

SUOMEN SOODAKATTILAYHDISTYS FINNISH RECOVERY BOILER COMMITTEE

**Finnish Recovery Boiler Committee** 

**Recovery boiler performance testing** Material and energy balance

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#### Foreword

This recovery boiler performance test procedure and material and energy balance calculation procedure has been compiled in the Finnish Recovery Boiler Committee's Black Liquor Sub-committee. The chairman was Keijo Salmenoja Oy Metsä-Botna Ab. The members were Esa Ruonala Stora Enso Oyj, Sanna Siltala UPM-Kymmene Oyj, Aki Hakulinen Kvaerner Power Oy, Kurt Siren Oy Keskuslaboratorio-Centrallaboratorium AB, Juha Koskiniemi Andritz Oy, Mika Salo Oy Metsä-Botnia Ab, Jyrki Rautkorpi Pöyry Forest Industry Oy, Mikko Hupa Åbo Akademi. Scretary for the subcommittee was Jens Kohlmann Pöyry Forest Industry Oy. Expertise was provided in creation of this document by Esa Vakkilainen Pöyry Forest Industry Oy.

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#### Summary

Recovery boiler mass- and energybalances are needed for performance testing of recovery boilers, mill energywide control systems and in calculating air emission data. There does not excist a suitable prodedure for modern recovery boilers. Current recovery boiler balances are mainly based on 1996 TAPPI publication "Performance Test Procedure: Sodium Base Recovery Units". The use of which is problematic because of English units and some erroneous views. General steam generator balances have been based on outdated DIN 1942 "Acceptance Test on Steam Generators", which fails to mention recovery boilers.

This recommendation includes borate autocausticization in the recovery boiler furnace. This type of operation takes currently place in some Skandinavian mills.

This recommendation is based on the newly accepted European standard for steam generator acceptance tests EN 12952-15:2003 "Water-tube boilers and auxiliary installations - Part 15: Acceptance tests". The balances are thus based on the as-fired liquor flow and as-fired liquor dry solids. Mass- and energybalances are made for unit mass flow of as-fired liquor.



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#### **1 INTRODUCTION**

Recovery boiler mass and energy balances are needed for performance testing of recovery boilers, mill energywide control systems and in calculating air emission data. There does not exist a suitable procedure for modern recovery boilers. Current recovery boiler balances are mainly based on 1996 TAPPI publication "Performance Test Procedure: Sodium Base Recovery Units". The use of which is problematic because of English units and some erroneous views. General steam generator balances have been based on expendable DIN 1942 "Acceptance Test on Steam Generators", which fails to mention recovery boilers.

This recommendation is based on the newly accepted European standard for steam generator acceptance tests EN 12952-15:2003 "Water-tube boilers and auxiliary installations - Part 15: Acceptance tests".

#### 1.1 Application

This procedure is meant for performance testing and efficiency analysis of modern recovery boilers. Therefore the following have been included

- Guidelines for performance testing
- Suggestion for applicable system boundaries
- Estimation of uncertaintities with measurements
- Recommendations on sample frequencies and sampling procedures
- Recommendations on applicable analysis

The recommendation is based on the as-fired liquor flow and the as-fired liquor dry solids. Mass and energy balances are made for unit mass flow of as-fired liquor. During the performance testing accurate black liquor flow measurement is not needed.

#### **1.2** Basis for balances

Basis for this recommendation is the as-fired black liquor flow and dry solids. Similarly the lower heating value is used as in EN 12952-15:2003. All balances are based on the unit flow of as-fired black liquor. During the performance test the accurate as-fired black liquor flow measurement is not needed.

Similarly the furnace heat load, HHRR is specified as lower heating value times mass flow per bottom area.

#### **1.3** Applicable boilers

Use of this procedure for other types of boilers than modern kraft recovery boilers needs careful thought. Its application without changes to other types of boilers is not possible. Modifications are needed to accommodate

- NSSC boilers
- Magnesium and calcium based recovery units
- Boilers with direct contact evaporators
- Gasification of black liquor



#### 1.4 Limitations

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#### **1.4.1** Additional flows to furnace

One of the biggest differences to earlier procedures is that this procedure includes all applicable flows to furnace. Typical additional flows to the furnace are

- Combustion of weak non condensable gases (DNCG or HVLC NCG)
- Combustion of strong non condensable gases (CNCG or LVHC NCG)
- Combustion of dissolving tank vent gases
- Combustion of methanol and turpentine

In addition to the above with black liquor other streams are burned

- Makeup
- Waste acids
- Biosludge
- Soap

Because the balances are based on as-fired liquor all the streams added to the virgin black liquor are automatically included. It is recommended that the maximum allowable flows for each stream during the performance testing are defined. Typically changes in these additional streams can not be accepted during performance testing. It is recommended that the testing is done with all typical additional flows on. Such flows are waste acids from chemical manufacture and biosludge. Similarly all individual flows to the furnace like DNCG, CNCG and dissolving tank vent gases should be operated during the performance testing.

