systems at recovery boilers, or as a nutrient (ammonium sulphate or phosphate) at the activated sludge plants.

The following illustrations from the Rempulp project will be inserted and explained to highlight nitrogen behaviour at selected process steps.

Table 2. Characterisation of pine kraft black liquors derived from laboratory pulping at 170 °C.

Compound (fraction)	Kappa number 134	Kappa number 87.5	Kappa number 20.6
Total nitrogen, mg/l	96	170	180
Ammonium nitrogen, 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

Table 3.2. The extent of ammonia formation during laboratory-scale cooking of different raw materials.

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

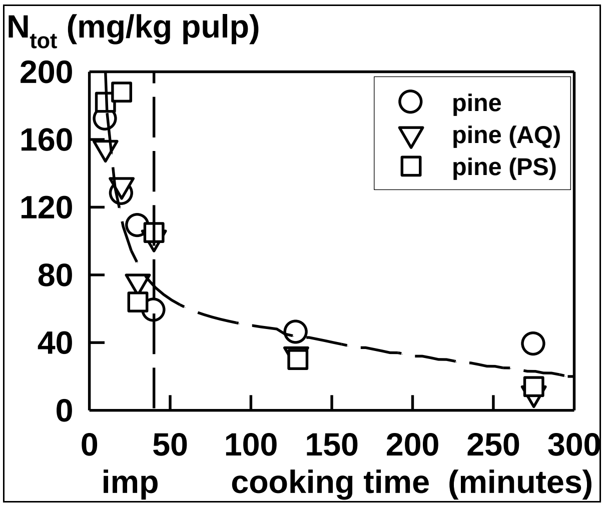
*Another final black liquor contained 162 and 24.1 mg/l of total and ammon. nitrogen, respectively.

**Another final black liquor contained 104 and 11.7 mg/l of total and ammon. nitrogen, respectively.

Table 3.4. The formation of ammonia (% of total nitrogen) after alkali treatment of selected model compounds at 160 or 170 °C for 30 min.

Material	160 °C, NaOH	170 °C, NaOH	170 °C, NaOH/Na_2S
4-Hydroxyproline	8.0	n.s.*	n.s.
Glycine	0.6	1.2	0.5
Serine	13.5	22.0	19.5
Valine	1.4	1.6	0.4
Aspartic acid	n.s.	7.4	n.s.
Glutamic acid	n.s.	1.4	n.s.
Proline	n.s.	2.3	n.s.
Phenylalanine	n.s.	3.6	n.s.
Lysine	n.s.	1.5	n.s.

*ns; not studied.



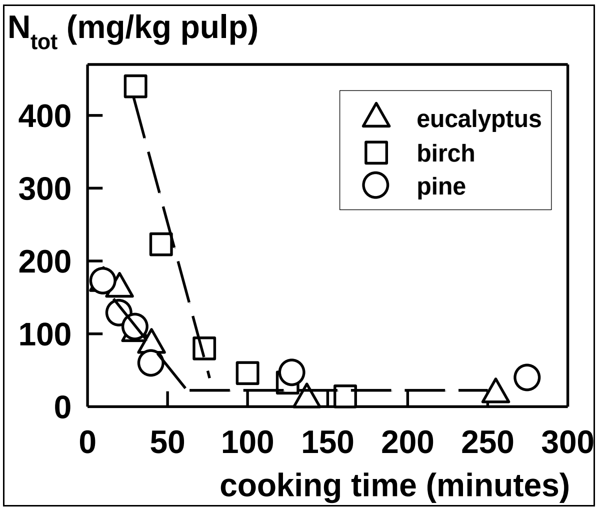
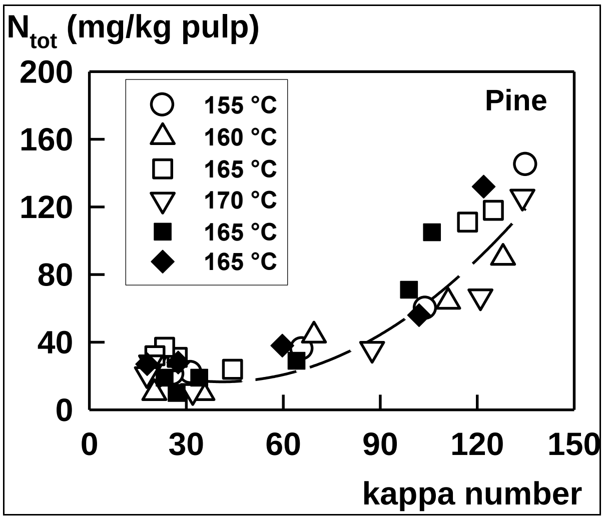


Fig. 3.1 (left). Release of nitrogen from wood chips vs. impregnation (imp) and cooking time for pine cooks with or without addition of anthraquinone (AQ) or polysulphide (PS), at 165 °C.

