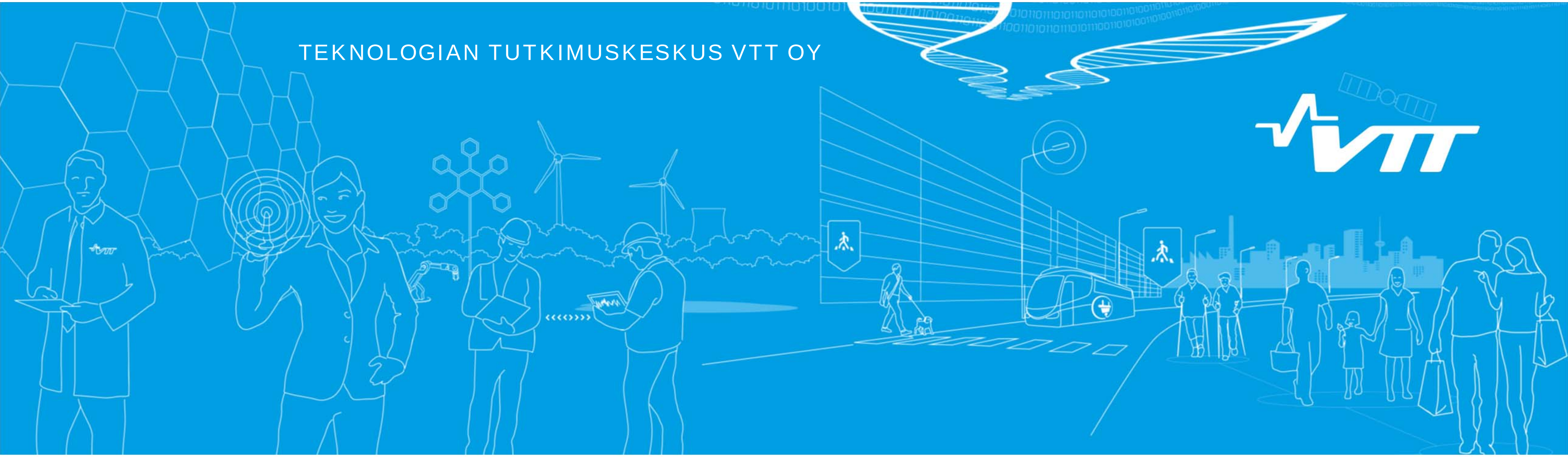
LIITE 1

VTT, Soodakattilan NOx-päästön riippuvuus puuraaka-aineen typpipitoisuudesta – tilanneraportti 30.9.2017

TEKNOLOGIAN TUTKIMUSKESKUS VTT OY



Typpikatsauksen tilanne

SKY/YTR 30.8.2017
Klaus Niemelä

Nitrogen in wood and its fate in kraft pulping

- Kolme pääaihetta
    - Puun typpipitoisuus ja sen vaihteluun vaikuttavat tekijät
    - Puun typpiyhdisteet (proteiinit, vapaat aminohapot, muut)
    - Puun typpiyhdisteiden käyttäytyminen keitossa

- Aineisto
    - Aikaisemmissa projekteissa kerätty
    - Uudet haut VTT:n käytössä olevista lähteistä
    - Rempulp-projektin (2000-2002) julkaisemattomat tulokset keiton ja haihdutuksen osalta

Tavoitteet vs. materiaalin kattavuus

- Niukan puoleisesti julkaistu:
  - Kotimaisen männyn ja koivun typpipitoisuuksia v. 2000-.
  - Lannoituksen vaikutuksia yksikössä ”% typpeä puussa” (usein kg/ha).
  - Proteiinien ja aminohappojen käyttäytyminen alkalissa korkeassa lämpötilassa, esim. ammoniakin muodostuminen.
  - Typpi keitossa, mustalipeätypen muodostuminen

- Runsaasti julkaistu:
  - Typpipitoisuuden vaihtelu puun eri osissa (esimerkkejä), ml. kuori. Aina ei taulukoituja lukuja vaan tulokset ”epätarkkoina” kuvina.
  - Typen yleinen merkitys puun kasvulle (aina ei typpipitoisuuksia analysoitu), typen kiertokulku metsissä.
  - Radiata-männyn ja muiden ulkomaisten puiden typpikysymyksiä (useita esimerkkejä otettu mukaan, kattava viiteluettelo).
  - Puun proteiinit yleensä, myös soluseinän rakennemateriaaleina (eritoten viim. 15-20 v. aikana), vastaavat analyysimenetelmät. Kuitenkin niukasti kotimaisista lajeista.

Raportin alkuperäinen rakenne

- Keskeiset luvut ”Nitrogen in softwood” ja ”Nitrogen in hardwood”
- Esim. ”Nitrogen in softwood” –luvun alkup. rakenne & tavoite:
  - Mukaan lähes kaikki löydetyt kuvat ja taulukot joissa jonkin havupuun typpipitoisuuksia (ympäri maailmaa)
  - → Esitetyissä taulukoissa usein mukana myös runsaasti lehtipuita
  - → Erityisesti taulukoissa (ja kuvissa) runsaasti myös tarpeetonta materiaalia
  - → Kotimaiset puulajit eksyvät helposti kaiken materiaalin sekaan; niistä erilliset yhteenvetotaulukot hankala koota

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⇨ Tuloksena vaikeaselkoinen ja sekava luku havupuun typestä

⇨ Erittäin vaikea jatkaa selkeästi lehtipuun typellä (ristikkäisviittaukset ym)

Raportin rakenne – uusittu versio

- ”Nitrogen in softwood” -luvun uusi rakenne
  - Alkuun yhteenvetotaulukko kotimaisen männyn ja kuusen typpi(pitoisuus)tutkimuksista
  - Tämän jälkeen mahdollisimman kattavasti julkaistut kotimaisten lajien typpitulokset (maittain, paikkakunnittain, lannoituksen vaikutus, jne)
  - Valikoituja kuvia typen jakautumisesta rungon eri osissa
  - Lopuksi vastaava kooste ulkomaisten havupuiden typpituloksista, kirjallisuusviitteet kuitenkin kattavasti
  - Erillinen lyhyt yhteenveto kuoren typpitoisuuksista
  - Ei skannattuja alkuperäistaulukoita

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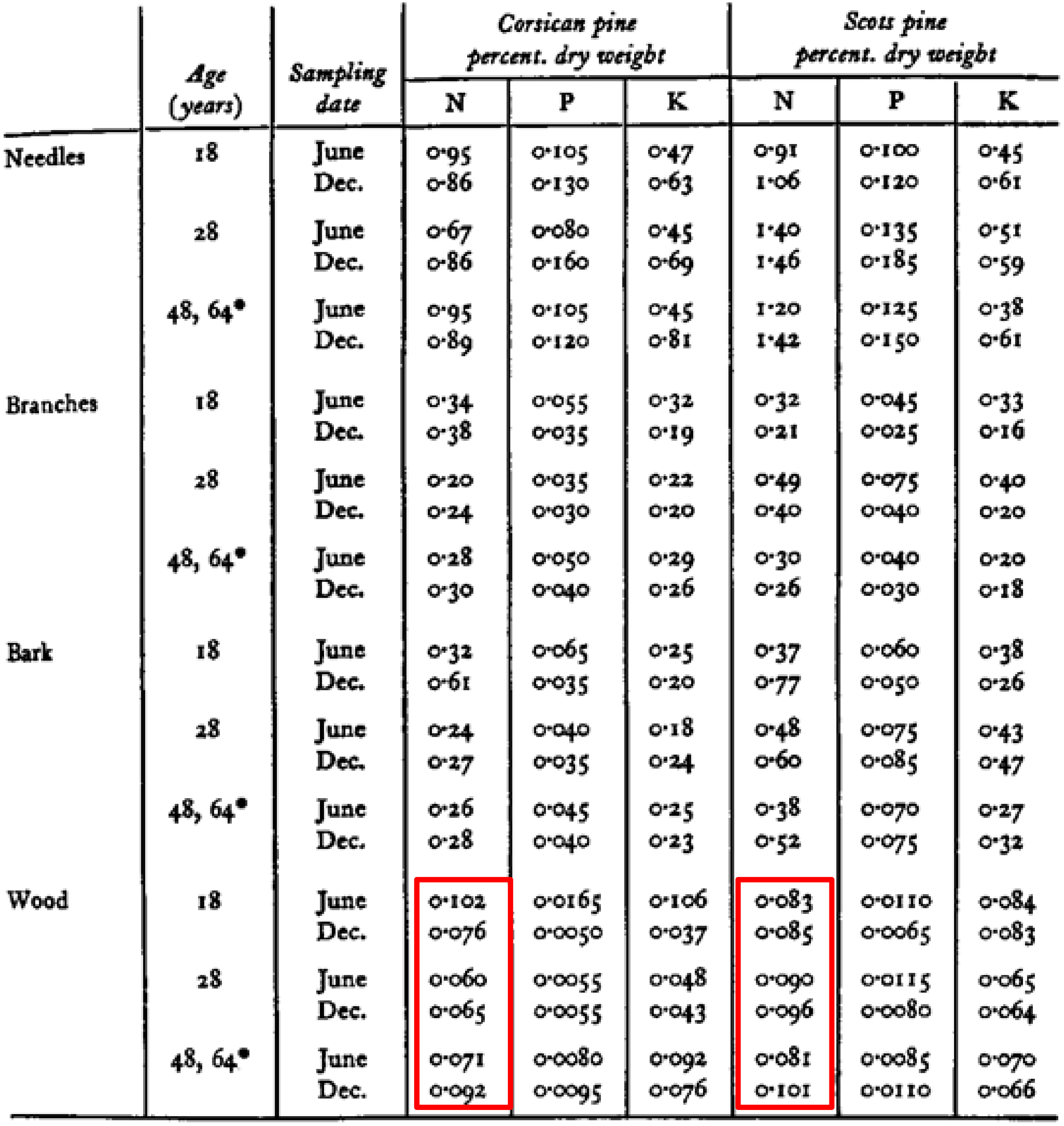
  - Ei skannattuja alkuperäistaulukoita

- ”Nitrogen in hardwood” -luku samalla periaatteella
  - Kotimaiset koivut, haapa ja leppä erikseen
  - Muut lehtipuut edustavasti vertailevaan yhteenvetotaulukkoon

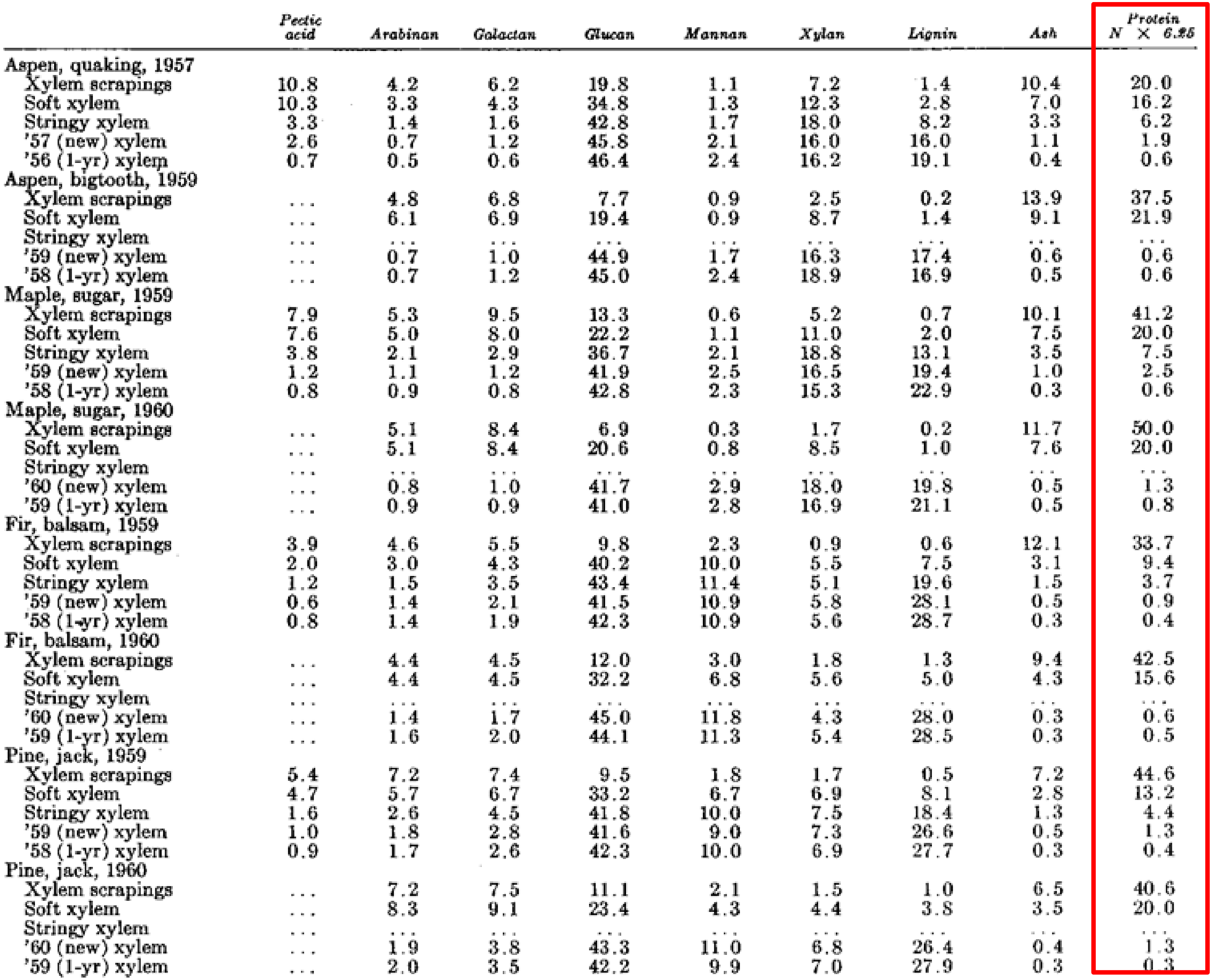
Table 3.10. Seasonal variation in contents of nitrogen and other nutrients in different parts of two pine species (Wright and Will 1958).

Esimerkki 1.



	Age (*years*)	*Sampling date*	*Corsican pine percent. dry weight*			*Scots pine percent. dry weight*		
			N	P	K	N	P	K
Needles	18	June	0·95	0·105	0·47	0·91	0·100	0·45
		Dec.	0·86	0·130	0·63	1·06	0·120	0·61
	28	June	0·67	0·080	0·45	1·40	0·135	0·51
		Dec.	0·86	0·160	0·69	1·46	0·185	0·59
	48, 64*	June	0·95	0·105	0·45	1·20	0·125	0·38
		Dec.	0·89	0·120	0·81	1·42	0·150	0·61
Branches	18	June	0·34	0·055	0·32	0·32	0·045	0·33
		Dec.	0·38	0·035	0·19	0·21	0·025	0·16
	28	June	0·20	0·035	0·22	0·49	0·075	0·40
		Dec.	0·24	0·030	0·20	0·40	0·040	0·20
	48, 64*	June	0·28	0·050	0·29	0·30	0·040	0·20
		Dec.	0·30	0·040	0·26	0·26	0·030	0·18
Bark	18	June	0·32	0·065	0·25	0·37	0·060	0·38
		Dec.	0·61	0·035	0·20	0·77	0·050	0·26
	28	June	0·24	0·040	0·18	0·48	0·075	0·43
		Dec.	0·27	0·035	0·24	0·60	0·085	0·47
	48, 64*	June	0·26	0·045	0·25	0·38	0·070	0·27
		Dec.	0·28	0·040	0·23	0·52	0·075	0·32
Wood	18	June	0·102	0·0165	0·106	0·083	0·0110	0·084
		Dec.	0·076	0·0050	0·037	0·085	0·0065	0·083
	28	June	0·060	0·0055	0·048	0·090	0·0115	0·065
		Dec.	0·065	0·0055	0·043	0·096	0·0080	0·064
	48, 64*	June	0·071	0·0080	0·092	0·081	0·0085	0·070
		Dec.	0·092	0·0095	0·076	0·101	0·0110	0·066

Table 3.19. Percentage composition of different hardwoods and softwoods (Haas and Kremer 1964). Most of the analysed trees were 25–100 years old.