#### 1.4.2 Borates

This recommendation includes borate autocausticization in the recovery boiler furnace. This type of operation takes currently place in some Skandinavian mills (Björk et al., 2005).

#### 1.4.3 Emissions

This procedure is assumes typical operation for modern kraft recovery boilers. This means that additional emission measurements are not needed. If the kraft recovery boiler generates atypically high incombustibles (CO, VOC), additional measurements and additional loss calculations are recommended.

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#### **1.5 Contract points**

This procedure has been meant as part of recovery boiler contract. Contracts are made long before the boiler takeover tests and performance tests occur. It is recommended that the contract mentions

- Applicable source for properties of water and steam
- Applicable source for gas enthalpies
- Emission measurement standard
- Applicable standards or methods for chemical analysis
- Reference temperature
- How the cleanliness of the recovery boiler is defined at the beginning of testing
- Total time of the testing period and length of each period
- Use of outside measurements and measuring services during testing
- Required sampling and measurement points
- Amount of blowdown and sootblowing during testing
- Such balance corrections that are calculated differently that this standard
- Frequency and type of sampling during testing
- Balance boundary if it is not the boiler enclosure

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#### 2 APPLICABLE STANDARDS

Performance test procedures and efficiency calculations are always based on the assumption that best available techniques are used and customary means applicable to the industry are followed. All measurements should be made following applicable standards. Analysis should be done according to the procedures for pulp mills. Sampling should be done as recommended. Emission measurements follow the applicable standards.

#### 2.1 General measurement standards

Recovery boiler balance procedure is based on the assumption that if the contract does not clearly state other vice the performance and acceptance tests are done according to the following guidelines and standards.

EN 837-1

EN 873-3	Pressure gauges -Part 1: Bourdon tube pressure gauges -Dimensions, me- trology, requirements and testing
EN 60751	Pressure gauges -Part 3: Diaphragm and capsule pressure gauges - Dimensions, metrology, requirements and testing
EN ISO 5167	Industrial platinum resistance thermometer sensors (IEC 751: 1983+ A1: 1986) 7-1
IEC 584-1	Measurement of fluid flow by means of pressure differential devices -Part 1: Orifice plates, nozzles and Venturi tubes inserted in circular cross- section conduits running full (ISO 5167-1: 1991)
IEC 584-2	Thermocouples -Part 1: Reference tables
ISO 5168	Thermocouples -Part 2: Tolerances
	Measurement of fluid flow -Estimation of uncertainty of a flow-rate meas- urement



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#### 2.2 Methods for analysis

SCAN-N 22:77

Determination of dry solids SCAN-N 33:94

Determination of effective alkali KCL 67:87

Determination of NaOH content SCAN-N 31:94

Determination of sulphide content SCAN-N 6:64 tai SCAN-N 6:85

Determination of sulphate content KCL 66:81

Determination of black liquor higher heating value SCAN-N 37:98

Sodium, potassium SCAN-N 35:96 tai ASTM D 4239 / LECO SC-444

Sulfur ASTM D 5373 / LECO CHN-1000 / LECO CHN-600

Hydrogen, carbon

ASTM D 4208

Cloride

SFS 3866, 3869, 5265, 5293 sekä 5624

Emissionsions

#### 2.3 Sampling guidelines

Smelt sampling should be done according to the "ETY-soodakattila valiokunta, Suositus sulan and viherlipeän reduktioasteen määrittämiseksi" VK-15 394V-02.



#### 2.4 Thermodynamical property values

The properties of water and steam shall be determined in accordance with the "Properties of Water and Steam, IAPWS-IF97: The Industrial Standard IAPWS-IF97 for the Thermodynamic Properties and Supplementary Equations for Other Properties" by W. Wagner and A. Kruse, Springer-Verlag Berlin and Heidelberg GmbH & Co. K, 1998, ISBN: 3540643397.

Properties for smelt compounds and gases can be found in web pages of the National Institute of Standards and Technology <u>http://webbook.nist.gov/</u>. NIST properties are mainly based on the newest edition of JANAF-tables (Chase, 1998).

### **3 BALANCE CALCULATIONS**

This balance procedure is based on the new European boiler balance standard EN 12952-15:2003 "Water-tube boilers and auxiliary installations - Part 15: Acceptance tests". Because this standard does not give answers to kraft recovery boiler specific questions some additional definitions have been made to e.g. calculate some heat losses.