Fig. 3.2 (right). Release of nitrogen from wood chips versus cooking time. The temperatures for eucalyptus and birch cooks were 147 and 162 °C, respectively.



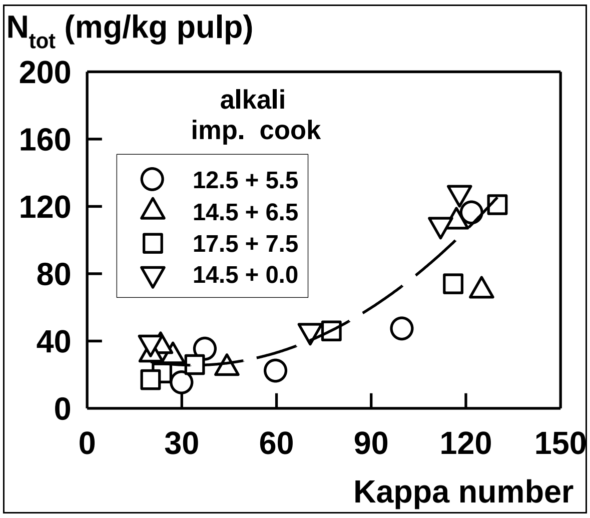


Fig. 3.3 (left). Release of nitrogen from pine wood vs. kappa number during cooking at different temperatures. Unfilled and filled symbols refer to the cooking experiments with synthetic and industrial white liquors, respectively.

Fig. 3.4 (right). Release of nitrogen from pine chips versus kappa number at different distributions of alkali charge (% of wood) between impregnation (first number) and cooking (second number). The cooking temperature was 165 °C.

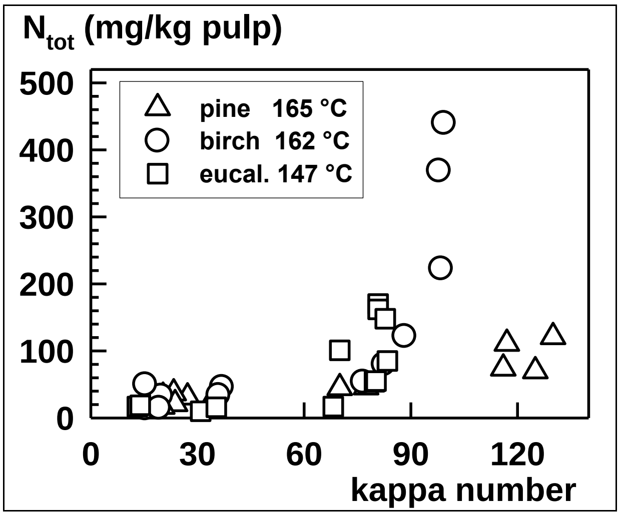


Fig. 3.8. Nitrogen remaining in pulp after cooking of Scandinavian pine and birch, and Portuguese eucalyptus versus kappa numbers. The cooking temperatures are also given.

Table 3.5. Concentrations (mg/l) of amino acids in selected softwood black liquors.

Amino acid	D8-1	D10	EV3
Dry solids, %	21.1	17.6	47.4
Aspartic acid	5.6	0.9	13.7
Glutamic acid	12.4	13.4	24.3
Serine	0.6	0.5	0.5
Glycine	13.7	6.9	7.8
Arginine	21.9	16.6	28.8
Alanine	9	6	12.1
Tyrosine	6.4	4.6	10.1
Cystine	51.5	10.4	8.4
Valine	4.7	2.2	6.6
Methionine	6.8	6.8	10.6
Isoleucine	2.4	1.1	3.6
Leucine	9.8	9.4	17.9
Phenylalanine	–	–	7
Total	135.8	78.8	151.4