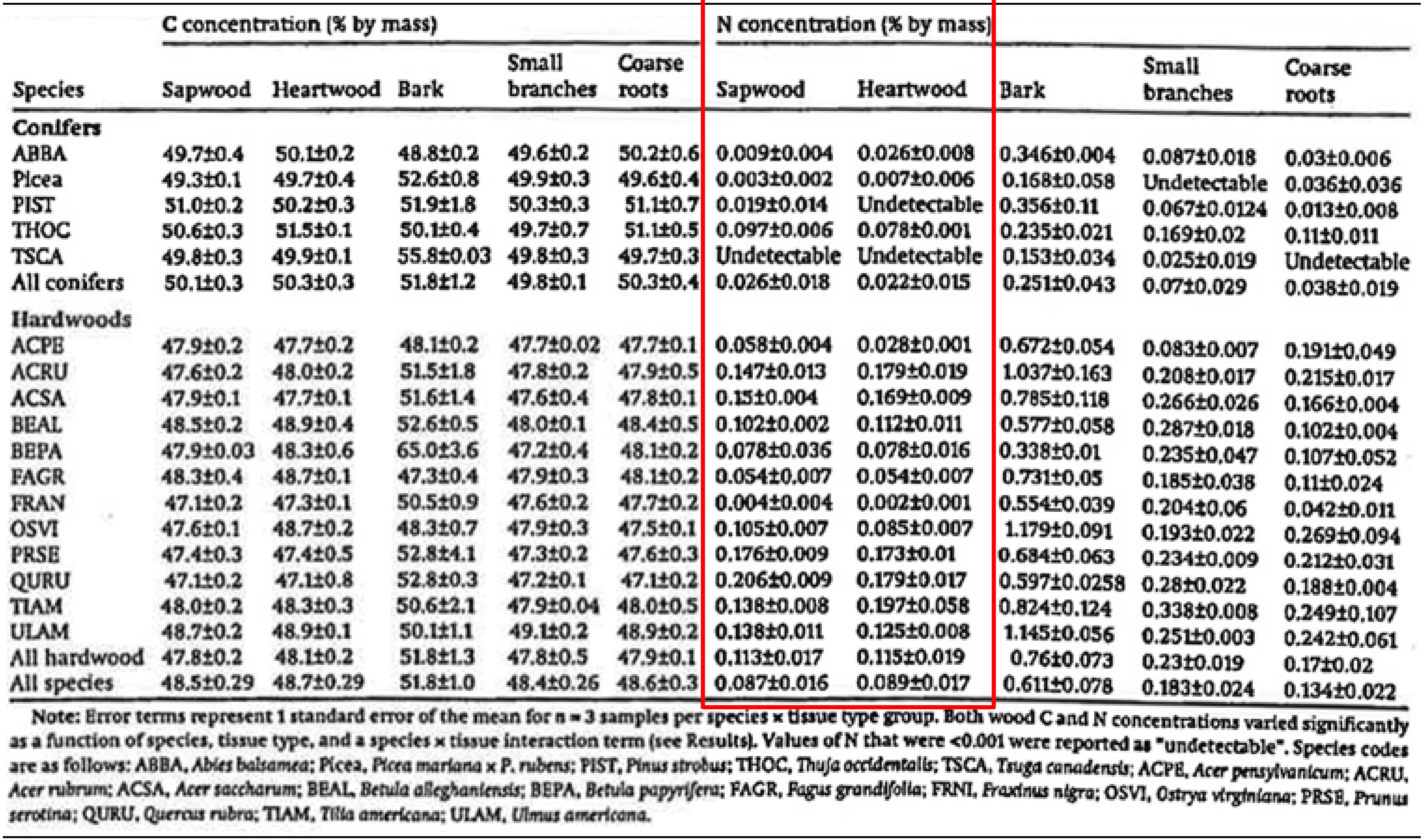


	Pectic acid	*Arabinan*	*Galactan*	*Glucan*	*Mannan*	*Xylan*	*Lignin*	*Ash*	*Protein* N × 6.25
Aspen, quaking, 1957									
Xylem scrapings	10.8	4.2	6.2	19.8	1.1	7.2	1.4	10.4	20.0
Soft xylem	10.3	3.3	4.3	34.8	1.3	12.3	2.8	7.0	16.2
Stringy xylem	3.3	1.4	1.6	42.8	1.7	18.0	8.2	3.3	6.2
'57 (new) xylem	2.6	0.7	1.2	45.8	2.1	16.0	16.0	1.1	1.9
'56 (1-yr) xylem	0.7	0.5	0.6	46.4	2.4	16.2	19.1	0.4	0.6
Aspen, bigtooth, 1959									
Xylem scrapings	...	4.8	6.8	7.7	0.9	2.5	0.2	13.9	37.5
Soft xylem	...	6.1	6.9	19.4	0.9	8.7	1.4	9.1	21.9
Stringy xylem	...	...	...	...	...	...	...	...	...
'59 (new) xylem	...	0.7	1.0	44.9	1.7	16.3	17.4	0.6	0.6
'58 (1-yr) xylem	...	0.7	1.2	45.0	2.4	18.9	16.9	0.5	0.6
Maple, sugar, 1959									
Xylem scrapings	7.9	5.3	9.5	13.3	0.6	5.2	0.7	10.1	41.2
Soft xylem	7.6	5.0	8.0	22.2	1.1	11.0	2.0	7.5	20.0
Stringy xylem	3.8	2.1	2.9	36.7	2.1	18.8	13.1	3.5	7.5
'59 (new) xylem	1.2	1.1	1.2	41.9	2.5	16.5	19.4	1.0	2.5
'58 (1-yr) xylem	0.8	0.9	0.8	42.8	2.3	15.3	22.9	0.3	0.6
Maple, sugar, 1960									
Xylem scrapings	...	5.1	8.4	6.9	0.3	1.7	0.2	11.7	50.0
Soft xylem	...	5.1	8.4	20.6	0.8	8.5	1.0	7.6	20.0
Stringy xylem	...	...	...	...	...	...	...	...	...
'60 (new) xylem	...	0.8	1.0	41.7	2.9	18.0	19.8	0.5	1.3
'59 (1-yr) xylem	...	0.9	0.9	41.0	2.8	16.9	21.1	0.5	0.8
Fir, balsam, 1959									
Xylem scrapings	3.9	4.6	5.5	9.8	2.3	0.9	0.6	12.1	33.7
Soft xylem	2.0	3.0	4.3	40.2	10.0	5.5	7.5	3.1	9.4
Stringy xylem	1.2	1.5	3.5	43.4	11.4	5.1	19.6	1.5	3.7
'59 (new) xylem	0.6	1.4	2.1	41.5	10.9	5.8	28.1	0.5	0.9
'58 (1-yr) xylem	0.8	1.4	1.9	42.3	10.9	5.6	28.7	0.3	0.4
Fir, balsam, 1960									
Xylem scrapings	...	4.4	4.5	12.0	3.0	1.8	1.3	9.4	42.5
Soft xylem	...	4.4	4.5	32.2	6.8	5.6	5.0	4.3	15.6
Stringy xylem	...	...	...	...	...	...	...	...	...
'60 (new) xylem	...	1.4	1.7	45.0	11.8	4.3	28.0	0.3	0.6
'59 (1-yr) xylem	...	1.6	2.0	44.1	11.3	5.4	28.5	0.3	0.5
Pine, jack, 1959									
Xylem scrapings	5.4	7.2	7.4	9.5	1.8	1.7	0.5	7.2	44.6
Soft xylem	4.7	5.7	6.7	33.2	6.7	6.9	8.1	2.8	13.2
Stringy xylem	1.6	2.6	4.5	41.8	10.0	7.5	18.4	1.3	4.4
'59 (new) xylem	1.0	1.8	2.8	41.6	9.0	7.3	26.6	0.5	1.3
'58 (1-yr) xylem	0.9	1.7	2.6	42.3	10.0	6.9	27.7	0.3	0.4
Pine, jack, 1960									
Xylem scrapings	...	7.2	7.5	11.1	2.1	1.5	1.0	6.5	40.6
Soft xylem	...	8.3	9.1	23.4	4.3	4.4	3.8	3.5	20.0
Stringy xylem	...	...	...	...	...	...	...	...	...
'60 (new) xylem	...	1.9	3.8	43.3	11.0	6.8	26.4	0.4	1.3
'59 (1-yr) xylem	...	2.0	3.5	42.2	9.9	7.0	27.9	0.3	0.3

Esim. 2.

Table 3.35. Mean carbon and nitrogen concentrations for 17 Canadian tree species across five woody issue types (Martin et al 2015). The nitrogen concentrations in some softwood materials are very low, i.e. 0.03% or below that.

Esim. 3.



Species	C concentration (% by mass) Sapwood	Heartwood	Bark	Small branches	Coarse roots	N concentration (% by mass) Sapwood	Heartwood	Bark	Small branches	Coarse roots
Conifers										
ABBA	49.7±0.4	50.1±0.2	48.8±0.2	49.6±0.2	50.2±0.6	0.009±0.004	0.026±0.008	0.346±0.004	0.087±0.018	0.03±0.006
Picea	49.3±0.1	49.7±0.4	52.6±0.8	49.9±0.3	49.6±0.4	0.003±0.002	0.007±0.006	0.168±0.058	Undetectable	0.036±0.036
PIST	51.0±0.2	50.2±0.3	51.9±1.8	50.3±0.3	51.1±0.7	0.019±0.014	Undetectable	0.356±0.11	0.067±0.0124	0.013±0.008
THOC	50.6±0.3	51.5±0.1	50.1±0.4	49.7±0.7	51.1±0.5	0.097±0.006	0.078±0.001	0.235±0.021	0.169±0.02	0.11±0.011
TSCA	49.8±0.3	49.9±0.1	55.8±0.03	49.8±0.3	49.7±0.3	Undetectable	Undetectable	0.153±0.034	0.025±0.019	Undetectable
All conifers	50.1±0.3	50.3±0.3	51.8±1.2	49.8±0.1	50.3±0.4	0.026±0.018	0.022±0.015	0.251±0.043	0.07±0.029	0.038±0.019
Hardwoods										
ACPE	47.9±0.2	47.7±0.2	48.1±0.2	47.7±0.02	47.7±0.1	0.058±0.004	0.028±0.001	0.672±0.054	0.083±0.007	0.191±0.049
ACRU	47.6±0.2	48.0±0.2	51.5±1.8	47.8±0.2	47.9±0.5	0.147±0.013	0.179±0.019	1.037±0.163	0.208±0.017	0.215±0.017
ACSA	47.9±0.1	47.7±0.1	51.6±1.4	47.6±0.4	47.8±0.1	0.15±0.004	0.169±0.009	0.785±0.118	0.266±0.026	0.166±0.004
BEAL	48.5±0.2	48.9±0.4	52.6±0.5	48.0±0.1	48.4±0.5	0.102±0.002	0.112±0.011	0.577±0.058	0.287±0.018	0.102±0.004
BEPA	47.9±0.03	48.3±0.6	65.0±3.6	47.2±0.4	48.1±0.2	0.078±0.036	0.078±0.016	0.338±0.01	0.235±0.047	0.107±0.052
FAGR	48.3±0.4	48.7±0.1	47.3±0.4	47.9±0.3	48.1±0.2	0.054±0.007	0.054±0.007	0.731±0.05	0.185±0.038	0.11±0.024
FRAN	47.1±0.2	47.3±0.1	50.5±0.9	47.6±0.2	47.7±0.2	0.004±0.004	0.002±0.001	0.554±0.039	0.204±0.06	0.042±0.011
OSVI	47.6±0.1	48.7±0.2	48.3±0.7	47.9±0.3	47.5±0.1	0.105±0.007	0.085±0.007	1.179±0.091	0.193±0.022	0.269±0.094
PRSE	47.4±0.3	47.4±0.5	52.8±4.1	47.3±0.2	47.6±0.3	0.176±0.009	0.173±0.01	0.684±0.063	0.234±0.009	0.212±0.031
QURU	47.1±0.2	47.1±0.8	52.8±0.3	47.2±0.1	47.1±0.2	0.206±0.009	0.179±0.017	0.597±0.0258	0.28±0.022	0.188±0.004
TIAM	48.0±0.2	48.3±0.3	50.6±2.1	47.9±0.04	48.0±0.5	0.138±0.008	0.197±0.058	0.824±0.124	0.338±0.008	0.249±0.107
ULAM	48.7±0.2	48.9±0.1	50.1±1.1	49.1±0.2	48.9±0.2	0.138±0.011	0.125±0.008	1.145±0.056	0.251±0.003	0.242±0.061
All hardwood	47.8±0.2	48.1±0.2	51.8±1.3	47.8±0.5	47.9±0.1	0.113±0.017	0.115±0.019	0.76±0.073	0.23±0.019	0.17±0.02
All species	48.5±0.29	48.7±0.29	51.8±1.0	48.4±0.26	48.6±0.3	0.087±0.016	0.089±0.017	0.611±0.078	0.183±0.024	0.134±0.022

Note: Error terms represent 1 standard error of the mean for n = 3 samples per species × tissue type group. Both wood C and N concentrations varied significantly as a function of species, tissue type, and a species × tissue interaction term (see Results). Values of N that were <0.001 were reported as "undetectable". Species codes are as follows: ABBA, *Abies balsamea*; Picea, *Picea mariana* × *P. rubens*; PIST, *Pinus strobus*; THOC, *Thuja occidentalis*; TSCA, *Tsuga canadensis*; ACPE, *Acer pensylvanicum*; ACRU, *Acer rubrum*; ACSA, *Acer saccharum*; BEAL, *Betula alleghaniensis*; BEPA, *Betula papyrifera*; FAGR, *Fagus grandifolia*; FRNI, *Fraxinus nigra*; OSVI, *Ostrya virginiana*; PRSE, *Prunus serotina*; QURU, *Quercus rubra*; TIAM, *Tilia americana*; ULAM, *Ulmus americana*.

Typpipitoisuuksista – mänty (P. sylvestris)

Yhteenvetotaulukkoa raportista (alkup.)

Country	N (%)	Table or Figure	Reference
Finland	0.07	Table 3.32	Nurmi et al. (1997)
Finland	0.048	Table 3.30	Telkkinen (1996, 1999)
Finland	0.045	Table 3.29	Varhimo (1988)
Finland	0.040	Table 3.29	Varhimo (1988)
Finland	0.043	Table 3.29	Varhimo (1988)
Finland	0.060	Table 3.29	Varhimo (1988)
Finland	0.050	Table 3.29	Varhimo (1988)
Finland	0.05-0.1	Figs. 3.31-3.36	Siltala (1988)
Finland	0.06		Häsänen and Huttunen (1989)
Sweden	0.19	Table 3.33, Fig. 3.45	Anon. (1999)
Sweden	0.078	Table 3.31	Hedenberg (1996)
Sweden	0.068	Table 3.31	Hedenberg (1996)
Sweden	0.048	Table 3.31	Hedenberg (1996)
Sweden	0.06	Fig. 3.39	Terziev (1995)
Germany	0.07	Table 3.22	Marutzky and Roffael (1977)
Germany	0.06-0.09	Table 3.21	Adelsberger and Petrowitz 1976
Germany	0.04-0.05	Figs. 3.6-3.11	Becker (1962)
England	0.07-0.097	Table 3.20	Bletchly (1969)
Switzerland	0.060	Table 3.36	Keller and Nussbaumer (1993)
Corsica	0.064	Fig. 3.3	Wright (1957)

Uudet taulukot

Esimerkki tutkimusyhteenvedoista (mänty, kuusi)

Table. Studies on the of nitrogen contents in Scots pine (P, *Pinus sylvestris*) and Norway spruce (S, *Picea abies*).

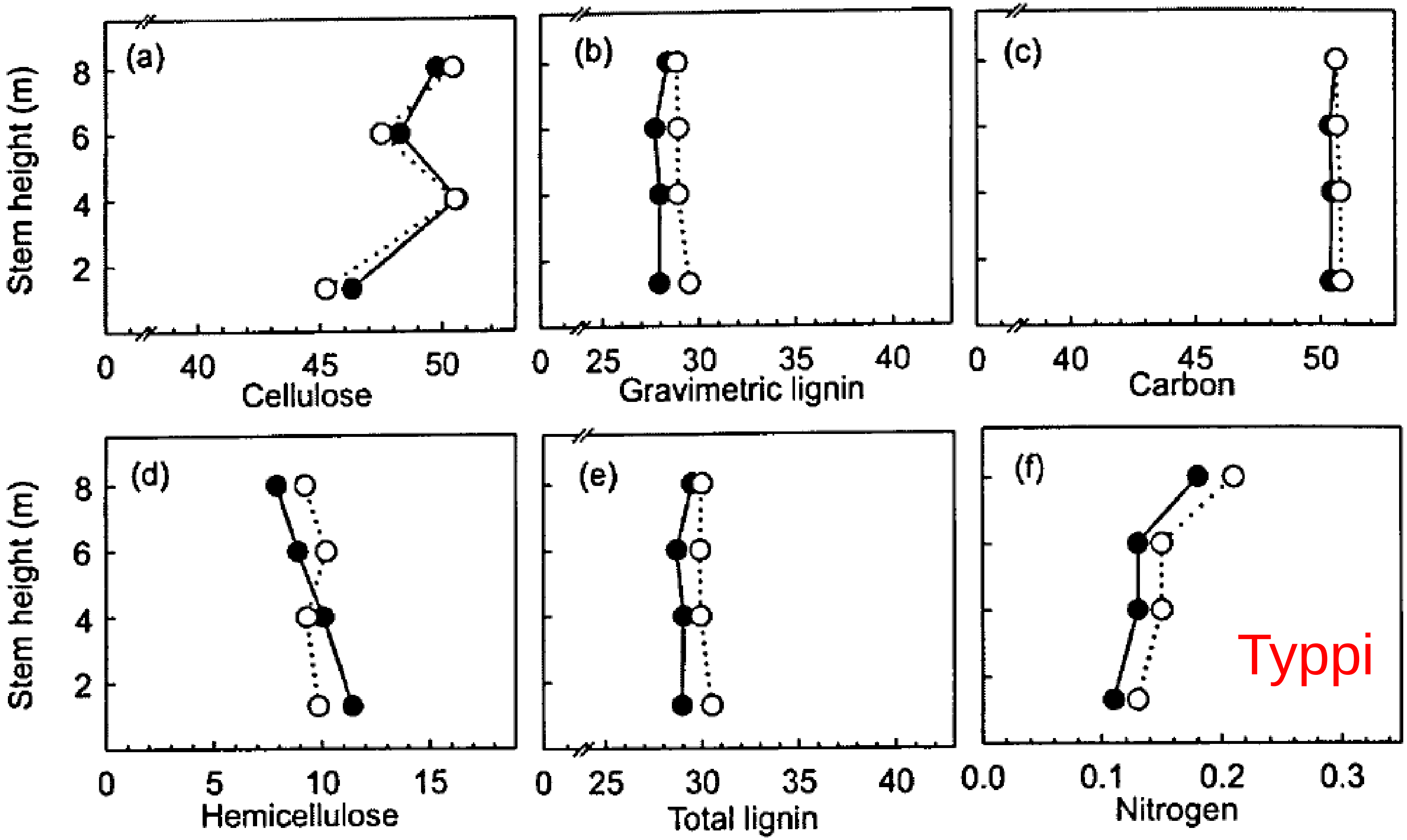
Reference	Species	Topic addressed
Gottlieb 1883	S	Wood composition
Schwalbe & Becker 1919	P	Wood composition
König & Becker 1919	S	Wood composition
Allsopp & Misra 1940	P	Cambium and sapwood composition
Ovington 1957	P	N content in several hard- and softwood species
Stewart 1957	P	N content sapwood and cambial zone
Wright and Will 1958	P	N content and distribution, also for Corsican pine
Nickel 1960	P	N and protein content across the stem
Becker 1962	P	N content across the stems, also for other SWs
Bletchly 1969	P	N content in sapwood
King et al. 1974	P, S	N content along the radius of the stems
Mälkönen 1974	P	N content (annual cycles of nutrients)
Adelsberger & Petr. 1976	P	N content and distribution, protein composition
Marutzky & Roffael 1977	P, S	N content
Magnussion et al. 1979	P, S	Typical N content ranges, incl. other NPEs
Paavilainen 1980	P	N content, effect of fertilisation on peatland (FI)
Westermark et al. 1986	S	N content in whole wood and some fractions
Varhimo et al. 1988	P, S	Wood composition of Finnish trees
Siltala 1988	P	N content, distribution and different factors
Helmisaari & Siltala 1898	P	English paper based on Siltala 1988
Finér 1989	P, S	N content, effect of fertilisation in Finland
Häsänen & Huttunen 1989	P	N content (and other elements)
Boutelje et al. 1990	P	N content in two planks, method comparisons
Keller & Nussbaumer 1993	P, S	N content analysed by chemiluminescence
Terziev et al. 1995	P	N in plank samples, fate in drying
Terziev et al. 1997	P	N content in sapwood
Telkkinen 1996, 1999	P, S	N content, fate in pulping
Hedenberg 1996	P, S	N content (also in bark) in Swedish trees
Anon. 1999	P, S	N contents, Swedish Ecocyclic pulp mill project
Nurmi et al. 1999	P, S	N content in different Finnish tree parts
Ingerslev 1999	S	N content, effect of fertilisation in Denmark
Anttonen et al. 2002	S	N content, effect of fertilisation in Sweden
Niemelä & Ulmgren 2002	P	N content, fate in pulping (E. globulus)
Kaakinen et al. 2007	S	N content, effect of fertilisation in Finland
Kaakinen et al. 2009	S	N content, effect of fertilisation in Sweden
Palviainen et al. 2010	P, S	N content in stump wood and bark

Uudet taulukot

- Typpipitoisuustutkimukset
  - Kotimaiset lajit (mänty ja kuusi)
  - Valikoidut ulkomaiset havupuut
  - Kotimaiset lajit (koivut, haapa, leppä)
  - Valikoidut ulkomaiset lajit (ml. eukalyptus)

- Julkaistut pitoisuustiedot
  - Kotimainen mänty
  - Kotimainen kuusi
  - Valikoidut muut havupuut
  - Havupuiden kuori
  - Kotimaiset lehtipuut
  - Valikoidut muut lehtipuut
  - Lehtpuiden kuori

Lannoituksen vaikutus – esimerkki kuusipuu



● Kontrolli ❍ Optimilannoitus (Kaakinen et al. 2009)

(Tällaisia esimerkkejä julkaistu varsin vähän)

Esimerkki vuodenaikaisvaihtelusta (pintapuu)