Calculation of material and energy balances is fundamental. Dimensioning of recovery boiler heat transfer surfaces can not be done if mass and energy flows are unknown. Proper calculation is important for mill energy and mass balances. These are needed to evaluate economics and running costs. Recovery boiler mass and energy balances have been presented by Gullichsen (1968b), Clement *et al.* (1963), Adams and Frederick (1988) and Vakkilainen (2000b). The only standard that covers exclusively recovery boiler mass and energy balance calculation is the so called Tappi standard (Performance, 1996).

This recommendation does not require a standard form for the way the recovery material and energy balance is presented. For a material and energy balance to conform this standard the physical properties and the calculations need to follow this document. An example calculation is shown as Annex to clarify the calculations.

#### **3.1 Standard state**

Term "standard state" is meant here to refer the zero-point of enthalpy Pn = 0,101325 MPa and tn = 0 °C. It is recommended that balances are calculated using 0 °C as reference temperature. The balance reference temperature can also be some other temperature defined in the contract.

#### **3.2 Boiler efficiency**

Boiler efficiency is a measure of the goodness of the chosen process and equipment to transfer combustion heat to the heat in steam. The best solid fuel boilers the boiler efficiency is close to 90 %. Oil and natural gas fired boilers can achieve 95 % efficiency.

Boiler efficiency can be defined as the ratio of the useful heat output to the total energy input.

$$\eta = \frac{Q_{abs}}{Q_{in}}$$

1

where

η	is boiler efficiency
$Q_{abs}$	is the useful heat absorbed (heat transferred to steam)
$Q_{in}$	is the heat and energy input into the boiler

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To determine the efficiency of a boiler, a system must be defined and the energy flows that cross the system boundaries must be resolved. System boundaries should be chosen so that it is possible to define all energy and mass flows in and out with sufficient accuracy. In practice many minor flows are usually neglected. When determining the boiler efficiency all internal reactions and recirculations can be neglected. Determination of boiler efficiency can be done with only flows though system boundaries.



#### Figure 3-1, Simplified boiler schematic

Figure 3-1 shows a simple boiler process. Fuel and required amount of combustion air are fed into the boiler. The fuel reacts with the oxygen in the boiler and flue gas is drawn out. Released heat is captured to the water pumped into the boiler transforming it to the steam that flows from the boiler.

It is clear that the system boundaries can be drawn in many ways. For example the boiler house might form a convenient system boundary. It has been pointed out that losses and heat input caused by fans, blowers and pumps should not affect the boiler efficiency. On the other hand, forced circulation pumps, flue gas recirculation fans and other internal process devices should be taken into account, because they play a role when boiler efficiency between different types of boilers is compared. Therefore the system boundary for boiler efficiency loosely includes some but not all equipment in the boiler house.

A system boundary for boiler efficiency measurement is determined in equivalent way to definition in EN 12952-15. Figure 3-2 shows a typical system boundary for recovery boiler. All flow values are recorded when they cross the system boundary. This is shown in Figure 3-3. Definitions for flows are shown in table 3-1.

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### Figure 3-2, Typical system boundaries for a recovery boiler

Comments for system boundary definition

- Black liquor handling, storing and feeding equipment are outside the boiler system boundary. Black liquor preheating and the associated equipment are within the system boundary as they are a part of an internal flow loop.
- Air fans and air ducts are outside the boiler system boundary. Equipment starting from the first heat transfer surface, air preheater is within the system boundary.
- Furnace with associated equipment is within the boiler system boundary. Smelt handling and dissolving tank is outside the boiler system boundary.

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- Flue gas cleaning equipment is outside the boiler system boundary. Possible fan for flue gas recirculation is outside the boiler system boundary.
- All steam and water heat exchangers that cool the flue gas are inside the boiler system boundary
- Forced circulation pumps are inside the system boundary.
- Control system, instrumentation and electrification are outside the boiler system boundary.



Figure 3-3, Recovery boiler diagram with input, losses and mass flows (normal envelope)

For recovery boiler efficiency calculations flow, pressure, temperature and composition of each flow must be known.