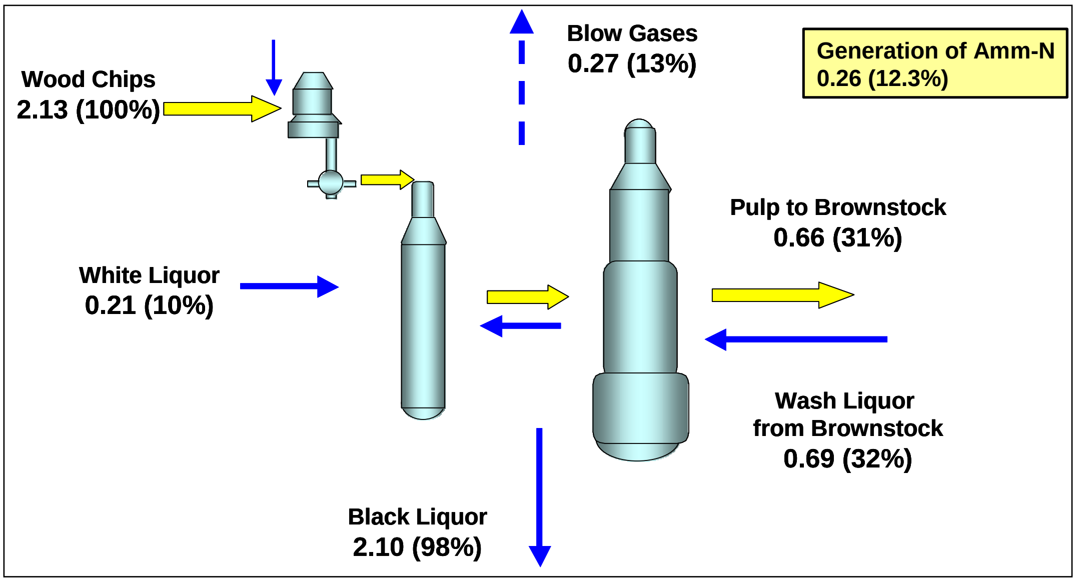


Fig. 3.20. Total nitrogen balances for the digester at one of the study mills. The figures are given as kg N/ton pulp and normalised to nitrogen in wood chips (100%).