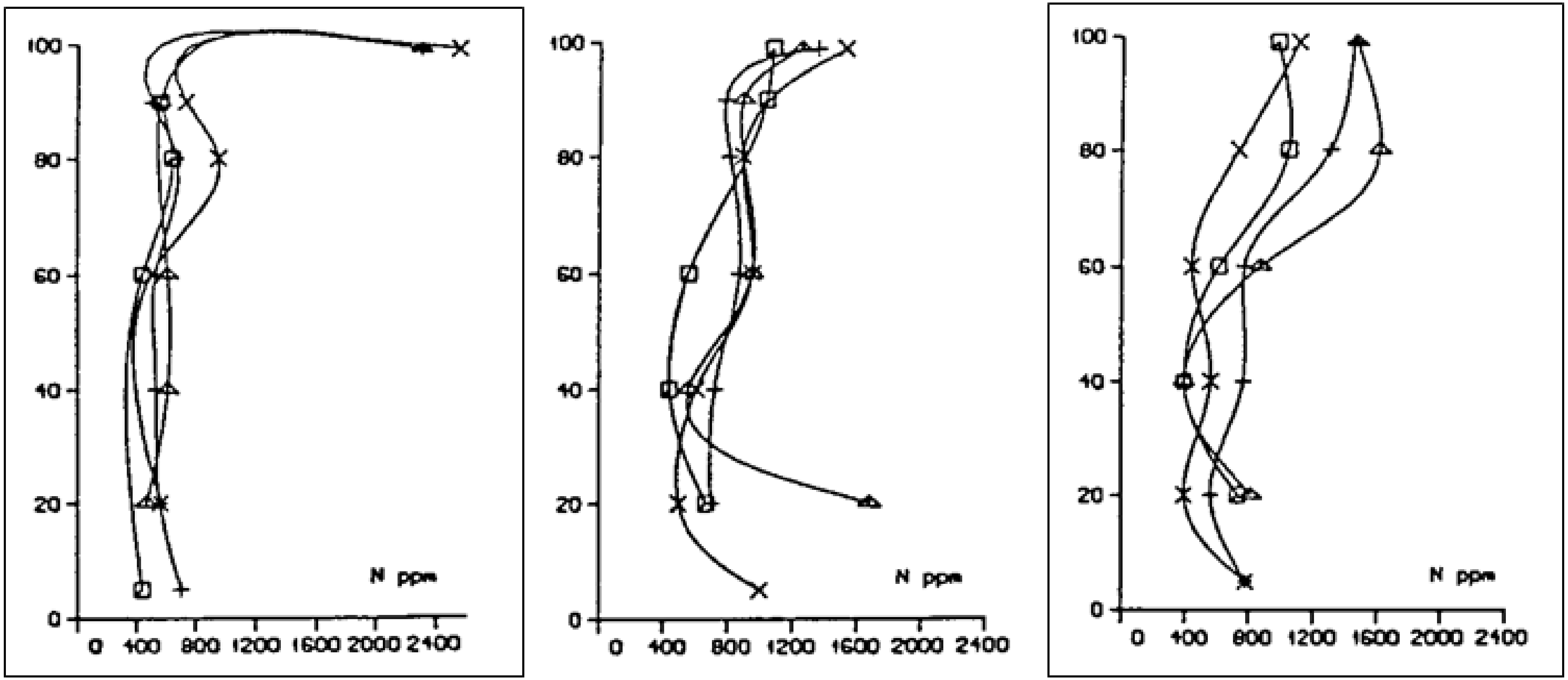


Fig. 3.36. Seasonal variation in vertical nitrogen content in outer sapwood of pine: mature trees (left), young trees (middle), and seedlings (right), according to Siltala (1988). Sampling in February (×), May (□), July (⊗), and September (+).

Esimerkki Pohjois-/Etelä-Suomi-vaihtelusta

(Kuusipuu, Kaakinen et al. 2007)

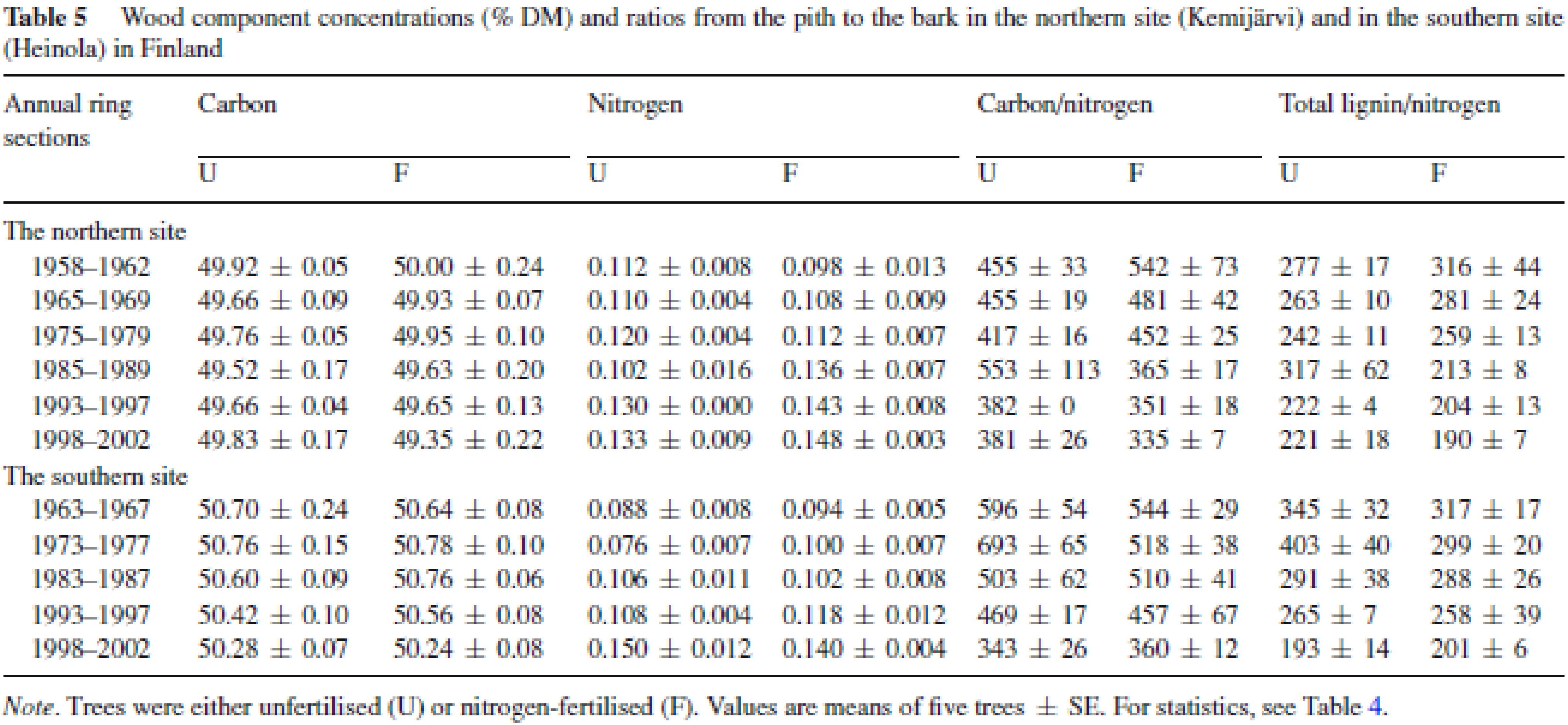


Table 5 Wood component concentrations (% DM) and ratios from the pith to the bark in the northern site (Kemijärvi) and in the southern site (Heinola) in Finland

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

Note. Trees were either unfertilised (U) or nitrogen-fertilised (F). Values are means of five trees ± SE. For statistics, see Table 4.

Puun typpiyhdisteet

- Proteiinit ja aminohapot tärkeimmät, hyvin vähän muita orgaanisia tai mitään epäorgaanisia yhdisteitä
- Vapaat aminohapot
    - Esiintyy jonkin verran, määritetty useista puulajeista
- Proteiinit
    - Puun proteiinit (rakenteet ja tehtävät) huomattavan mielenkiinnon kohteina viim. 20 v. aikana
    - Tunneituimmat ryhmät extensins, glycine-rich proteins, proline-rich proteins ja arabinogalactan proteins.
    - Useita eri tehtäviä.
    - Osa ilmeisesti kovalenttisesti sitoutuneina ligniiniin (soluseinässä).

Esimerkki havupuiden soluseinäproteiineista (aminohappokoostumukset, Loopstra 2000)

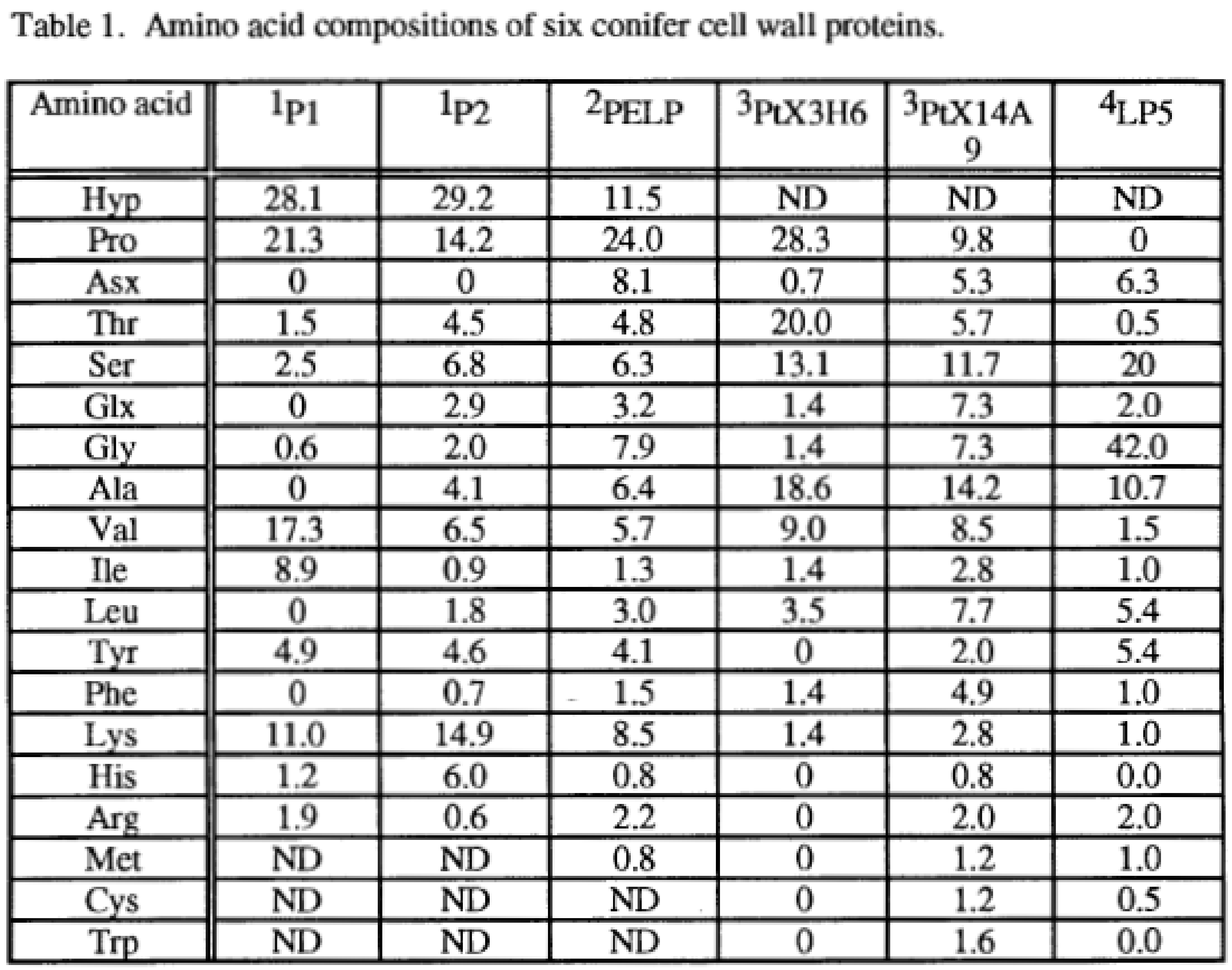


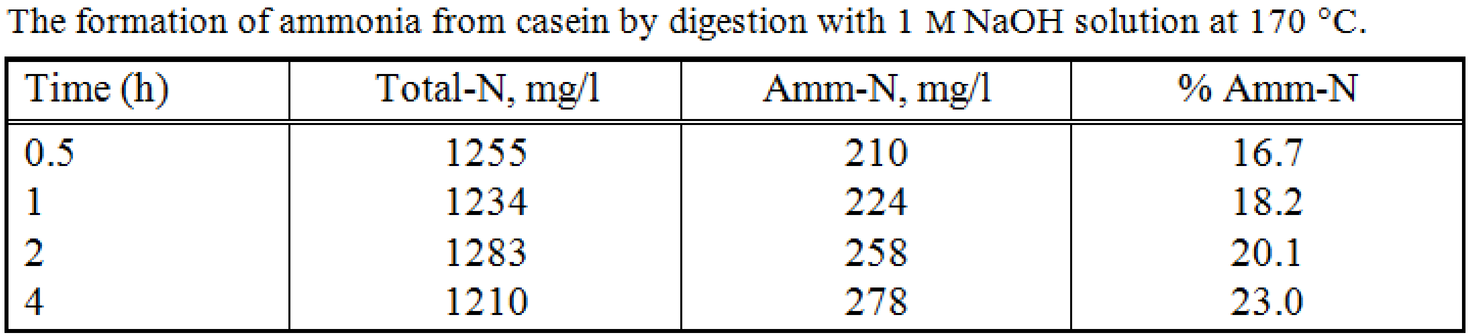
Table 1. Amino acid compositions of six conifer cell wall proteins.

Amino acid	^{1}P1	^{1}P2	^{2}PELP	^{3}PtX3H6	^{3}PtX14A9	^{4}LP5
Hyp	28.1	29.2	11.5	ND	ND	ND
Pro	21.3	14.2	24.0	28.3	9.8	0
Asx	0	0	8.1	0.7	5.3	6.3
Thr	1.5	4.5	4.8	20.0	5.7	0.5
Ser	2.5	6.8	6.3	13.1	11.7	20
Glx	0	2.9	3.2	1.4	7.3	2.0
Gly	0.6	2.0	7.9	1.4	7.3	42.0
Ala	0	4.1	6.4	18.6	14.2	10.7
Val	17.3	6.5	5.7	9.0	8.5	1.5
Ile	8.9	0.9	1.3	1.4	2.8	1.0
Leu	0	1.8	3.0	3.5	7.7	5.4
Tyr	4.9	4.6	4.1	0	2.0	5.4
Phe	0	0.7	1.5	1.4	4.9	1.0
Lys	11.0	14.9	8.5	1.4	2.8	1.0
His	1.2	6.0	0.8	0	0.8	0.0
Arg	1.9	0.6	2.2	0	2.0	2.0
Met	ND	ND	0.8	0	1.2	1.0
Cys	ND	ND	ND	0	1.2	0.5
Trp	ND	ND	ND	0	1.6	0.0

Sulfaattikeitossa…

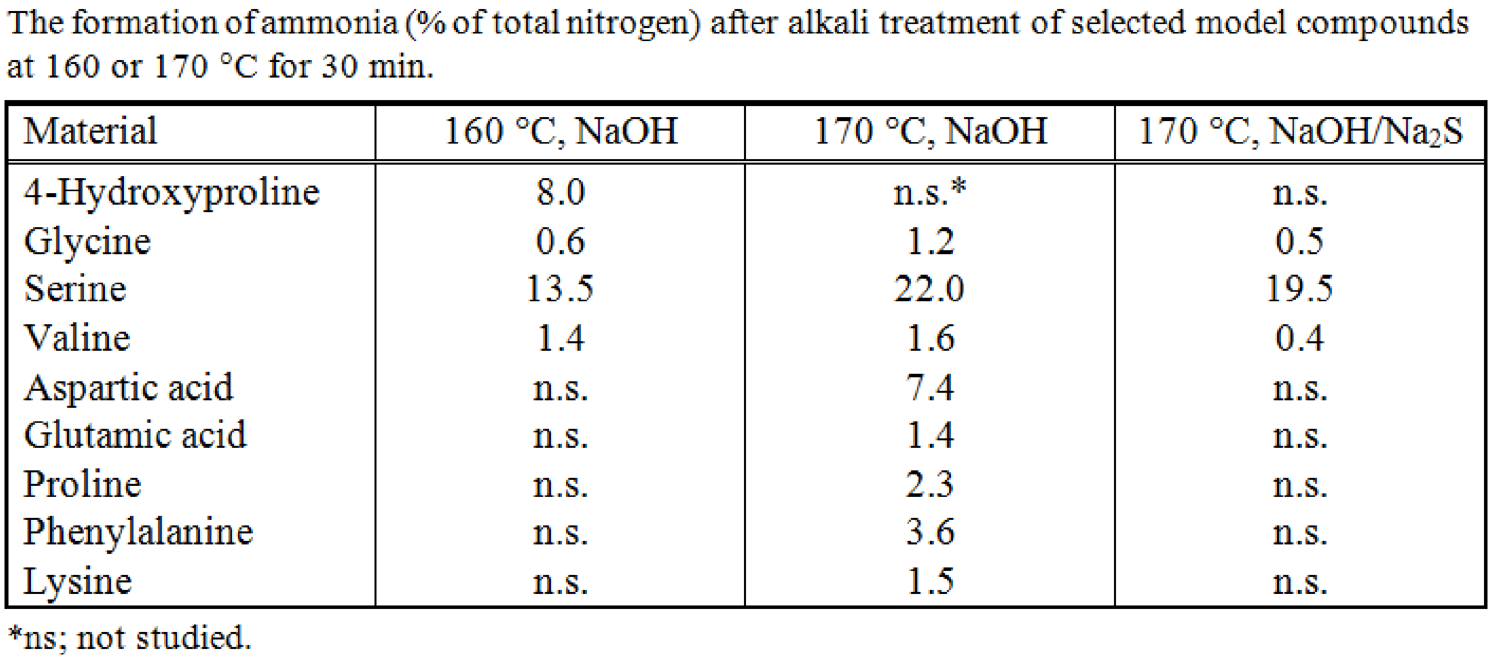
- Puun typestä yli 95% vapautuu keittoliemeen, massassa jäämät mahdollisia
- Osa proteiineista pilkkoutuu, aminohappoja vapautuu, osa aminoryhmistä vapautuu ammoniakkina
- Osa jää ligniiniin kiinni (kerasaostuu ligniinin kanssa pH:ta laskettaessa)
- Näitä kysymyksiä on tutkittu lähemmin ainoastaan Rempulp-projektissa (2000-2002); päätulokset raportissa
- Ammoniakki poistuu lipeästä haihdutuksessa (metanolin tärkein typpiyhdiste)
- Typen käyttäytymiseen itse keitossa ei juuri voida vaikuttaa; haihdutuksessa ammoniakin syntyä (ja siirtoa lauhteisiin) voidaan hieman lisätä erillisellä lipeän lämpökäsittelyvaiheella.

Ammoniakin muodostumisesta



The formation of ammonia from casein by digestion with 1 M NaOH solution at 170 °C.