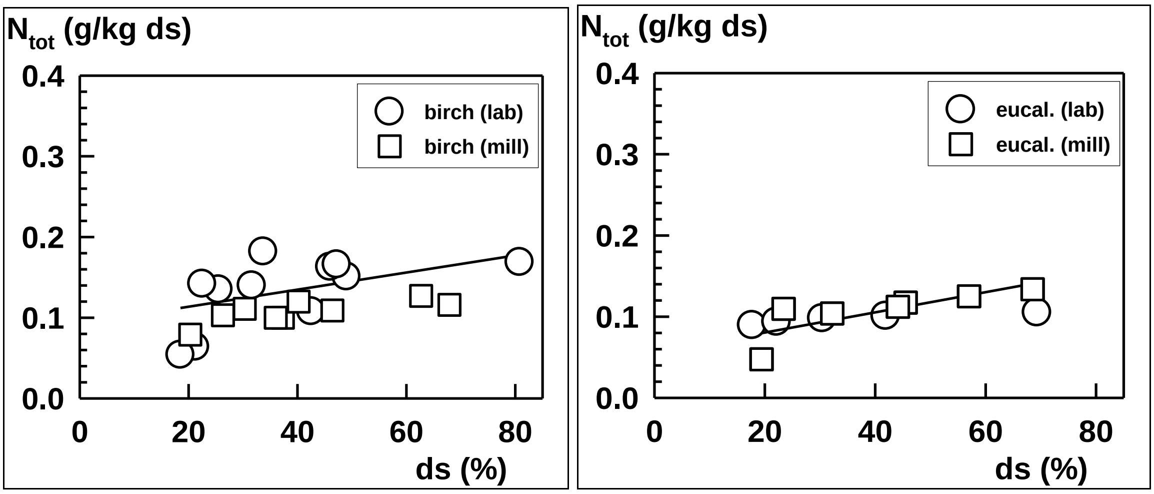


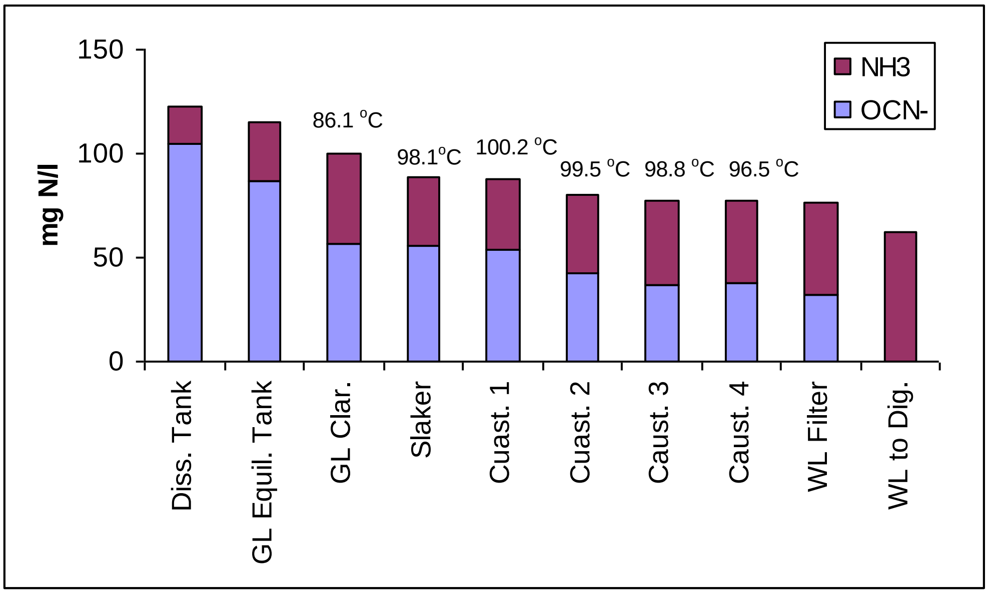
Fig. 3.25 and 3.26. Total release of nitrogen into condensate during laboratory evaporation of birch and eucalyptus black liquors (versus ds). The original nitrogen contents of the liquors were 0.069% for birch lab, 0.083% for birch mill, 0.051% for eucalyptus lab, and 0.086% for eucalyptus mill.

Table 3.10. Release of total nitrogen in laboratory evaporation of black liquors, with and without heat treatment. Procedure: pre-evaporation to 30–50% ds, then heat treatment (HT) and finally evaporation to about 70% ds. N released, amount of N released from the liquors in the laboratory evaporator; –, not determined. The numbers given must be considered rather rough since variations in total nitrogen concentrations in condensates under the same experimental conditions were common.

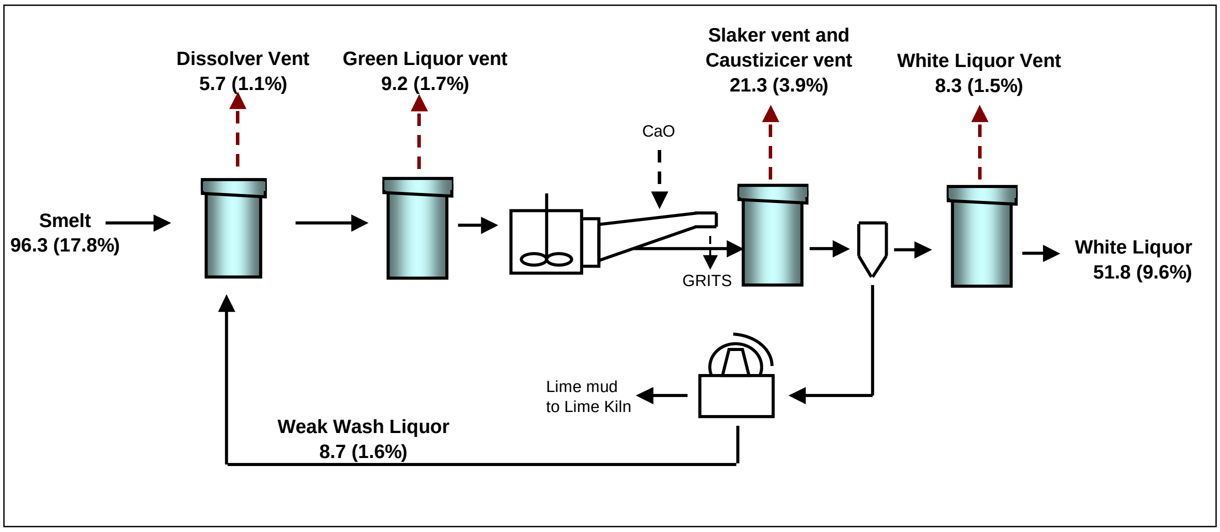
Black liquor	N_{tot} in BL, g/kg ds	Released, no HT	Released, with HT at 200 °C, 3 h	Released, with HT at 200 °C, 16 h	Released, with HT at 300 °C, 2 h
Pine lab	0.59	0.21 (35%)	0.25 (42%)	0.30 (51%)	–
Softw. mill	0.57	0.10 (18%)	0.25 (44%)	0.30 (53%)	–
Birch lab	0.71	0.17 (24%)	0.45 (63%)	–	–
Birch mill*	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%)	–	–

Table 3.22. Rough concentrations (mg/l) of organic nitrogen compounds (calculated as nitrogen) idenified in the investigated methanol samples.

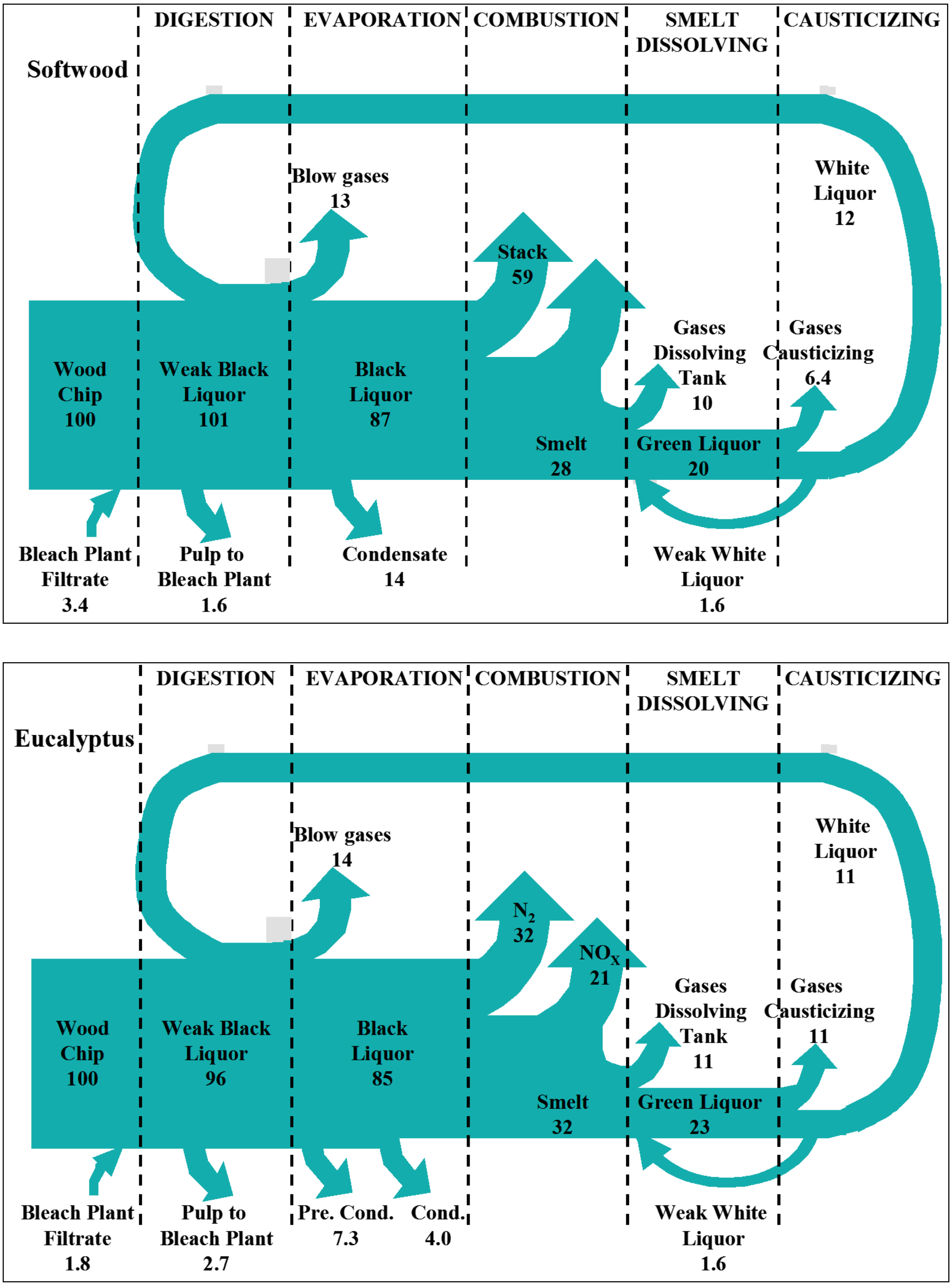
Compound (category)	Mill 1	Mill 2	Mill 3
Pyrrole	65	20	70
1-Methylpyrrole	20	–	30
Miscellaneous heterocyclic	traces	traces	traces
Aliphatic amines	220	150	190
Total	305	170	290



Figs. 3. Concentration of OCN^- and NH_3 in causticising liquors at at one of the study mills.



Figs. 3.132–3.134. Total nitrogen balance for the causticising areas at one of the study mills. The figures are given as kg N/ton of white liquor produced, and in brackets as percent of nitrogen entering the mills with wood chips.