Time (h)	Total-N, mg/l	Amm-N, mg/l	% Amm-N
0.5	1255	210	16.7
1	1234	224	18.2
2	1283	258	20.1
4	1210	278	23.0

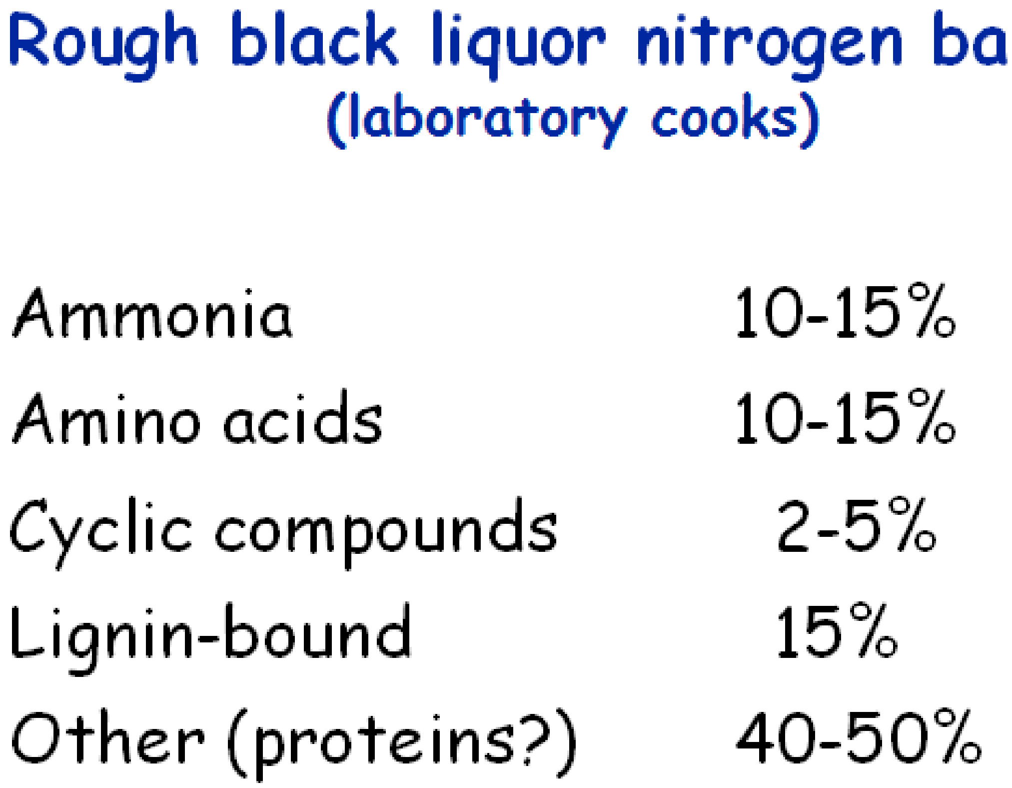


The formation of ammonia (% of total nitrogen) after alkali treatment of selected model compounds at 160 or 170 °C for 30 min.

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.

Laboratoriokeiton mahdollinen typpitase

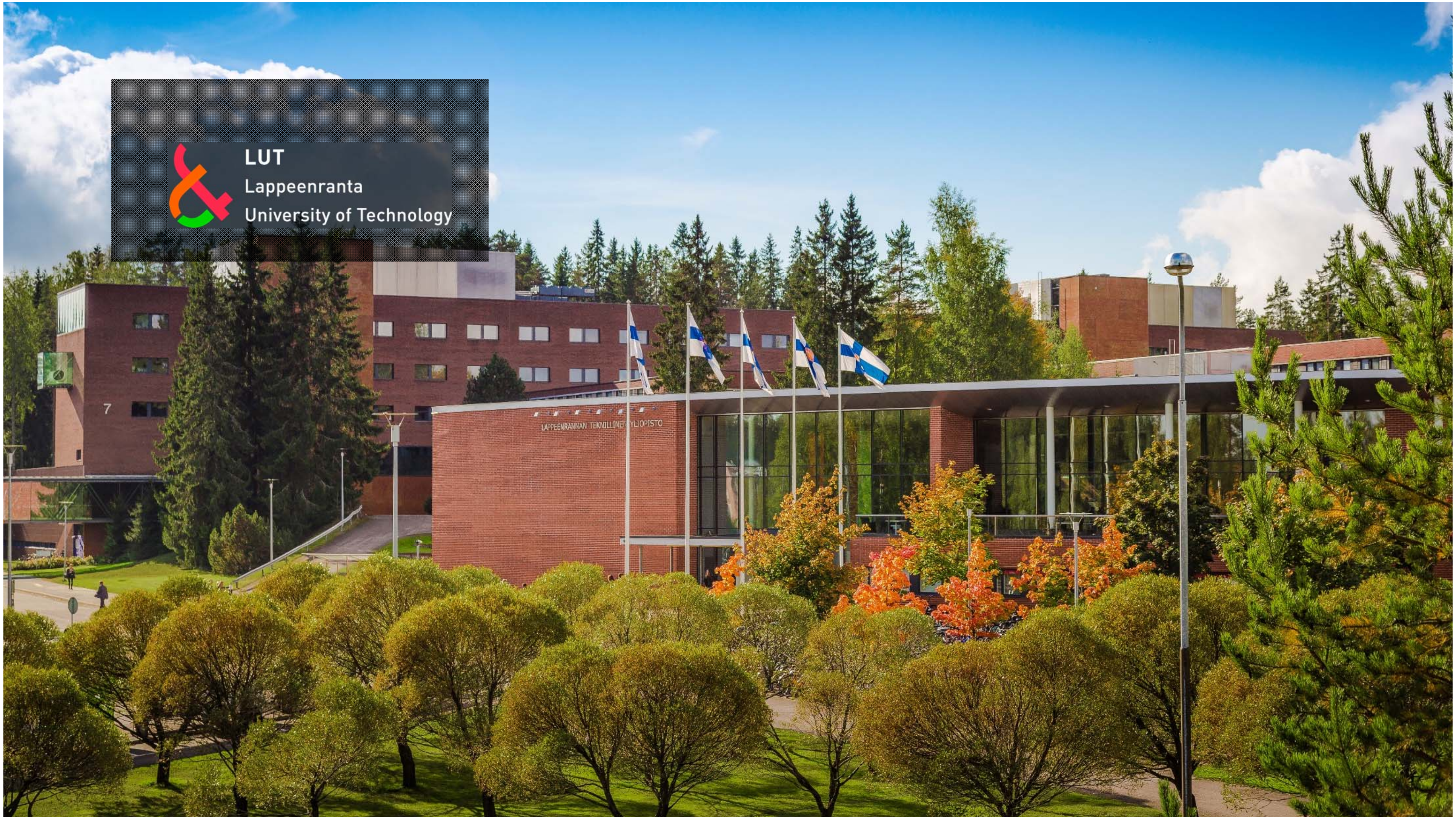


Rough black liquor nitrogen balance
(laboratory cooks)

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

LIITE 2

LUT, Selvitys tyypillisistä savukaasuvirroista [m3/ADt] eri puulajeilla – tilanneraportti 30.9.2017



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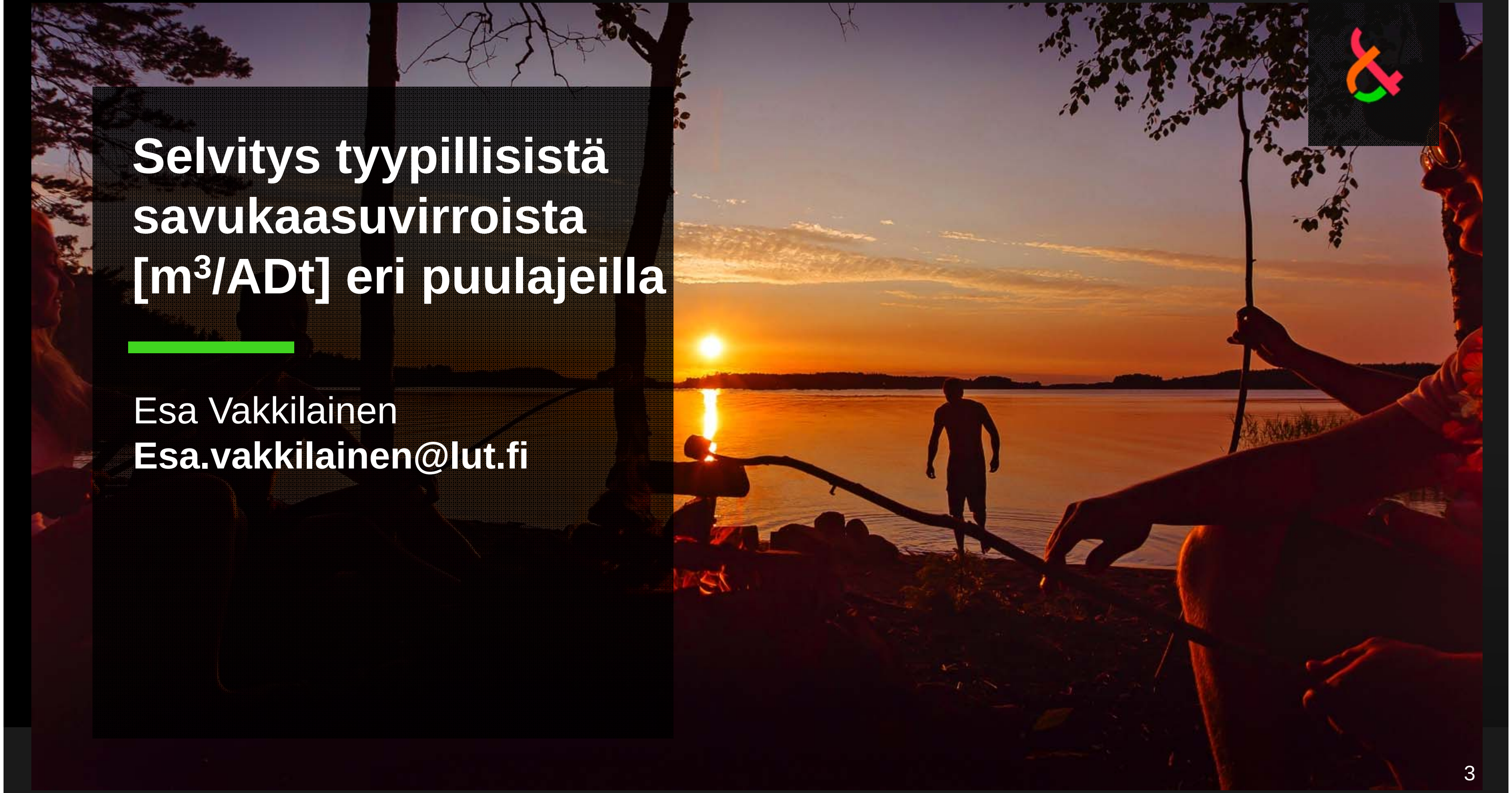
University of Technology

LAPPEENRANTA

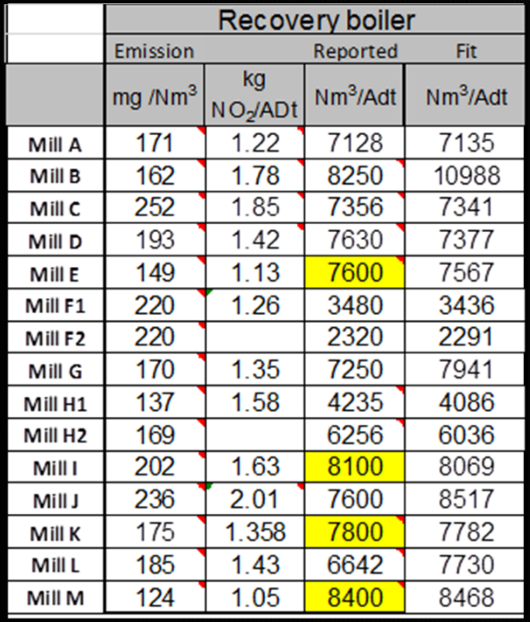
International crossroads



Selvitys tyypillisistä savukaasuvirroista [m^3/ADt] eri puulajeilla

Esa Vakkilainen
Esa.vakkilainen@lut.fi

ETSIMME VASTAUSTA SAVUKAASUMÄÄRÄN VAIHTELUUN



	Recovery boiler			
	Emission		Reported	Fit
	mg /Nm^3	kg NO$_2$/ADt	Nm^3/Adt	Nm^3/Adt
Mill A	171	1.22	7128	7135
Mill B	162	1.78	8250	10988
Mill C	252	1.85	7356	7341
Mill D	193	1.42	7630	7377
Mill E	149	1.13	7600	7567
Mill F1	220	1.26	3480	3436
Mill F2	220		2320	2291
Mill G	170	1.35	7250	7941
Mill H1	137	1.58	4235	4086
Mill H2	169		6256	6036
Mill I	202	1.63	8100	8069
Mill J	236	2.01	7600	8517
Mill K	175	1.358	7800	7782
Mill L	185	1.43	6642	7730
Mill M	124	1.05	8400	8468

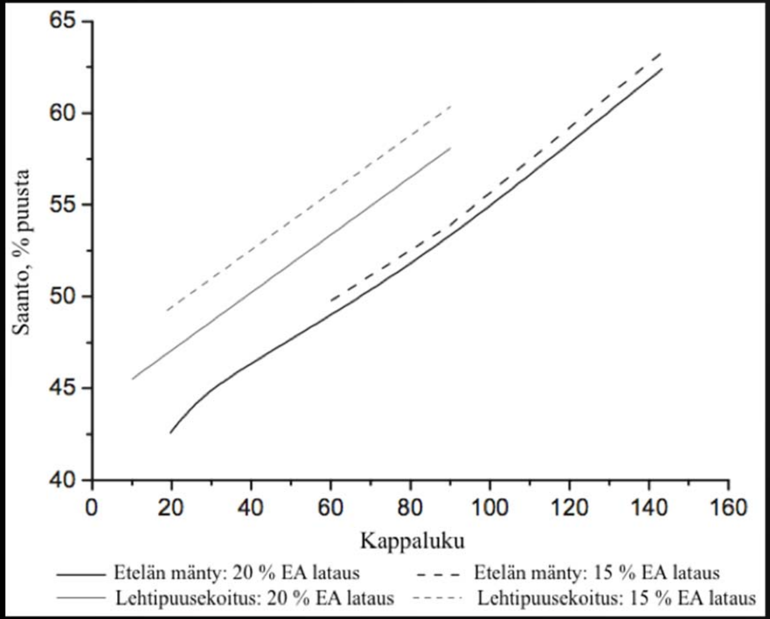
Työssä selvitetään erityisesti seuraavia seikkoja

Vaihe 1. Laaditaan excel laskentamalli savukaasuvirtauksen laskentaan.

Vaihe 2. Kerätään Soodakattilayhdistyksen kanssa Suomen tehtaiden tyypilliset savukaasuvirrat. Käydään tehtailla vierailuilla läpi laskentaa ja mitattuja tuloksia

Vaihe 3. Laaditaan uuden n. 1 200 000 ADt/a modernin sekä perinteisen Suomeen sopivan sellutehtaan vuosikeskiarvotaseet ja arvioidaan savukaasumäärää eri puulajeille sekä tehtaan ajomalleille. Toistetaan laskenta yhdistyksen määrittämissä tilanteissa.

Keiton saanto – orgaaninen savukaasuksi



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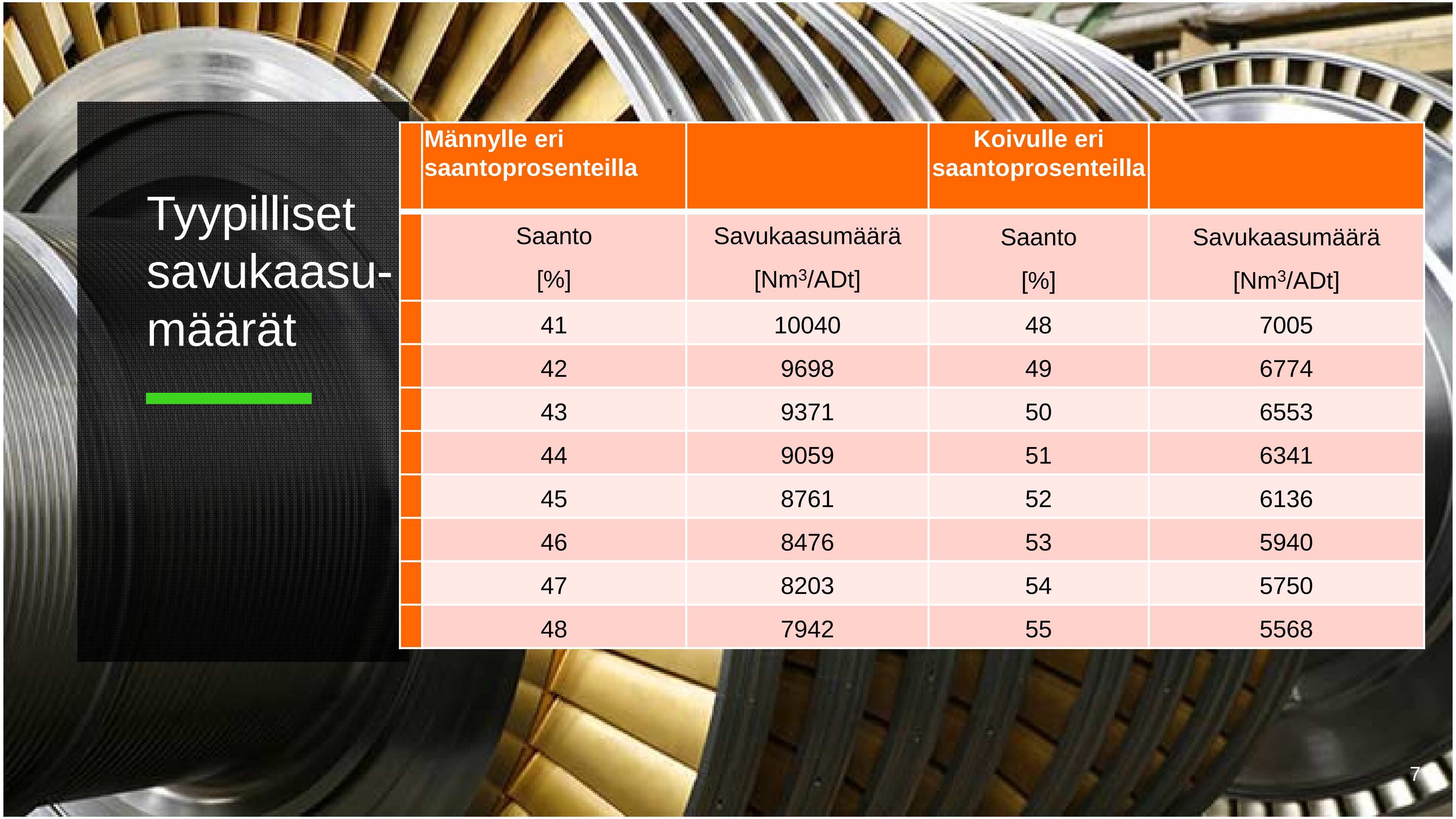

Tyypilliset savukaasu-määrät

Männylle eri saantoprosenteilla		Koivulle eri saantoprosenteilla	
Saanto [%]	Savukaasumäärä [Nm^3/ADt]	Saanto [%]	Savukaasumäärä [Nm^3/ADt]
41	10040	48	7005
42	9698	49	6774
43	9371	50	6553
44	9059	51	6341
45	8761	52	6136
46	8476	53	5940
47	8203	54	5750
48	7942	55	5568

Tilanne 30.8.2017

- Sovittu että aloitetaan diplomityö, Sauli Repo
- Ensimmäinen versio excelistä tehty

Jatko

- DI-työntekijä töissä syyskuun alusta
- Käynnit tehtailla syksyllä 2017 / keväällä 2018?
  - muut tiedot paitsi ominaissavukaasumäärä luottamuksellisia (kerätään datana koivu ja havusellun tuotanto)
  - excel versio tehtaasta jää tehtaalle