Figs. 3.136 and 3.137. Normalised total nitrogen balances for two study mills. Nitrogen intake with wood chips normalised to 100%.

4. Summary and conclusions

The present review focused on the contents of nitrogen in the Nordic pine, spruce and birch trees, as well as on the nature of organic nitrogen constituents and their behaviour in the kraft process. For comparison, a lot of material was also collected addressing other softwood and hardwood materials, but the corresponding concentrations are not tabulated in detail.

During the comprehensive literature searches it became evident that there is a huge amount of information available on nitrogen contents in dozens of different softwood and hardwood species covering numerous industrially important genera. It also became clear that the studies cover all different tree parts, including twigs and branches, bark, roots, and needles. Furthermore, it is evident that practically taken all the main wood species contain equally low amounts of nitrogen in mature stemwood, as the figures above >0.25–0.3% have only seldom been reported.

For the Nordic wood species, the nitrogen contents in stemwood usually vary from c. 0,05-0,15%, although somewhat higher amounts have also been reported. For the variation, there are apparently many reasons, depending for example on the following factors:

- different applied analytical methods used at different laboratories
- different geographical locations, soil type, and potential fertilisation
- age of wood
- specific sampling point in wood, vs. a bulk sample
- purity of sample, e.g. carefully sorted sample vs. industrial chips

All those factors (known or unknown) make it hard to reach sufficiently detailed or correct final conclusions on the most representative values for the nitrogen contents of wood, especially for pulpwood used at the current pulp mills. Therefore it is now recommended to conduct a national sampling and analysis campaign to cover chips and black liquor samples from all national pulp mills, to be all analysed in the same laboratory. For the black liquors, VTT (KCL) has developed an improved Kjeldahl method (Niemelä and Tuominen 2005).

Appendix 1. Nitrogen and other nutrient concentrations (%) in a number of softwood and hardwood species (Meerts 2002). Softwoods cover genera from Abies to Tsuga.