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LIITE 3

Pöyry Finland, Soodakattilan päästömittausten menetelmät – tilanneraportti 30.8.2017

PÖYRY

SOODAKATTILAN PÄÄSTÖMITTAUSTEN MENETELMÄT

Elokuu / 2017

SISÄLTÖ

Alustava sisällysluettelo

1. Lainsäädäntö ja standardointi
    - Muutoksia tapahtunut sitten edellisen selvityksen

2. Laskentaperiaatteet

3. Mitattavat päästökomponentit: mitä, milloin

4. Mittausepävarmuus: perusteet, miten tehdään ja sovelletaan

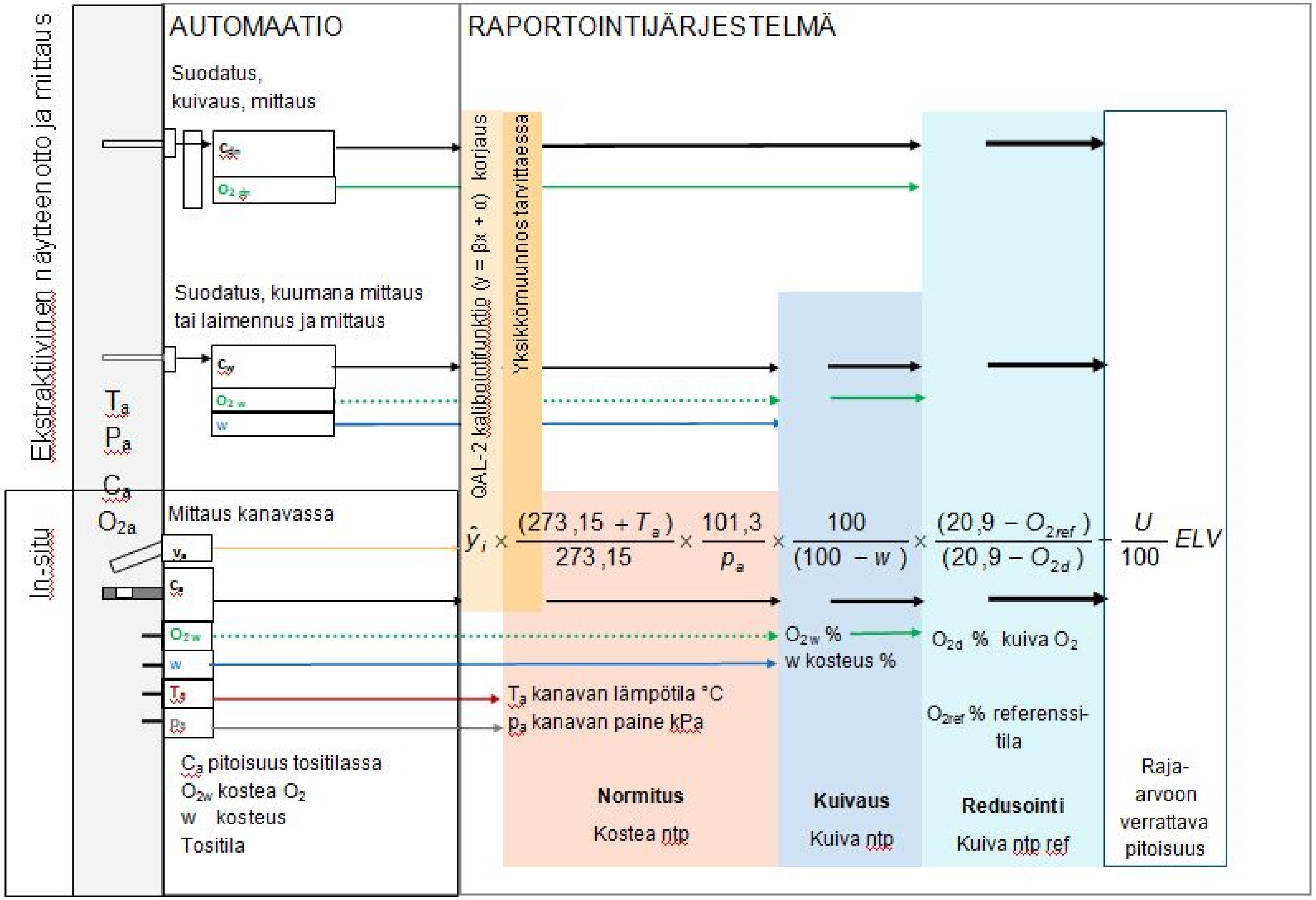
5. Mittalaitteet ja niiden käyttökokemukset, ongelmakohdat

6. Raportointi (VAHTI, E-PRTR)

1. LAINSÄÄDÄNTÖ JA STANDARDOINTI

- BAT-päätelmät ja uudet ympäristöluvat
- PP revised BREF 2015
- Lupamääräykset em. dokumentin jälkeen myönnetyissä luvissa
- Tarkkailuvelvoitteet uusissa luvissa
- Tarkkailuvelvoitteiden toteutusta ohjaavat standardit
  - Laitteistovaatimukset (AMS) (EN 15267-1, -2, -3)
  - Laadunvarmennus (EN 14181 ja kansallinen tulkinta)
  - Mittausten toteutus ja mittauspaikat (EN 15259)
  - Tulosten käsittelyn (AMS) standardoinnin tila
  - Menetelmäkohtaiset (EN…..)
- Tarkkailun yhtenäistämistä EU:n taholta
  - JRC Reference Report on Monitoring of Emissions to Air and Water from IED installations (Revised final draft 2017-06-05) Joint Research Centre http://eippcb.jrc.ec.europa.eu/reference/mon.html

2. LASKENTAPERIAATTEET



Ekstraktiivinen näytteenotto ja mittaus

In-situ

T_a
P_a
C_a
O_{2a}

AUTOMAATIO

Suodatus,
kuivaus, mittaus

C_{dn}
$O_{2\,dn}$

Suodatus, kuumana mittaus
tai laimennus ja mittaus

C_y
$O_{2\,w}$
w

Mittaus kanavassa

v_a
C_a
O_{2w}
w
T_a
p_a

C_a pitoisuus tositilassa
O_{2w} kostea O_2
w kosteus
Tositila

RAPORTOINTIJÄRJESTELMÄ

QAL-2 kalibointifunktio ($y = \beta x + \alpha$) korjaus

Yksikkömuunnos tarvittaessa

$$\hat{y}_i \times \frac{(273,15+T_a)}{273,15} \times \frac{101,3}{p_a} \times \frac{100}{(100-w)} \times \frac{(20,9-O_{2ref})}{(20,9-O_{2d})} - \frac{U}{100} ELV$$

T_a kanavan lämpötila °C
p_a kanavan paine kPa

O_{2w} %
w kosteus %

O_{2d} % kuiva O_2

O_{2ref} % referenssi-tila

Normitus
Kostea ntp

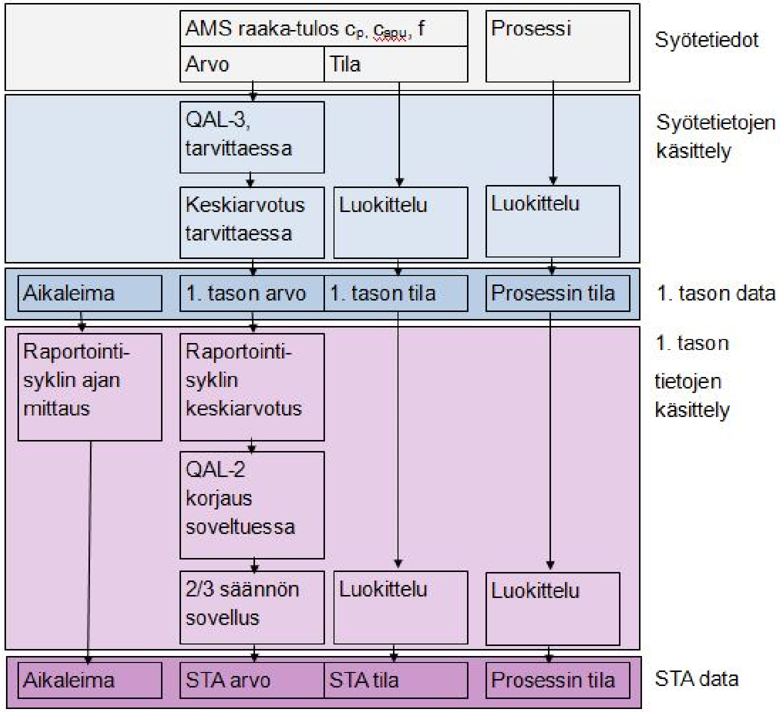
Kuivaus
Kuiva ntp

Redusointi
Kuiva ntp ref

Raja-arvoon verrattava pitoisuus

DATAN KÄSITTELYÄ

Periaatteita prEN 00264076-1:2017



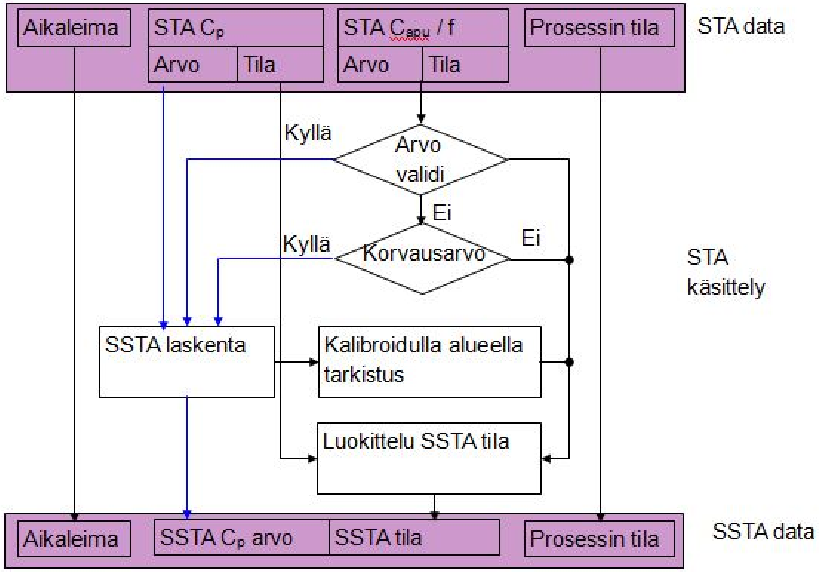
AMS raaka-tulos c_p, c_{apu}, f
Arvo | Tila
Prosessi
Syötetiedot

QAL-3, tarvittaessa
Keskiarvotus tarvittaessa
Luokittelu
Luokittelu
Syötetietojen käsittely

Aikaleima | 1. tason arvo | 1. tason tila | Prosessin tila
1. tason data

Raportointi-syklin ajan mittaus
Raportointi-syklin keskiarvotus
QAL-2 korjaus soveltuessa
2/3 säännön sovellus
Luokittelu
Luokittelu
1. tason tietojen käsittely

Aikaleima | STA arvo | STA tila | Prosessin tila
STA data



Aikaleima | STA C_p (Arvo | Tila) | STA C_{apu} / f (Arvo | Tila) | Prosessin tila
STA data

Arvo validi
Kyllä
Ei
Korvausarvo
Kyllä
Ei
SSTA laskenta
Kalibroidulla alueella tarkistus
Luokittelu SSTA tila
STA käsittely

Aikaleima | SSTA C_p arvo | SSTA tila | Prosessin tila
SSTA data

STA lyhyen jakson keskiarvo
SSTA lyhyen jakson keskiarvo referenssitilassa

3. MITATTAVAT KOMPONENTIT

- BREF ja ympäristöluvat
- Tarkkailusuunnitelmat
  - Ympäristöraportointi E-PRTR

- Jatkuvat mittaukset: NOx, SO_2, TRS, hiukkaset, apusuureet O_2, virtaus, T, p
  - Mittausperiaatteita ja -järjestelmiä

- Jaksottaiset: hiukkaset erilaisista matriiseista, vertailut NOx, SO_2, TRS, O_2,
- ’Satunnaiset’ E-PRTR: metallit , PCDD/F, HCl, N_2O, NH_3

4. EPÄVARMUUSTARKASTELU

Menetelmäkohtaiset

epävarmuuden osatekijät
on-line mittaukset

- Epälineaarisuus
- Virityksen nollasiirtymä
- Virityksen aluesiirtymä
- Näytevirtauksen vaikutus
- Ilmanpaineen vaikutus
- Ympäristölämpötilan vaikutus
- Jännitteen vaihtelun vaikutus
- Interferenssit
- Toistettavuus laboratoriotasolla
- Kalibrointikaasun epävarmuus

- Osatekijöiden neliöiden summa
- Laajennettu epävarmuus = edellinen x 2
  - k = 2

$$S_{\mathrm{int,n}} > S_{\mathrm{int,p}}$$

$$u(C_{\mathrm{CO,ppm}}) = \sqrt{\begin{aligned}&u^2(Corr_{\mathrm{fit}}) + u^2(Corr_{\mathrm{0,dr}}) + u^2(Corr_{\mathrm{s,dr}}) + u^2(Corr_{\mathrm{rep}}) + u^2(Corr_{\mathrm{adj}}) + u^2(Corr_{\mathrm{s,vf}})\\ &+ u^2(Corr_{\mathrm{a,press}}) + u^2(Corr_{\mathrm{temp}}) + u^2(Corr_{\mathrm{volt}}) + S_{\mathrm{int,n}}{}^2\end{aligned}}$$

- Vaatimukset laitosjärjestelmille ja referenssimenetelmille taulukkona

5. MITTALAITTEET

Laitetoimittajille esitetty kysely heidän tämän hetkisestä tarjonnastaan metsäteollisuuden mittauskohteeseen SK

Kontram Oy

Suomi Analytics Oy

Sick Oy

- Päivitystä mittausjärjestelmien kokoonpanoon
- Vertailuissa havaittua
  - Hiukkaset
  - Kaasut
  - Apusuureet
- Käyttökokemuksia ?

6. RAPORTOINTI

- VAHTI ??

- E-PRTR ??
- Tuottamismenetelmät
- Ohjeistus raportoinnista

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LIITE 4

LUT, NCG-järjestelmien turvallisuusauditointi, syntyvät hajukaasumäärät ja koostumukset, tyypilliset onnettomuuteen johtavat syyt – prosessikonseptitarkastelut – tilanneraportti

30.8.2017

UNIVERSITY OF
TECHNOLOGY AND BUSINESS

”NCG-järjestelmien turvallisuusauditointi, syntyvät hajukaasumäärät ja koostumukset, tyypilliset onnettomuuteen johtavat syyt - prosessikonsepti-tarkastelut”

Kirsi S. Hovikorpi, Esa Vakkilainen
30.08.2017

Yliopisto Saimaan-rannalla

Tähän mennessä - yhteenveto

- Projektissa, ”*NCG-järjestelmien turvallisuusauditointi, syntyvät hajukaasumäärät ja koostumukset, tyypilliset onnettomuuteen johtavat syyt - prosessikonsepti-tarkastelut*”, pyritään luomaan yleisesti käytettävä tapa, jolla suoritettaisiin sulfaattisellutehtaiden turvallisuusauditointi, samalla selvittäen tehtaan sen hetkisen hajukaasujen keräilyn, käsittelyn ja polttoon johtamisen nykytila.

Tähän mennessä - yhteenveto

- Tarkoituksena tehdä suositusluonnos Soodakattilayhdistyksen valitseman, tehtaista ja toimijoista koostuvan, ryhmän valvonnassa tavasta käydä läpi hajukaasujärjestelmien mahdolliset vaaraa aiheuttavat tilanteet, niin että hajukaasujärjestelmille tehtävissä turvallisuusauditoinneissa muistetaan ottaa huomioon erilaiset vaaratilanteet.

Tähän mennessä - yhteenveto

- Samalla selvitetään
  - mistä,
  - miten paljon ja
  - millä pitoisuuksilla

  moderneilla tehtailla hajukaasuja syntyy ja käsitellään ennen polttoon johtamista.
- Lisäksi mietitään onko erilaisilla keräilytavoilla keräilyprosessista syntyviä, niille tyypillisiä vaaratyyppejä.

Tähän mennessä - yhteenveto

- Auditointikäyntejä on tehty tammikuusta lähtien tähän mennessä eri laajuuksilla viidelle eri Suomen sellutehtaalle (2 pohjoisessa ja 3 etelässä), lisäksi on saatu sähköpostitse aineistoa katsottavaksi kahdelta muulta tehtaalta (1 etelästä, 1 lännestä), ja alustavasti suunniteltu 2-3 muulle tehtaalle vielä käyntejä.

Tähän mennessä - yhteenveto

- Lisäksi on haastateltu yksittäisiä eri yrityksien ja siellä olevien eri osastojen (tehtaiden, laitetoimittajien) henkilöitä, joilla on substanssiosaamista niin käytänteenä kuin projekteissa hajukaasuista, saaden mahdollisimman laajan ja ajanmukaisen kuvan, josta jatkaa syvemmälle hajukaasujen pariin.
- ”Jos ei saa ajanmukaista ymmärrystä alkulähteiden prosesseista ja ajotavoista, on vaikea sisäistää ja ymmärtää mahdollisten syy-yhteyksien aiheuttamat seuraukset matkan varrella ja loppupoltossa.”

Tähän mennessä - yhteenveto

- Erityisesti pyritään selvittämään tarvittavin osin:

1. Esitetään perusteita sellutehtaan eri prosessiosastojen hajukaasumäärien
    a) syntyyn
    b) rikkipitoisuuksiin
    c) Analyyseihin

Tähän mennessä - yhteenveto

… jatkoa edelliseen sivuun

Vaatinee mittauksia tehtailla (milloin tehty viimeksi?), joillakin tehtailla toteutettukin jo osittain.

Kesän 2017 aikana on tehty yhdelle tehtaalle ehdotukset eri hajukaasukohteiden mittauspisteille ja yhdemallille. Listaa voitaisiin käyttää pohjana muilla tehtailla tehtäville, jotta saataisiin vertailukelpoisia aineistoja läpikäytäväksi.

Tähän mennessä - yhteenveto

2. Kartoitetaan tyypilliset hajukaasujen (väkevät ja laimeat)
    a) keräilyjärjestelmät
    b) käsittelyjärjestelmät

Tästä on jo tehty kansainväliseen ICRC Halifax, Canada seminaariin 24.-26.05.2017 artikkeli ja pidetty seminaarissa esitelmä 26.05.2017. Artikkelissa ei menty eri toimittajien detaljeihin ratkaisuihin.

Tähän mennessä - yhteenveto

3. Dokumentoidaan kirjallisuudesta erilaisia hajukaasuonnettomuuksia.

Tämä on työn alla.

Lisäksi toivoisimme tehtailta omia kokemuksia ja vähältä piti/lähetä piti -tilanteita eri osastoilta. Vaatii henkilöhaastatteluita.

Tähän mennessä - yhteenveto

4. Selvitetään hajukaasukattiloiden ja soihtujen toimintaa.

Tämä on alkutekijöissään. Haastateltu jo hieman poltintoimittajia.

5. Dokumentoidaan syitä miksi ja mistä hajuja on päässyt ”karkuun” tehtailta.

Tämä on jo aloitettu auditointikäyntien yhteydessä.

Tähän mennessä - yhteenveto

LOPUKSI

”Ja eihän se ole peräaukon syy jos se ripuloi, vaan täytyy selvittää, että mitä on tullut laitettua suun kautta sisään.”

- Kirsi S. Hovikorpi –

peräaukko = polttopää

suu = keräilylähteet

LIITE 5

Åforsk, Techniques for reducing intake of ammonia-nitrogen in strong gases and methanol to kraft recovery boilers – raportti 2.12.2014

REPORT

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Ångpanneföreningens Forskningsstiftelse

Techniques for reducing intake of ammonia-nitrogen in strong gases and methanol to kraft recovery boilers

ÅFORSK Ref N° 13-426

ÅF Industry AB

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Preface

This study is sponsored by Ångpanneföreningens Forskningsstiftelse (ÅForsk), a Swedish foundation that promotes research and development primarily within the field of energy, environment, safety, sustainability, materials, processes and products from renewable resources.

The objectives of this study are to identify and evaluate methods for reducing the amount of ammonia-nitrogen entering the kraft recovery boiler. Two methods for reducing the ammonia-nitrogen content of non-condensable gases and/or methanol which are often incinerated in the recovery boiler were identified, evaluated and compared with a reference case. The refernce case was based on the bleached softwood market kraft pulp model mill as defined in the FRAM (STFI-Packforsk, 2005) research programs (2 000 ADt bleached SW pulp/d). The study was performed as a desk-top study utilizing data from public articles and in ÅF files data archives.

Special thanks to Hans Norrström and Lars E Andersson for suggestions and constructive input during the work and their final review of the report.

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Alt 2 nitrogen mass balance block diagram

1 Executive Summary

The aim of this study was to identify and evaluate efficient ways to reduce the ammonium-nitrogen content in gases and methanol fed to kraft recovery boilers or dedicated incinerators within the kraft pulp mill. The effect-goal if a feasible process is implemented could be a reduction in NO_X-formation but was not within the scope of present the study. The study was performed as a desk-top study utilizing data from public articles and in ÅF files data archives.

A reference mill wide nitrogen mass balance was developed for the bleached softwood market kraft pulp model mill as defined in the FRAM (STFI-Packforsk, 2005) research programs (2 000 ADt bleached SW pulp/d). Identification and configuration of mill areas, process systems and production rate was thereby identical to the FRAM model mill. Regarding foul condensate, strong gases and methanol the model mill includes steam stripping of foul condensates followed by condensation of stripper gases and further distillation in a methanol column. Basic input data for the reference balance was mainly nitrogen content in Scandinavian softwood and concentration of nitrogen in foul condensate. Concentration of total nitrogen in other process streams was based on mass balance and data on nitrogen-split between process streams, e.g. strong black liquor to recovery boiler and smelt to dissolving tank etc.

Softwood pulping generally implies less nitrogen intake to the process than compared to hardwood pulping but is also well correlated to the amount of bark residues that is a very important factor. Most nitrogen is released in the cooking process as organic- and reduced nitrogen compounds. More than 90% of the reduced nitrogen (mainly as ammonia) is found in the foul condensate and the stripped clean condensate is virtually ammonia-free. Consequently, the majority of nitrogen is in volatile form and ends up in the stripper off-gas stream. In order to decrease ammonia-nitrogen in the Stripper Off Gases (SOG), the two processes identified and evaluated were 1) Acidification of the foul condensate prior to steam stripping and 2) Acidification of methanol and separation of the volatile and ammonia-free methanol phase.

Key results from the study are summarized in table 1 below. For the reference model mill case, approximately 30% of the nitrogen fed to the recovery boiler via black liquor and gases is due to intake of ammonia in low volume, high consistency (LVHC) gases, including the methanol fraction. Both studied alternatives were shown to efficiently reduce the intake of ammonium-nitrogen in LVHC gases by 85-90 %.

		Model mill Reference (2 000 ADt/d at MCR)	Alternative 1: Acidification of foul condensate	Alternative 2: Acidification of methanol
Black liquor dry solids	g N/ADt	1181	1181	1181
LVHC gases	g N/ADt	526	64	85
HVLC gases	g N/ADt	153	201	118
Total nitrogen to recovery boiler	g N/ADt	1860	1446	1384
Nitrogen to waste water treatment plant	g N/ADt	66	413	421
Investment costs	kEUR	-	~50 - 75	~790 - 825
Operating costs	EUR/ADt		0.47	0.31

Table 1. Related key values for nitrogen streams, estimated investment- and operation costs for the two alternative processes.

Both processes are considered feasible from a process technology point of view. Alternative 1, comprising acidification of foul condensate prior to steam stripping, indicate much lower investment costs than Alternative 2, which comprises acidification of methanol from the methanol recovery system and further acidification and separation of the volatile methanol phase from the ammonium-containing water phase prior to firing in recovery boiler (or dedicated incinerator). The main reason for the higher investment for Alternative 2 is due to additional required equipment such as mixing tank and stripping column as well as required piping, pumps, valves etc. The new equipment for Alternative 1 is minor and does only comprise a pump for sulfuric acid, pH-control, distributor, piping and valves.

Both processes produce ammonium-enriched clean condensate streams that are assumed to be used for pulp washing in the bleach plant. The bleach plant wash filtrates thereby contain higher concentration of aqueous reduced nitrogen (i.e ammonia) which we have assumed to partially replace N-containing chemicals added as nutrients to the effluent treatment. A minor amount of ammonia will however be recovered to the HVLC vent.

It is assumed that acidification in both Alternative 1 and Alternative 2 is made by using fresh sulfuric acid. We have assumed that all freshly added sulfur must be compensated for by addition of sulfur-free sodium as NaOH. In table 1 below some central nitrogen key values as well as alternative costs are listed for the alternate processes.

2 Background and objectives

2.1 Background

NO_X emissions to air have a negative impact on the environment. Therefore all kraft pulp mills must monitor and report NO_X emissions in order to ensure compliance with environmental license limits. Since the recovery boiler is the main source of NO_X emissions from a pulp mill, the reduction of NO_X from recovery boilers is a high priority for pulp mills and for environmental authorities.

The EU IPPC BAT recommendations for the pulp and paper industry (2001) are 0.6-1.8 kg NO_X /ADt, or 50-80 mg NO_X /MJ of energy input to the recovery boiler (as NO_2). The variation in the BAT recommendations is relatively large, because recovery boiler NO_X emissions depend on a number of factors such as the nitrogen content of the black liquor to the recovery boiler, the recovery boiler design, and how the recovery boiler is operated. The design and operation of auxiliary systems in the mill, such as the non-condensable gas (NCG) and condensate systems also impact NO_X emissions from the recovery boiler. NCG can be incinerated in the recovery boiler, power boiler, lime kiln, or a separate incinerator. The incineration point and the nitrogen content of the NCG impact the overall nitrogen balance in the mill, including the nitrogen content of the black liquor to the recovery boiler. Determination of the most appropriate incineration point is mill specific, and depends on factors such as the sulphur balance in the mill, and sulphur emission limits for the alternatives. In some mills NCG incineration in the kiln is suspected to cause ring formation, so the kiln is not always an option. A separate incinerator has relatively high investment- and operating costs which must be considered. In this study it assumed that NCG is incinerated in the recovery boiler.

Mill experiences and studies have shown that NO_X emissions can increase when the total amount of nitrogen from black liquor and NCG, (excluding air nitrogen) entering the recovery boiler increases (Clement & Barna, 1993). Of this reason cost effective techniques which can reduce the amount of nitrogen to the recovery boiler (Andersson & Norrström, 2010) without having a negative impact on other important environmental parameters are of interest to most kraft pulp mills.

The main problem by intake of fuel-nitrogen to a boiler is the risk for NO_X-formation and emissions. Present practices for handling NO_X-emissions comprise e.g. optimized configuration of air system and SNCR - selective non-catalytic reduction with urea or ammonia. Selective catalytic reduction is a technology employed in coal fired boilers but is due to safety reasons not recommended for kraft recovery boilers and is additionally also virtually impossible to install in existing recovery boilers, *ibidem*. In addition to firing in the recovery boiler, strong gases/liquefied methanol can also be fired in dedicated incinerators which can be of conventional type or specially designed for low-NO_X emissions.

The main suppliers to the pulp industry, as well as some of the pulp producers themselves have developed a number of alternatives for nitrogen capture from the foul condensate and methanol systems in kraft pulp mills. Some processes target foul condensate treatment before or in the foul condensate stripper system while other processes focus on either the resulting SOG or the liquefied methanol, if a methanol recovery plant is available.

2.2 Project objectives

The objectives of this study are to identify and evaluate methods for reducing the amount of nitrogen entering the recovery boiler (excluding air nitrogen as N_2). In particular, cost effective methods for reducing the nitrogen content, mainly as ammonia (NH_3), of non-condensable gases and/or methanol which are often incinerated in the recovery boiler are identified and evaluated.

The main activities in this project are:

1. Define a base case nitrogen balance for a model mill, including the non-condensable gas system. This balance is mainly based on reference material and ÅF data from various studies. Note that quantification of NO_X emissions from the recovery boiler is not included in the scope of this project.

2. Define and evaluate alternatives for reducing nitrogen into the recovery boiler for the model mill, based on research articles, patents, and ÅF experience.

Two main alternatives are considered:

Alt 1: Acidification of foul condensate before stripping, or in the stripper column, to convert volatile ammonia compounds to non-volatile ammonia ions which remain in the stripped condensate.

Alt 2: Acidification and separation of ammonia from SOG, or the mill's methanol by product.

Evaluation of each of the two process alternatives covers the following:

- Process description, including a general equipment specification
- Nitrogen balance to estimate the reduction of nitrogen to the recovery boiler
- Potential process consequences in other mill areas and operating experiences
- Equipment and operating cost estimates

3 Base case

3.1 Mill Description

The model mill considered is a Nordic softwood bleached kraft pulp mill. The design of the mill is based on best available and commercially proven technology. A detailed description of the mill is given in the 2005 FRAM project (STFI-Packforsk, 2005) and the update in 2010 "Energy consumption in the pulp and paper industry - Model mills 2010; Bleached kraft market pulp mill" (ÅForsk, 2010). Key design factors which are relevant to this study are summarized below.

- Production: 2000 ADt/d bleached softwood market kraft pulp, maximum continuous rate (MCR)
- Wood supply: 50% pine / 50% spruce
- Deknotted digester yield 47%, final bleached yield 44%
- The evaporation plant produces 80% dry solids liquor, and operates at 771 t H_2O/h. All of the intermediate condensate is used in the recausticizing plant for dregs washing, lime mud dilution, and as shower water on the lime mud filter. The clean condensate is used as wash liquor in the brown stock and bleach plant, and any excess is discharged as effluent.
- There is a stripping system for foul condensate from the digester and evaporation plant and a methanol rectification column with turpentine decanter and foul methanol liquor storage. Liquid methanol is incinerated in the recovery boiler.
- Non condensable gases are collected throughout the mill. Both low volume high concentration (LVHC) and high volume low concentration (HVLC) gases are burned in the recovery boiler.
- The smelt dissolving tank vent is returned to the recovery boiler.
- Primary effluent treatment consists of a clarifier to remove fiber sludge, cooling, and neutralization. Effluent flow after primary treatment is approx. 22 m^3/ADt and COD is approximately 26 kg/ADt.
- Biological effluent treatment consists of a bio-film reactor with suspended carriers and an activated sludge system (aeration basin and secondary clarifier). The system is designed for low bio-sludge production and low nutrient discharges. COD reduction is approximately 65-70%.
- The biological sludge from the secondary clarifier is dewatered to about 10% in a centrifuge and mixed with intermediate black liquor in the evaporation plant, before firing in the recovery boiler. Primary sludge is fired in the power boiler.

3.2 Nitrogen balance

The nitrogen balance for the base case is presented in Appendix 1.

Several studies have been done regarding the nitrogen chemistry in the kraft pulping process including nitrogen balances. There are some differences from study to study, for example, quantification of HVLC gases, however the general fate of nitrogen is similar. Following is a description of the nitrogen balance for the model mill.

3.2.1 Fiber line

The main source of nitrogen to the kraft pulping process is the wood chips to the digester. The nitrogen content of wood chips depends on, for example, whether the wood is hardwood or softwood, wood species, and bark content of the chips. Hardwoods generally have higher nitrogen content than softwood, and bark contains about ten times more nitrogen than wood, on a dry weight basis. The nitrogen content in wood can vary from 0.4 - 2.0 kg N/ t wood. In this study, softwood containing 693 g N / kg dry wood corresponding to 1 300 g N / ADt has been taken into account. The nitrogen in the wood is mainly in the form of peptides in the wood proteins and enzymes.

In addition to the nitrogen entering the digester with the wood chips, there is also nitrogen which enters the digester with white liquor. Since the chemical recovery system in the kraft pulping process is basically a closed cycle, the nitrogen in the white liquor originates from the wood chips. Nitrogen in the white liquor is mainly in the form of ammonia.

Approximately 90-95% of the nitrogen in the wood chips is released during the cooking process and exits the digester with the blow gases and the black liquor. Some nitrogen leaves the digester with the pulp to brownstock washing, but the majority of that nitrogen returns to the digester with the brownstock wash liquor.

A portion of the wood nitrogen which is released during the cooking process is converted to ammonia, and the remaining wood nitrogen is contained in organic nitrogen compounds. According to DeMartini et al. (2004) approximately 10-15% of the wood nitrogen is converted to ammonia. About half of the ammonia in the digester is released with the digester blow gases, while the organic nitrogen compounds and the remaining ammonia exit the digester with the weak black liquor to the evaporation plant.

3.2.2 Liquor cycle

Studies have also found that some additional ammonia is formed in the early effects of evaporation. According to Demartini et al. (2004) the amount of ammonia generated during evaporation is equivalent to approximately 12 - 13% of the wood nitrogen. Essentially all of the ammonia in the black liquor from the digester plus the additional ammonia formed during evaporation is released to the evaporation plant condensates.

The evaporated black liquor is fired in the recovery boiler. Approximately one third of the nitrogen in the black liquor leaves the recovery boiler as smelt to the smelt dissolving tank (Kymälainen et al. (1999)).

The nitrogen in the smelt is mainly in the form of cyanates which are mostly converted to ammonia during the smelt dissolving / recausticizing processes. According to Kymälainen et al.

(2004), green liquor nitrogen corresponds to approximately 40% of the black liquor nitrogen. Approximately 60% of the green liquor nitrogen remains in the white liquor to the digester, approximately 20% of the green liquor nitrogen is returned to the smelt dissolving tank as weak wash, and approximately 20% of the green liquor nitrogen exits the process as gaseous NH_3 around the slaker and causticizer vessels.

3.2.3 Condensate and Gas Handling systems

In the model mill, the evaporation plant condensates are divided into clean, intermediate, and foul condensates, depending on the level of contamination. Clean condensates typically have a COD of approximately 200 mg/L, and intermediate condensates can range from 500 - 1000 mg/L. Foul condensate from the digester and the evaporation plant contain methanol, malodorous sulphur compounds, turpentine, and potentially minor quantities of tall oil resins, thus the foul condensate COD is far higher. The foul condensate is stripped in a steam stripper where most volatile contaminants are recovered to the SOG. The stripped foul condensate is clean enough to be mixed with the clean condensate.

Evaporation condensate segregation varies from mill to mill, depending on how condensates are reused and on the quality requirements for condensate released as effluent. In general, new evaporation plants have condensate segregation designed so that all of the intermediate condensate which is generated can be consumed in recausticizing, since it is not acceptable to release intermediate condensate as effluent. In some mills there may be an excess of intermediate condensate which is stripped with the foul condensate, or even in a separate stripper, to produce clean condensate.

In the model mill all intermediate condensate is used in the recausticizing plant for dreg washing, lime mud dilution, and shower water on the lime mud filter. The clean condensate including the stripped condensate is used for post oxygen washing and bleach plant washing. Only a minor amount of the condensate used for washing is returned to the liquor cycle via the digester. Any excess clean condensate is released as effluent from the mill.

Digester blow gases contain about half of the ammonia that is in the digester. Essentially all of this ammonia remains with the digester foul condensate. The evaporation plant condensates contain the remaining half of the ammonia from the digester plus ammonia formed during evaporation of the black liquor. Studies made show (Gautreaux et al. (2004)) that all ammonia is released to the SOG during foul condensate stripping and that the stripped condensate is essentially nitrogen free. Based on Kymäläinen et al. (1999), it has been assumed that the foul condensate contains approximately 75% of the total condensate nitrogen while remaining nitrogen is found in the clean and intermediate condensates.

In the base case it has been assumed that half of the intermediate and clean condensates are used in the recausticizing plant while the remaining intermediate and clean condensates together with stripped condensate are used in the fiber line for washing in brownstock and bleaching. Fiber line wash filtrates that are not recycled are sent to the waste water treatment plant. A minor amount of the nitrogen in the fiber line wash filtrates is released to the HVLC collection system. It is assumed that the washing and bleaching operations do not absorb any nitrogen to the pulp.

There are some references, such as Kymäläinen et al. (1999), which describe nitrogen losses to the HVLC collection system in the recausticizing plant area. Unfortunately, no information regarding nitrogen HVLC losses in other mill areas has been found, thus the amount of nitrogen released from both the fiber line and evaporation plant is scaled proportionally to the recausticizing area HVLC nitrogen.

In most mills the HVLC gases are collected and in most modern pulp mills the HVLC gases from both the fiber line and evaporation plant are well covered as well as the vent gas from the dissolving tank. Unfortunately not all pulp mills cover the recausticizing plant area to the same extent. This is due to several reasons such as installation cost and primary focus on collecting the most extensive odor sources. In general the installation of a HVLC gas collection system implies a lot of piping and ducting that must be carefully designed in order to avoid high material cost etc. The cost for piping, ducting and the design thereof can be more expensive than the investment cost for the main equipment. For this reason, HVLC gas collection systems are often expanded gradually.

There are few specific technologies for reduction of LVHC nitrogen (Blomström & Lundahl, 2006). Most of these technologies are based on absorption of ammonia by simple water spraying since ammonia is readily soluble in water. This absorption process is somewhat similar to a HVLC cooling scrubber. Measurements and studies made on HVLC nitrogen are however extremely rare since most are focused on TRS and other parameters of interest. Resulting HVLC condensates, depending on the moisture content, are normally low volume and if not too odorous these condensates can be taken either to the waste water treatment plant or to the mill foul condensate collection system.

The SOG is treated in a methanol recovery system where the methanol is recovered as liquid methanol. Liquefied methanol is a more concentrated fuel than compared to SOG and the liquefied form facilitates both temporary storage and implies stable incineration in terms of stable heat input and reduced flame fluctuations. The recovered methanol is burned in the recovery boiler, alternatively the lime kiln or in a dedicated incinerator.

3.2.4 Effluent treatment

The amount of nitrogen required for the biological effluent treatment to function properly depends on the COD of the incoming effluent. A normal nitrogen requirement in a bleached kraft mill bio treatment is approximately 0.5 kg N/ADt. The incoming effluent contains some nitrogen and is added either as urea, Nutriol™ or a similar commercial nitrogen mixture.

The bio sludge from effluent treatment is taken back to the evaporation plant, dewatered, hydrolyzed and mixed with black liquor that is sent to the recovery boiler. Approximately half of the effluent nitrogen, 0.25 kg/ADt, is bound to the bio sludge according to ÅF file data. The bio sludge contains about 10 % as reduced ammonia nitrogen (Kymäläinen et al. (2000)), and the remaining 90 % of the bio sludge nitrogen is considered organically bound nitrogen with somewhat similar behavior and properties as the organic nitrogen found in black liquor.