		Concentrations in sapwood (s) and heartwood (h) (mg kg^{-1})										Heartwood/sapwood				
Species	Taxon	N_s	N_h	P_s	P_h	K_s	K_h	Ca_s	Ca_h	Mg_s	Mg_h	N	P	K	Ca	Mg
Abies firma	1					3000	2000			110	100			0.67		0.91
Abies firma	1			20	2	250	1000	300	400	100	100		0.10	4.00	1.33	1.00
Abies sacchalinensis	1					630	1000	800	1200	150	200			1.59	1.50	1.33
Callitris columellaris	1			10	10	320	230	3170	3710	460	510		1.00	0.72	1.17	1.11
Callitris hugelii	1			55	10	600	380	2960	4710	160	480		0.18	0.63	1.59	3.00
Cedrus deodara	1							1500	300						0.20	
Chamaecyparis obtusa	1					600	500	400	300	75	100			0.83	0.75	1.33
Chamaecyparis thyoides	1							600	200	80	40				0.33	0.50
Cryptomeria japonica	1							606	562	93	184				0.93	1.98
Cryptomeria japonica	1					1600	5600	1000	800	100	200			3.50	0.80	2.00
Cryptomeria japonica	1			70	5.5	375	1150	950	900	85	200		0.08	3.07	0.95	2.35
Larix decidua	1			280	30	678	140	709	600	164	167		0.11	0.21	0.85	1.02
Larix laricina	1			185	20	754	490	559	652	151	323		0.11	0.65	1.17	2.14
Larix leptolepis	1					600	200	400	200	100	50			0.33	0.50	0.50
Metasequoia glyptostroboides	1							800	450	160	100				0.56	0.63
Picea abies	1	1600	800	95	5	900	300	600	700			0.50	0.05	0.33	1.17	
Picea rubens	1					873	522	936	810	166	412			0.60	0.87	2.48
Picea rubens	1							500	800	62	60				1.60	0.97
Picea rubens	1			67	33	776	875	597	673	74	85		0.49	1.13	1.13	1.15
Pinus densiflora	1					450	250	700	900	100	200			0.56	1.29	2.00
Pinus nigra	1	950	910	94	20	900	400	570	660	180	255	0.96	0.21	0.44	1.16	1.42
Pinus rigida	1	870	970	70	20	490	240	810	1040	275	146	1.11	0.29	0.49	1.28	0.53
Pinus strobus	1	1000	450									0.45				
Pinus sylvestris	1	1060	640	100	17	740	130	580	710	240	230	0.60	0.17	0.18	1.22	0.96
Pinus sylvestris	1	790	600	68	33	473	385	796	969	106	140	0.76	0.49	0.81	1.22	1.32
Pinus sylvestris	1	470	400	61	3	300	3	500	600	150	150	0.85	0.05	0.01	1.20	1.00
Podocarpus archboldii	1	1800	2000	110	70	840	1080	1480	1080	220	170	1.11	0.64	1.29	0.73	0.77
Thuyopsis dolobrata	1							706	1330	40	239				1.88	5.98
Tsuga diversifolia	1	750	400									0.53				
Acer rubrum	2	900	400									0.44				
Acer saccharum	2					1260	1502	2874	2812	643	1084			1.19	0.98	1.69
Acer saccharum	2			80	25			8000	1000				0.31		0.13	
Ackama paniculata	2			53	53	1100	210	610	490				1.00	0.19	0.80	
Aesculus turbinata	2					500	1000	1250	3200	500	700			2.00	2.56	1.40
Ardisia sp.	2	1250	1620	90	30	860	130	420	440	160	70	1.30	0.33	0.15	1.05	0.44
Banksia serratifolia	2			58	15	1300	170	580	710				0.26	0.13	1.22	
Betula lenta	2	950	500									0.53				
Carya sp.	2	2500	1500									0.60				
Castanea crenata	2							366	363	210	20.1				0.99	0.10
Castanea crenata	2					1250	560	300	200	300	20			0.45	0.67	0.07
Castanea sativa	2	1588	762	124	6	607	220	377	291	292	115	0.48	0.05	0.36	0.77	0.39
Casuarina cristata	2			70	43	770	1800	8800	8600				0.61	2.34	0.98	
Casuarina torulosa	2			40	10	450	10	630	720	120	140		0.25	0.02	1.14	1.17
Cedrela tonduzii	2	1200	600									0.50				
Ceiba pentendra	2	3900	1100									0.28				
Ceratopetalum apetalum	2			209	113	1940	1695	187	944				0.54	0.87	5.05	
Ceratopetalum apetalum	2	1700	1400	45	40	800	1100	3210	1930	240	370	0.82	0.89	1.38	0.60	1.54
Cornus florida	2	2000	2000									1.00				
Cryptocarya sp.	2	1000	1570	140	120	960	990	700	1200	950	3400	1.57	0.86	1.03	1.71	3.58
Dryadodaphne crassa	2	1370	1030	60	10	2300	540	540	4300	1220	710	0.75	0.17	0.23	7.96	0.58
Elaeocarpus ptilanthus	2	1200	1230	100	40	1180	720	1030	1700	210	1030	1.03	0.40	0.61	1.65	4.90
Eucalyptus cameronii	2			53	3	370	25	240	30				0.06	0.07	0.13	
Eucalyptus campanulata	2			53	3	160	32	60	25				0.06	0.20	0.42	
Eucalyptus dalrympleana	2	2000	1000	615	870	2250	600	580	1430	470	360	0.50	1.41	0.27	2.47	0.77