For mills that do not recover bio sludge, it is estimated that the nitrogen content in most streams would be about 20% lower than the base case presented in this report. This observation seems indirectly to correlate with other studies made in this field where for example the flue gas NO concentration has been observed to increase by 21 % after bio sludge intake to the recovery cycle (Vähä et al. (2012).

4 Alternative 1 - Acidification of foul condensates and SOG

4.1 Process Description

In this alternative, the foul condensate is acidified to pH less than or equal to 6.5 prior to steam stripping. At this pH, most of the ammonia is captured as NH_4^+ in the liquid clean condensate from the stripper. The clean condensate is used in the bleach plant, and then sent to the waste water treatment plant. The added acid neutralizes the ammonia and in some cases, minor amounts of other alkaline compounds. There is some neutralizing heat formed however the temperature increase is relatively insignificant, mainly due to the large volume of foul condensate. In the M-Real process (Alfthan & Sjölander, 1999) the acid is added directly to the foul condensate tank, whereas the acid is added to the upper part of the stripper column in the Södra Cell process (Olsson & Zacchi, 2004). The chemical principle is however the same even if there may be some minor differences when it comes to equipment details etc. In general these processes do not require any special equipment except for acid preparation and dosing equipment.

The quality of the acid and the purity demand seems to vary somewhat in these methods. The M-Real process used sulfuric acid but the Södra Cell process seems open to a wide range of different types of acids. Theoretically any acid would work, but due to corrosion problems some acids such as hydrochloric acid are less suitable. A dilute sulfuric acid seems to be the most commonly used acid for these types of applications. A standard material such as ASTM 316 or similar material seems to be the preferred material and should be suitable as long as the acid control operates as expected.

There are some other potential problems which may occur in these processes. In softwood mills the foul condensate may contain extractives. These extractive compounds as well as TRS compounds present in the foul condensate may partly polymerize when acid is added and cause clogging problems or unwanted scaling from where the acid is added and downstream. If clogging occurs in the stripper the cleaning procedure may be complicated and time consuming. These types of problems are however not fully documented but recorded in ÅF file data. Neutralization of ammonia by sulfuric acid may also cause precipitation of ammonium sulfate that may cause local problems, especially in the acid mixing zone, thus proper mixing seems important. For this reason, even if the ammonium sulfate is very soluble, there is a small but not negligible risk that the stripper trays, especially in the inlet region, may be exposed to deposit formations that may clog valves, downcomers or else disturb the stripper operation.

4.2 Nitrogen Balance

The nitrogen balance for this alternative is illustrated in enclosure 2. The balance is mainly based on the M-Real patent, but similar results are expected with the Södra Cell process. The nitrogen content for some of the key streams compared to the base case is shown in table 2 below.

	Base case g N/Adt	M-Real process g N/ADt	change, %
Wood	1300	1300	-
White liquor	368	294	-20
Weak black liquor	1362	1346	-1
Biosludge intake	250	250	-
Digester foul condensate	236	220	-7
Evaporation foul condensate	247	237	-4
SOG	480	13	-97
Stripped condensate	10	446	4360
Clean/intermediate condensates	155	586	278
MeOH to recovery boiler	451	12	-97
LVHC to recovery boiler	75	52	-31
Black liquor to recovery boiler	1181	1181	-
Total nitrogen to recovery boiler	1860	1446	-22
Green liquor	614	490	-20
Lime mud	31	26	-16
Purchased N to effluent treatment	434	87	-80

Table 2. Nitrogen amounts for some key process streams for the M-Real process compared to the base case.

According to the balance the total nitrogen fed to the recovery boiler (excl. nitrogen as N_2) can be reduced by about 22 % or about 400 g N/ADt by the acidification of the foul condensates and the SOG. The amount of ammonia is markedly increased in the stripped and intermediate condensates. The method is simple and requires a minimum of additional process equipment. The nitrogen as ammonia in foul condensate is captured to the stripped clean condensate for further use in the fiber line operations. Some nitrogen will be recovered to the fiber line HVLC collection system but most nitrogen will finally be found in the effluents taken to the waste water treatment plant.

4.3 Potential consequences in other mill areas

According to the balances the HVLC nitrogen increases by about 30 % due to the use of the nitrogen enriched condensate in the fiber line. Unpublished Swedish mill experience indicates that the process decreases the clean condensate COD. Even if this is expected due to improved removal of acidic TRS compounds it should be a welcomed side effect.

In terms of nitrogen, the optimal scenario would be if the nitrogen enriched clean condensate from the stripper can be taken directly to the waste water treatment. In this case however, the clean condensate used in the fiber line washing and bleaching processes would have to be replaced with fresh water, and the mill’s total fresh water consumption would increase.
If acidulation is made with fresh sulfuric acid, additional NaOH will be required as make-up in order to maintain the Na/S balance.

5 Alternative 2 - Nitrogen condensate recovery from Kraft methanol

Metso (Brucher & Norberg, 2009) has developed a process for capture of nitrogen from liquid methanol. A.H. Lundberg (Der & Jensen, 2010) has developed a process similar to Metso’s but it is however not considered in this study. Andritz (Saviharju & Eneberg, 2003) has developed a process for nitrogen capture which is based on acid scrubbing of the SOG. The Metso and Andritz processes differ from each other but both result in a more nitrogen concentrated condensate compared to Alternative 1. The lower volumetric flows and higher nitrogen concentration implies in new possibilities, such as sending the nitrogen enriched condensate directly to the waste water treatment plant without first passing the bleach plant.

5.1 Process Description

5.1.1 The Metso “PuriMeth™” process

In the Metso process liquid methanol is processed, and a methanol recovery plant is a first requisite for the process. The purpose of the Metso “PuriMeth™” process is to remove the nitrogen in a first stage and oxidation of odorous TRS compounds in a second stage. In this study only the nitrogen removal stage is considered. The resulting nitrogen and odor -free methanol can then be further processed or incinerated without causing increased NO_X.

The process is relatively simple; initially the methanol from the methanol storage tank is mixed with sulphuric acid, and then transferred to a column where the volatile methanol and TRS phase is separated from the ammonium containing water phase. The gas phase is condensed for further use whereas the ammonium containing condensate can be used for nitrogen replacement in the waste water treatment plant or further refined and sold as a fertilizer if sufficiently free from TRS compounds and other impurities.

5.1.2 The Andritz process

In the Andritz process the SOG is scrubbed with acid, resulting in an enriched nitrogen condensate. The amount of condensate from the ammonia scrubber is higher compared to the Metso process, but still much lower compared to the M-Real and the Södra Cell methods. According to ÅF file data the nitrogen capture efficiency seems to correlate to the gas- liquid contact arrangement inside the scrubber system. Similar to the Metso process the resulting condensate can be taken to the waste water treatment plant to replace purchased nitrogen.

5.2 Nitrogen Balance

A nitrogen balance, mainly based on the Metso “PuriMeth™” process, is shown in enclosure 3. Depending on the scrubbing efficiency the Andritz process balance should in general appear somewhat similar. According to ÅF file data the resulting methanol is more or less totally free from nitrogen and depending on the amount of water present in the system and steam used in the column the condensate nitrogen concentration is approximately. 30 - 45 g/l. There is a minor increase in both nitrogen and other volatile TRS compounds to the LVHC collection system due to the vent from the condenser. The condensate is sent to the water treatment plant.

Table 3 below summarizes the nitrogen content for some of the key streams in relation to the base case.

	Base case	**Metso Power process**	
	g N/Adt	**g N/ADt**	**change, %**
Wood	1300	1300	-
White liquor	368	280	-24
Weak black liquor	1362	1317	-3
Biosludge intake	250	250	-
Digester foul condensate	236	191	-19
Evaporation foul condensate	247	219	-11
SOG	480	408	-15
Stripped condensate	10	8	-20
Clean/intermediate condensates	155	136	-12
MeOH to recovery boiler	451	0	-100
LVHC to recovery boiler	75	85	13
Black liquor to recovery boiler	1181	1181	-
Total nitrogen to recovery boiler	1860	1384	-26
Green liquor	614	467	-24
Lime mud	31	25	-19
Purchased N to effluent treatment	434	85	-82

Table 3. Nitrogen amounts for some key steams for the Metso “PuriMeth™” process compared to the base case. The total amount of nitrogen to the recovery boiler is decreased by about one fourth.

In the Metso “PuriMeth™” process, the total nitrogen to the recovery boiler is reduced by approximately 26 % or about 475 g N/ADt compared to the base case and about 4 % more than compared to Alternative 1. The installation does however require more equipment to be installed and the higher investment cost has to be evaluated relatively the small increase in efficiency. The Metso “PuriMeth™” process may however be justified if the nitrogen free methanol shall be further purified with respect to sulfur but this case has not been examined in this study.

As in Alternative 1, most process streams contain lower nitrogen amounts and the nitrogen enriched condensate from the Metso “PuriMeth™” process can be sent directly to the waste water treatment plant since this relatively concentrated nitrogen stream will not affect the water balance significantly.

5.3 Potential consequences in other mill areas

According to ÅF file data there are no known Metso “PuriMeth™” installations. There is however one Swedish mill that has been operating an Andritz installation for a couple of years. The mill operating the Andritz installation has had extensive clogging problems and because of this the system is presently not in operation but by-passed. The Metso “PuriMeth™” only processes the methanol after the methanol recovery process, not the total SOG, so there are reasons to believe that such clogging issues may be less serious, or possibly not an issue at all.

The mill that was operating the Andritz installation started to recover bio sludge to the evaporation plant in 2004 and it was observed that the overall nitrogen level in the mill increased. After installation of the Andritz process the resulting nitrogen condensate was taken to the waste water treatment and no related serious consequences has been reported in this matter.

Ordinary “Low-NO_X” incinerators are generally expensive but the Metso “PuriMeth™” process enable relatively cheap “low-NO_X” incineration of the kraft methanol since treated methanol can be taken to almost any ordinary mill incineration system such as the lime kiln. Sulfur capture is however required in order to keep the SO_2 emissions at a fairly low level.

Similar to Alternative 1, if fresh sulfuric acid is used for acidulation a corresponding amount of NaOH is required for maintaining the Na/S balance.

6 Economic evaluation

The investment- and operating costs for both Alternative 1 and 2 has been estimated. The investment cost covers all estimated costs for a "turnkey" delivery designed for the mill capacity as presented in section 3.1.

The reduced NO_X in the recovery boiler flue gas may in some countries, such as Sweden, also affect the operating costs. The Swedish NO emission fee in relation to both Alternative 1 and 2 is discussed in section 6.2.

6.1 Alternative 1

6.1.1 Investment cost

Even if the M-Real process has not been specified in detail it is assumed that the process comprises the following equipment:

- Centrifugal pump
- pH controlling equipment incl. control valve
- Liquid distributor
- Piping, incl. manual valves

It is assumed that sulfuric acid, mixed to approximately 30 w% is available within a reasonable distance from the installation. The assumed base material is ASTM 316. The turnkey cost is estimated to between 50 - 75 kEUR. The piping cost is the biggest uncertainty since it depends on the existing layout.

6.1.2 Operating cost

The operating cost has been estimated in table 4 below. It has been calculated that about 413 g N/ADt of the nitrogen enriched condensate sent to the fiber line is finally sent to the waste water treatment plant, thus savings due to replacement of urea or similar chemicals can be made. This process requires somewhat more acid than compared to the Alternative 2. Due to the use of clean condensate in the bleach plant area this process implies increased nitrogen losses to the HVLC collection system, thus slightly less amounts of nitrogen for use in the waste water treatment plant than compared to Alternative 2.

		EUR/ADt
Sulfuric acid (as 100-w %)	0.14 EUR/kg	0.27
NaOH (as 100-w %)	0.39 EUR/kg	0.61
Electricity	0.07 EUR/kWh	0.01
Nitrogen replacement	-1.0 EUR/kg	-0.41
TOTAL		0.47

Table 4. Estimated costs for consumables based on typical figures.

The operating cost is estimated to about 0.5 EUR/ADt, corresponding to an annual operating cost of about 620 kEUR but reduced to about 330 kEUR if the waste water treatment plant and the nitrogen saving is taken into account. Typical figures have however been used and may vary. The NaOH consumption for neutralization is conservatively estimated. It is assumed that neutralization of the condensate flow is required irrespective if recycled to the black liquor or

discharged with bleach plant wash filtrates to the effluent treatment and as seem from table 4 the NaOH cost is the biggest.
In the study there has not been any attempt to quantify the recovery boiler NO_X-formation effect with aspect to decreased ammonium-nitrogen intake. Accordingly, any costs associated with recovery boiler NO_X-formation are disregarded.

6.2 Alternative 2

6.2.1 Investment cost

It is assumed that the Metso "PuriMeth™" process comprises the following equipment:

- Mix tank
- Column with internals
- Condenser
- Centrifugal pumps
- Field instrumentation incl. control valves (8 loops assumed)
- Piping incl. manual valves
- Steel structure

It is assumed that diluted acid is available relatively close to the installation site and only additional piping and control valve is needed. The assumed base material is Duplex or LDX type of steel for the Mix tank, upper part of the column and the condenser. The turnkey cost for this system is estimated to about 790 - 825 kEUR. As for Alternative 1 there are uncertainties in not only the piping cost but also in required steel structures etc.

6.2.2 Operating cost

The Metso "PuriMeth™" process operation cost has been estimated in table 5 below. Similar to Alternative 1 typical values for consumables has been assumed and may vary between different mills. A cost for NaOH for neutralization of freshly added sulfuric acid is also included. The first stage of the Metso "PuriMeth™" process, results in an increased annual operation cost estimated to about 512 kEUR/a but taking the waste water treatment nitrogen savings into account the annual operating cost is reduced to about 217kEUR/a. Perhaps the operation cost looks more attractive if the second stage of this process, where TRS-free methanol is produced, is taken into account. The second stage is however beyond the scope for this study and has not been considered. Due to the minor amount of acid used in this process less neutralizing NaOH is required than compared to Alternative 1. Since it is assumed that the recovered nitrogen condensate is sent directly to the waste water treatment this process also implies less nitrogen losses to the HVLC collection system. Similar to Alternative 1 the NaOH cost is the biggest.

		EUR/ADt
Sulfuric acid (as 100-w %)	0.14 EUR/kg	0.18
NaOH (as 100-w %)	0.39 EUR/kg	0.41
Electricity	0.07 EUR/kWh	0.004
Low pressure steam	0.01 EUR/kg	0.13
Nitrogen replacement	1.0 EUR/kg	-0.42
(Warm water production	0.5 m^3/ADt	-)
TOTAL		0.31

Table 5. The estimated operation cost related to the first stage of the Metso "PuriMeth™" process.

There have not been any attempts to quantify effects on NO_X-formation in the recovery boiler resulting from lower intake of ammonium-nitrogen to the recovery boiler. Accordingly, any costs associated with recovery boiler NO_X-formation are disregarded.

7 Conclusions

Over the years several processes and technologies to reduce the nitrogen intake (excl. air N_2) to kraft pulp mill recovery boilers have been developed. Such reduction is expected to result in a decreased recovery boiler NO_X emission.

Most processes apply acidification of foul condensates, gases or methanol and produce nitrogen (ammonium) enriched condensate. In cases where there is a waste water treatment plant using reduced nitrogen it seems possible to make savings if the recovered nitrogen can be replace a purchased nitrogen source. Most of the main suppliers have developed technologies for nitrogen capture as a part of a bigger scope where TRS free methanol is recovered. Some of these technologies are however still under development, especially when it comes to the refining of the methanol. There seems however to be a negative operating cost when considering the nitrogen removal stage only and A.H. Lundberg is the only known supplier where such a concept has been commercialized.

The processes evaluated in this study demonstrate that it theoretically seems possible to reduce the recovery boiler nitrogen load by 20-25 % at relatively low capital and operating costs. There are however several factors that affect the total result. The potential use of the recovered nitrogen streams is of great importance since reuse in internal mill processes tends to suppress the benefit due to losses either to HVLC or other condensates that are recirculated back to the evaporation plant. For this reason, the waste water treatment plant, where reduced nitrogen is consumed, is perhaps the most obvious consumer. Acidification of foul condensates, SOG or kraft methanol may however not be problem free. According to ÅF file data some mills suffer from clogging due to polymerization of TRS compounds and extractives. In one mill, where the SOG is scrubbed with diluted sulfuric acid, these problems have caused serious disturbances and today the nitrogen capture system is bypassed.

If a NO_X regulation with an emission fee is effective, there can be significant operating cost savings when the nitrogen to the recovery boiler is reduced. Therefore further work to overcome the practical problems with the technologies reviewed in this study is highly recommended.

8 Further studies

The effect from decreased nitrogen intake to the recovery boiler (or to a dedicated incinerator) on NO_X emissions was not part of this study. A continuation of this study could be to perform practical field studies on the effect of decreased ammonium nitrogen intake in relation to the NO_X-generation.

In Sweden bigger incinerator systems with an annual capacity of more than 25 GWh are covered by an additional emission fee for flue gas NO. Depending on several factors such as the recovery boiler reduction efficiency, type of processed wood etc. the emission fee may be high or low. The NO emission and the resulting NO emission fee is generally higher for older recovery boilers in mills where hardwood pulp is produced. Further studies are however required to clarify the relation between the results from the present study and the NO_X generation. Such study would be of great importance to verify both environmental aspects and potential economical savings.

9 References

09-163, Å. R. (u.d.). *Energy Consumption in the Pulp and Paper Industry - Model mills 2010, Bleached Kraft Market Pulp Mill.*

Alfthan, C. J., & Sjölander, C. (1999). *Patentnr 9800190-2.* Sweden.

Andersson, L., & Norrström, H. (2010). Metoder för NOx reduktion på sodapannor. *Sodahuskonferensen 2010* (ss. 23 - 35). Stockholm: ÅF Industry AB.

Blomström, S., & Lundahl, R. (2006). *Patentnr WO/2010/016786.* US.

Brucher, J., & Norberg, A. (2009). *Patentnr SE531478.* Sweden.

Clement, J. L., & Barna, J. L. (1993). The effect of black liquor fuel-bounding nitrogen on NOx emissions. (ss. 653 - 660). TAPPI Proc Int Environ Conf Exhib, Book 2.

Demartini, N., Forssen, M., Hupa, M., Niemela, K., & Ulmgren, P. (u.d.). Distribution and Release of Nitrogen Compounds at Kraft Pulp Mills - A Survey of Three European Mills.

Der, B., & Jensen, A. (2010). *Patentnr WO2010091492.*

Gautreaux, W. T., Matthews, J. L., Hardee, J. L., & Bunting, K. P. (2004). *Ammonia Scrubber for Condensate Stripper Off-Gases.* North Charleston, South Carolina: MeadWestaco Corporation, Kraft Division.

Kristoffer Svedin, C. I. (2009). *LIME KILN MODELING CFD & One-dimensional simulations.* Stockholm: Värmeforsk.

Kymäläinen, M., Forssén, M., & Hupa, M. (1999). The fate of Nitrogen in the Chemical Recovery process in a Kraft pulp mill: Part 1: A general view. *Journal of Pulp and Paper Science 25 (12)*, 410-417.

Kymäläinen, M., Forssén, M., Demartini, N., & Hupa, M. (2000). *Effects of differences in the Kraft recovery process on harmful nitrogen.* Process Chemistry Group. Turku, FINLAND: Åbo Akademi University.

Olsson, J., & Zacchi, G. (2004). *Patentnr 9903676-6.* Sweden.

Saviharju, K., & Eneberg, H. (2003). *Patentnr EP001424435.*

Vähä-Savo, N., Demartini, N., & Hupa, M. (2012). Fate of biosludge nitrogen in black liquor evaporation and combustion. *TAPPI JOURNAL; 11, 9*, p 53-59.

ÅForsk. (2010). *Energy Consumption in the Pulp and Paper Industry - Model mills 2010, Bleach Kraft Market Pulp Mill.* Reference 09-163.

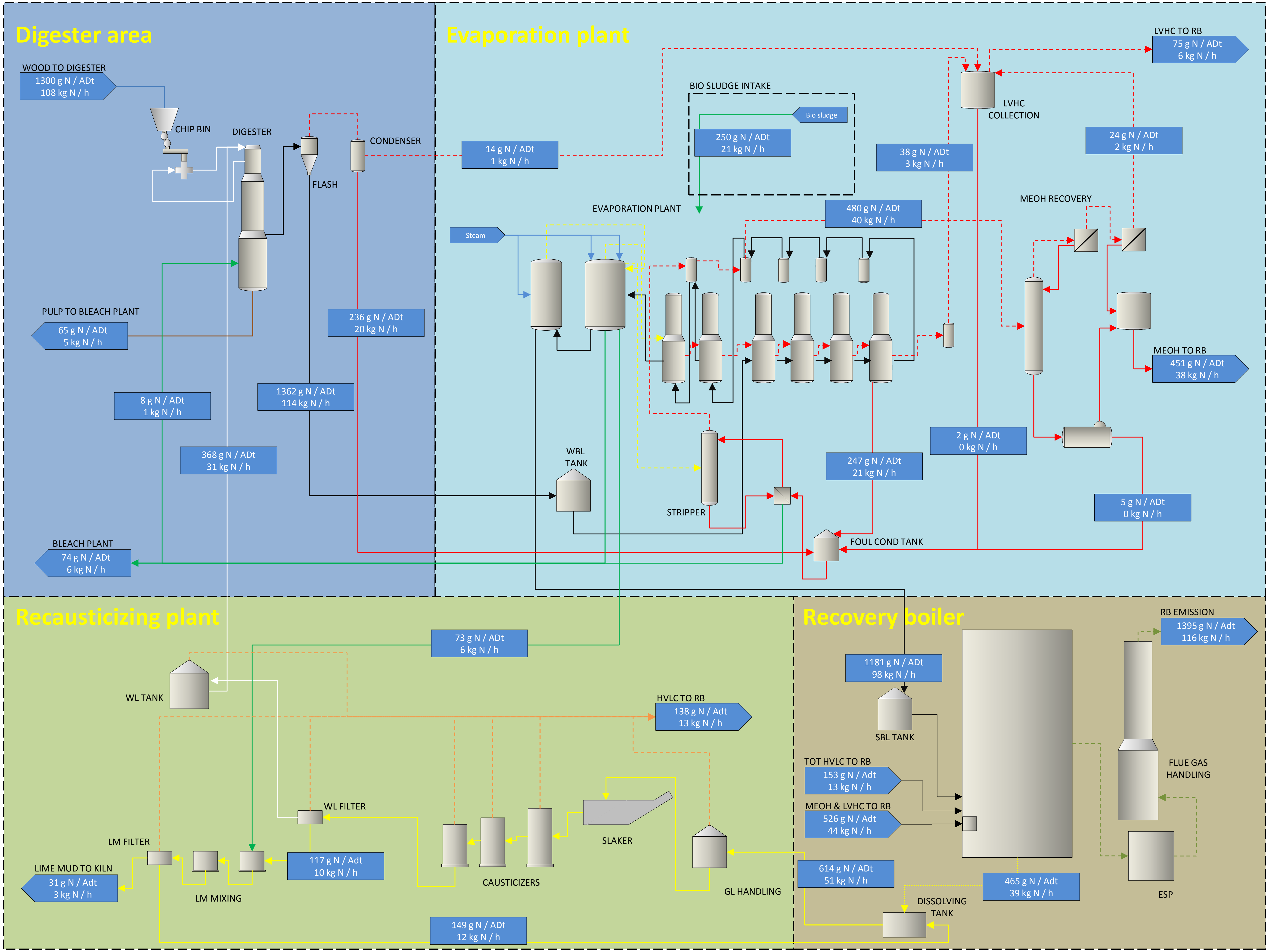
10 Enclosures

No 1 - Reference nitrogen mass balance block diagram

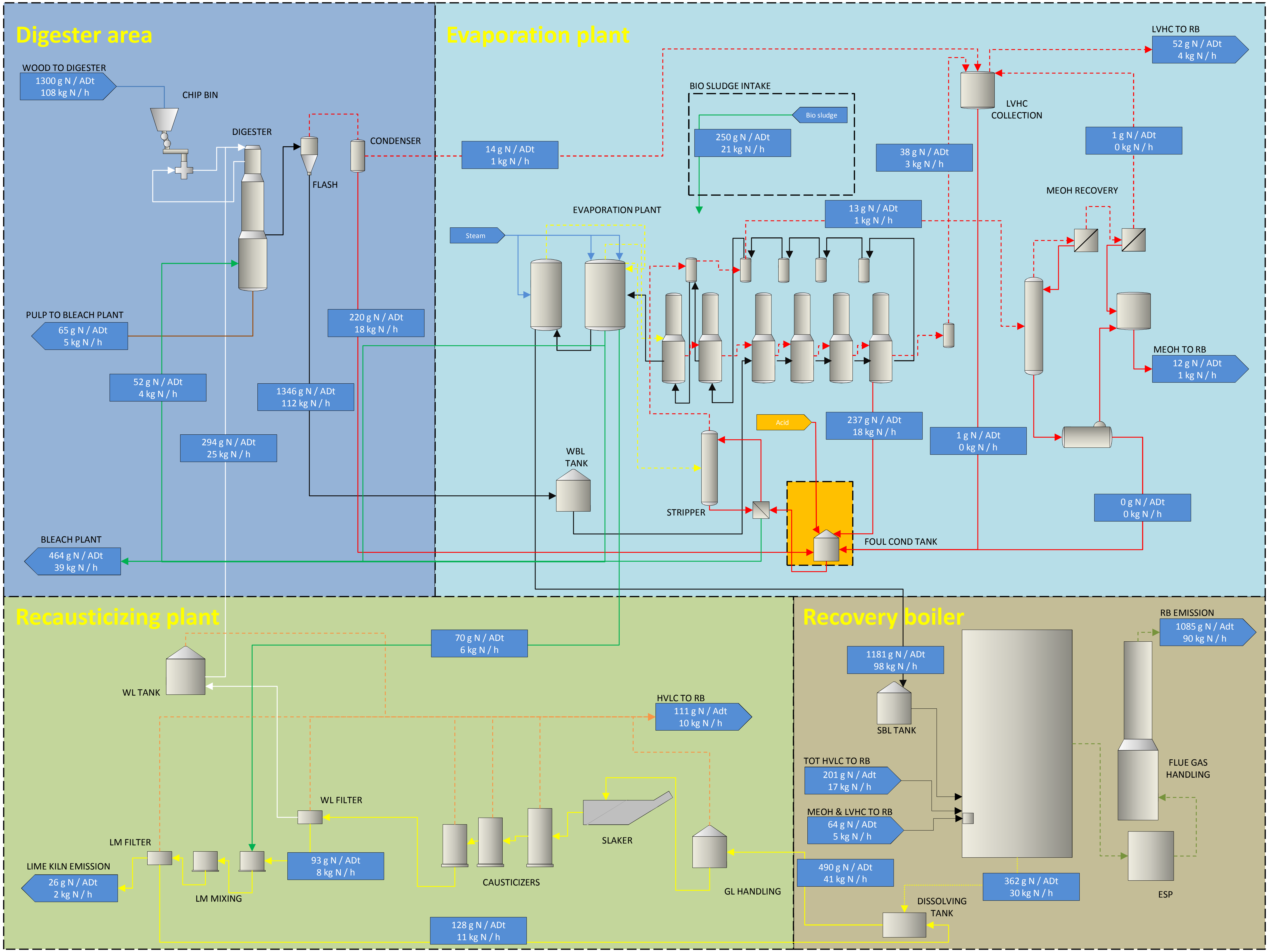
No 2 - Alternative 1 nitrogen mass balance block diagram

No 3 - Alternative 2 nitrogen mass balance block diagram

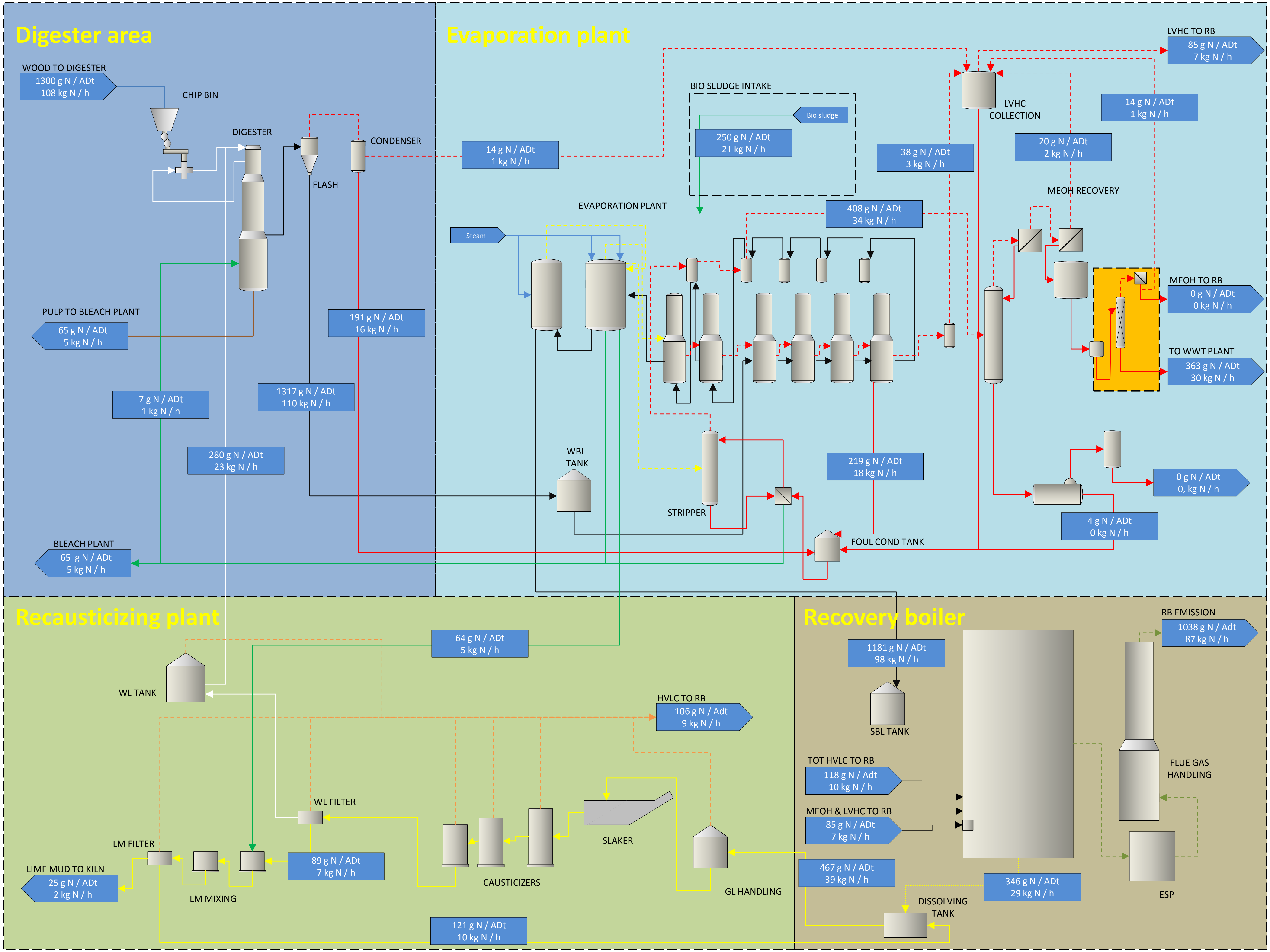
Enclosure 1: Reference nitrogen mass balance block diagram



Enclosure 2: Alternative 1 nitrogen mass balance block diagram



Enclosure 3: Alternative 2 nitrogen mass balance block diagram



LIITE 6

Esitys: Muiden työryhmien kuulumiset ja tulevat tapahtumat

Muiden työryhmien kuulumiset

Projekti	KTR: Hitsauspinnoitettujen putkien käyttö soodakattiloissa, VTT
Tavoite	Selvittää hitsauspinnoitettujen putkien käytettävyyttä / soveltuvuutta soodakattiloihin
Tekijä	VTT
Kustannus (bud. / tot.)	12 000 eur / 12 000 eur (+alv) (kirjallisuustutkimus) 8 000 eur / 9700 eur (+alv) (karakterisointitutkimus) 52 500 eur / - eur (+alv) (vanhennuskokeet)
Tilanne / Aikataulu	1. Kirjallisuuskatsaus valmistui 5/2016 2. Karakterisointitutkimus valmistui 01/2017 (KMP esitys) 3. Vanhennuskokeet käynnissä -> lämpötila 650 C tehty 4. Jännityskorroosiokokeet (syksy 2017) Kolmelta toimittajalta (Uhlig, AZZ/WSI, Areva Uddcomb) saatu 625, 825 ja 309 pinnoitettuja putkia • Referenssiputkina San38/San28/304L kompound • Vanhennuskokeet tehdään kolmessa eri lämpötilassa (600, 650, 700 C) ja kolmella eri pitoajalla (10, 100, 1000 h)

Projekti	KTR: Selvitys sularännien toiminnasta vaihtelevalla kuormalla
Tavoite	Selvitetään lämpövuon (sulavirtauksen/lämpötilojen vaihtelu) vaikutusta sularännien vaurioitumiseen Pyritään löytämään syitä miksi sularännit eivät kestä edes 12 kuukautta
Tekijä	LUT, diplomityö Eetu Rantanen
Kustannus (bud. / tot.)	12 000 eur / - eur (+alv)
Tilanne / Aikataulu	Tehtailta pyydetty dataa jäähdytysvesivirtauksista ja sitä kautta laskettu lämpötehon muutoksia -> riittävä määrä isoja muutoksia -> säröily Sunilassa tehty lämpökameramittauksia

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Projekti	KTR: Sularännisuositus
Tavoite	1. Kerättiin tietoa tapahtuneista vaurioista ja niiden syistä kyselyn avulla 2. Tehty SKY:n suositus BRLBAC:n ohjeen pohjalta
Tekijä	KTR
Kustannus (bud. / tot.)	2 000 eur / 5 000 eur (+alv)
Tilanne / Aikataulu	25.01.17 Ohjeen esittely vauriokeskustelussa 22.03.17 Ohje päivitetty keskustelun perusteella 05.04.17 KTR kokouksessa lisäykset tekstiin 28.09.17 KTR kokous suosituksen hyväksyntä ja julkaisu

Projekti	KTR: Soodakattilan tiiveydenvalvontaselvitys, Varo Oy
Tavoite	Tehdä yhteenveto käytössä olevista menetelmistä tehtailla (vuoden 2001 raportin päivitys) sekä esitellä saatavilla olevat parhaat tekniikat ja menettelyt
Tekijä	Timo Karjunen, Varo Oy
Kustannus (bud. / tot.)	12 000 eur / - eur + alv
Tilanne / aikataulu	• Kysely tiiveydenvalvonnan nykytilasta lähetettiin tehtaille 11/2016 • Esitys tuloksista Konemestaripäivillä Oulussa 1/2017 • Timo odottaa vielä tietoja laitetoimittajilta (kokemuksia viimeisimmistä projekteista) • Tulosten esittely KTR:n 28.9 kokouksessa
Päätökset	

Projekti	LTR: Black Liquor Evaporation Book
Tavoite	The book provides introductory text to the basic principles (handbook) of black liquor evaporation for young engineers in chemical recovery. Cost includes Niko DeMartini’s portion of the work
Tekijä	Åbo Akademi, Nikolai DeMartini Table Mountain Consulting, Jim Frederick
Kustannus (bud. / tot.)	14 750 eur / - eur (+alv)
Tilanne / Aikataulu	Hallitus tehnyt esityksen, että kirjan on valmistuttava tämän vuoden aikana – rahoitusvaraus ei siirry enää ensi vuoden budjettiin.
Johtopäätökset Toimenpiteet	• Lopullinen versio on tulossa kommentoivaksi 7/2017 • Versio lähetetään myös ulkopuolisille arvioijille Lars Olauson and David Clay.
Päätökset	

Projekti	LTR: Understanding Low Temperature Corrosion in BL Combustion – Phase 3
Tavoite	Työn tarkoitus on saada varmistus toisen osan saaduille tuloksille (24 tunnin kokeet) suorittamalla 1000 tunnin koe. Oletus on, että matalalämpötilakorroosio ilmenee nopeasti eli 24 tunnin kokeiden tulokset vastaavat 1000 tunnin koe tuloksia. Projektin aiemmissa osissa on selvinnyt, ettei rikkihapolle löydy kastepistettä soodakattiloissa ja alin mahdollinen savukaasujen lämpötila määräytyy teräspinnoilla korroosiota aiheuttavien suolojen hygroskooppisen luonteen mukaan.
Tekijä	Åbo Akademi: Nikolai DeMartini, Emil Vainio
Kustannus (bud. / tot.)	18 100 eur / - eur (+alv)
Tilanne / Aikataulu	1000 tunnin koe valmistui kesäkuussa ja raportti saatiin ÅA:sta elokuussa Raportin esittely 7.9 LTR kokouksessa

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Työryhmien projektiehdotuksia

- Kuumien lauhteiden käsittely ja puhdistaminen kalvotekniikalla
- Soodakattilatyöntekijän suojavaatetuksen kehitys
- Ääninuohous soodakattiloissa
- Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport

Muut asiat ja ilmoitukset

Opinnäytetyöpalkinto 2017

- Palkintoa voi hakea Suomessa korkeakoulussa tai yliopistossa tutkintonsa suorittavat opiskelijat, joiden opinnäytetyö liittyy sulfaattisellutehtaan kemikaalien talteenottoon.
- Työn tulee olla valmistunut 1.6.2016 ja 31.5.2017
- Palkinnon arvo 2000 euroa
- Opinnäytetöitä arvosteltaessa tarkastellaan seuraavia seikkoja:
  a) Tekniset ansiot
  b) Tulokset
  c) Uutuusarvo

Soodakattilapäivä 2017

- Aika: 2.11.2017
- Paikka: Clarion Helsinki (Jätkäsaari)

- Konemestaripäivät Veitsiluodossa tammikuu 2018

- Soodakattilaoperaattoreiden kokemustenvaihtopäivät
  - Järjestetään myös maaliskuu 2018

Vuositavoitteiden 2017 määrittely

1. Aktiivisuus:
   - Työryhmillä vähintään 3 kokousta vuodessa
   - Seminaarien osallistujamäärä >200 henkilöä
   - Työryhmillä 2 uutta projektia toteutettu 2017
2. Toiminnan laatu:
   - Jäsenistön palautteen keskiarvo vähintään 8.5
   - Palautteen kohteista valittu oleelliset kehityskohteet ja sovitut toimenpiteet tehty
3. Taloudelliset edellytykset:
   - Pysytään budjetissa ja rahoitus terveellä pohjalla.

4. Tuloksellisuus:
   - Vuoden lopussa kirjataan mitä on saavutettu ja miten saavutukset toteuttaa yhdistyksen päätehtävää
   - Korostettu teemoja hajukaasujärjestelmien turvallisuus sekä pitkät ajojaksot

17.10.2017 klo 13-15
Skype