Eucalyptus dives	2	1200	700	75	10	1050	180	640	180	180	40	0.58	0.13	0.17	0.28	0.22
Eucalyptus grandis	2	3100	1500	130	5	1250	200	650	750	200	230	0.48	0.04	0.16	1.15	1.15
Eucalyptus gummifera	2			60	5	900	50	310	160	110	90		0.08	0.06	0.52	0.82
Eucalyptus laevopinea	2	1900	1100	70	15	650	20	260	240	130	80	0.58	0.21	0.03	0.92	0.62
Eucalyptus maculata	2	1800	1000	50	5	800	220	1240	2370	340	770	0.56	0.10	0.28	1.91	2.26
Eucalyptus oleosa	2			45	3	1600	540	1600	2700				0.07	0.34	1.69	
Eucalyptus saligna	2			110	3	1000	35	500	100				0.03	0.04	0.20	
Fagus sylvatica	2	1500	800	165	70	1100	950	700	850	180	225	0.53	0.42	0.86	1.21	1.25
Flindersia maculosa	2			70	43	900	790	4200	3500				0.61	0.88	0.83	
Flindersia pimenteliana	2	730	1710	60	20	640	20	170	1350	190	170	2.34	0.33	0.03	7.94	0.89
Fraxinus americana	2	1700	900									0.53				
Galbulimima belgraveana	2	1450	1470	50	330	2410	2070	1170	890	830	480	1.01	6.60	0.86	0.76	0.58
Geijera parviflora	2			190	120	900	3200	15000	12000				0.63	3.56	0.80	
Hovenia dulcis	2					2000	2000	1000	1600	450	450			1.00	1.60	1.00
Jacaranda copaia	2	1600	1400									0.88				
Kalopanax pictus	2							1090	2050	241	243				1.88	1.01
Kalopanax pictus	2					1500	1250	1000	1600	250	310			0.83	1.60	1.24
Licaria cayennensis	2	1100	1100									1.00				
Liriodendron tulipifera	2	1500	1000									0.67				
Maclura pomifera	2			390	10			4600	2700	700	300		0.03		0.59	0.43
Magnolia obovata	2					800	125	450	210	80	2			0.16	0.47	0.03
Nothofagus truncata	2	630	375			1200	550	1000	650	200	250	0.60		0.46	0.65	1.25
Ochroma lagopus	2	1800	500									0.28				
Orites excelsa	2			94	27	1300	400	92	270				0.29	0.31	2.93	
Orvenia acidula	2			81	11	1000	290	4900	7000				0.14	0.29	1.43	
Oxydendron arboreum	2	2500	2300									0.92				
Phellodendron amurense	2					1500	300	910	800		200			0.20	0.88	
Planchonella firma	2	1400	2500	100	70	1470	1900	750	1350	400	710	1.79	0.70	1.29	1.80	1.78
Populus robusta	2			390	44	980	1760	1400	4000	240	730		0.11	1.80	2.86	3.04
Populus trichocarpa	2			107	39	970	2800	980	1920	180	400		0.36	2.89	1.96	2.22
Prunus sargentii	2							510	532	233	68.5				1.04	0.29
Prunus avium	2	1100	600	130	10	800	400	1100	1800	230	180	0.55	0.08	0.50	1.64	0.78
Quercus alba	2			115		1311	900	1050	708	92	17		0.00	0.69	0.67	0.18
Quercus alba	2	1530	1880	190	50	1160	730	850	1020	178	113	1.23	0.26	0.63	1.20	0.63
Quercus alba	2			188	12	1609	548	994	713	108	19		0.06	0.34	0.72	0.18
Quercus alba	2	900	550	100	70	1000	700	3300	1000	140	150	0.61	0.70	0.70	0.30	1.07
Quercus alba	2	4000	1500									0.38				
Quercus coccinea	2	1000	1400	27	20	1360	610	520	500	165	56	1.40	0.74	0.45	0.96	0.34
Quercus coccinea	2			162	6.3	1056	485	532	201	140	22		0.04	0.46	0.38	0.16
Quercus coccinea	2	3000	2000									0.67				
Quercus petraea	2					1100	640	3000	2000	140	25			0.58	0.67	0.18
Quercus prinus	2	2000	1000									0.50				
Quercus robur	2	2500	1200	200	20	2200	600	600	400	300	30	0.48	0.10	0.27	0.67	0.10
Quercus robur	2	2150	1450	160	30	1750	900	1250	950	600	165	0.67	0.19	0.51	0.76	0.28
Quercus robur	2	1800	1100	325	52	1750	650	525	395	190	42	0.61	0.16	0.37	0.75	0.22
Quercus robur	2	2750	900	180	10	1500	300	340	220	160	50	0.33	0.06	0.20	0.65	0.31
Quercus rubra	2	3100	800									0.26				
Quercus rubra	2	950	650	100	70	800	650	1250	600	110	80	0.68	0.70	0.81	0.48	0.73
Quercus rubra	2	2300	900									0.39				
Quercus serrata	2					1600	1600	630	450	100	20			1.00	0.71	0.20
Robinia pseudoacacia	2			310	30	1800	1500	1700	1300	190	160		0.10	0.83	0.76	0.84
Sloanea pulleniana	2	830	860	80	150	1650	2460	4040	2700	710	880	1.04	1.88	1.49	0.67	1.24
Sorbus alnifolia	2							1000	1500	300	400				1.50	1.33
Sphenostemon papuanum	2	1560	1610	110	180	3800	4500	1410	1610	1290	2300	1.03	1.64	1.18	1.14	1.78
Symphonia globulifera	2	1900	500									0.26				
Syncarpia glomulifera	2			70	5	950	45	600	130	250	75		0.07	0.05	0.22	0.30
Tarretia actinophylla	2			91	80	2600	900	760	750				0.88	0.35	0.99	
Tristania conferta	2	1800	1700	75	5	1050	1050	800	1750	130	600	0.94	0.07	1.00	2.19	4.62
Vouacapoua americana	2	1300	1200									0.92				
Zelkova serrata	2							1600	1000	560	320				0.63	0.57

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