Table 3-1,	Numbers in Figure 3-3	3
, , ,	<b>.</b>	-

No	Description	Symbols
1	Spray water	$m_{SS}, h_{SS}$
4	Blow down	$m_{BD}, h_{BD}$
5	External cooling	$Q_{EC}$
6	Atomizing steam	$m_{AS}, h_{AS}$
7	Oil, gas	$m_H, \mathbf{H}_{(N)H}, h_H$
12	Loss due smelt	$Q_{SL}$
18a	Useful heat	$Q_N$
19	Air heater	
22	Steam air heater	
23	External steam	
25	Condensate	$h_{SA2}$
26	FD Fan	$P_{FD}$
27	Steam (MP&LP)	$m_{AS}, h_{AS}$
28	ID fan	$P_G$
29	Loss due to flue dust	$Q_{FA}$
30	Dust collector	$Q_{DC}$ , $P_{DC}$
31	Loss due to carbon monoxide	$m_F, h_G$
32	Recirculating gas fan	$P_{UG}$
33	Leakage air	$m_{LA}, h_{LA}$
34	Other electric power	Р
35	Feed water	$m_{FW}, h_{FW}$
36	Reheat steam inlet	$m_{RH1}, h_{RH1}$
37	HP-feedwater preheat	$Q_{HPFW}$
38	Loss due radiation and convection	$Q_{RC}$
40	Spray water reheat steam	$m_{SR}, h_{SR}$
41	Normal envelope boundary	
42	Reheat steam outlet	$m_{RH2}, h_{RH2}$
44	Main steam	$m_{ST}, h_{ST}$
45 <b>*</b>	DNCG	$m_{DG}, h_{DG}$
46*	CNCG	$m_{CG}, \mathbf{H}_{(N) CG}, h_{CG}$
47 <b>*</b>	Methanol	$m_{ME},  \mathbf{H}_{(N)ME},  h_{ME}$
48 <b>*</b>	Turpentine	$m_{TP}, \mathbf{H}_{(N)TU}, h_{TP}$
49 <b>*</b>	Black liquor pump power	$P_M$
50 <b>*</b>	Black liquor	$m_{BL}, \mathbf{H}_{(N)BL}, h_{BL}$
51 <b>*</b>	Black liquor recirculation	$m_{BR}, h_{BR}$
52 <b>*</b>	Dissolving tank vent gases	$m_{DT}, h_{DT}$

\*numbering according to EN 12952-15 except 45 and above

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No	Description	Value
1	Spray water	10 kg/s , 120 °C, 13 MPa
4	Blow down	2 kg/s, 12,5 MPa(sat)
5	External cooling	0 MW
6	Atomizing steam	0 kg/s
7	Oil, gas	0 kg/s
12	Loss due smelt	$Q_{SL}$
18a	Useful heat	$Q_N$
19	Air heater	
22	Steam air heater	-> 120 °C
23	External steam	
25	Condensate	$h_{SA2}$ (60 $^{o}C$ )
26	FD Fan	$P_{FD}$
27	Steam (MP&LP)	$m_{AS}, h_{AS}$
28	ID fan	$P_{G}(\eta=0,6)$
29	Loss due to flue dust	$100 mg/m^3 n(dry)$
30	Dust collector	
31	Loss due to carbon monoxide	2 MW
32	Recirculating gas fan	0
33	Leakage air	5 %, 30 °C
34	Other electric power	4 MW
35	Feed water	т <sub>FW</sub> , 120 °С, 13 МРа
36	Reheat steam inlet	0 kg/s
37	HP-feedwater preheat	0 MW
38	Loss due radiation and convection	2 MW
40	Spray water reheat steam	0 kg/s
41	Normal envelope boundary	
42	Reheat steam outlet	0 kg/s
44	Main steam	<i>m<sub>ST</sub></i> , 500 °C, 10 MPa
45*	DNCG	$15 m^3/s$
46*	CNCG	0,6 kg/s, 20 MJ/kg
47*	Methanol	0 kg/s
48*	Turpentine	0 kg/s
49*	Black liquor pump power	$P_{M}(\eta=0,6)$
50*	Black liquor	4000 tds/d, 13 MJ/kgds, 140 °C
51*	Black liquor recirculation	0 kg/s
52*	Dissolving tank vent gas	$0,3 \ m^3/kgds, \ 50 \ ^oC$

#### **Table 3-2, Example values for flows in Figure 3-1**

\*numbering according to EN 12952-15 except 45 and above

In addition to these values one needs to know the analysis for as fired black liquor and other fuel flows. Typical non condensable gases, methanol and turpentine analysis are listed in Annex I. Making reliable analysis for non condensable gases is expensive and time consuming. If mutually agreed upon can example analysis be used if the amount of formed flue gases is only a small portion of total flue gases.

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#### **3.3** Material balance

Control of combustion requires air flow that matches fuel flow. The amount of air required to burn a mass unit of black liquor depends mainly on water content and the heating value of the fuel. It is only the organics in black liquor that combust. Black liquor higher heating value increase, Figure 3-4, means more air for combustion is needed. Figures like Figure 3-4 can be used to estimate the required air flow for dimensioning the fans. More importantly they should be used to estimate the possible range of air flows. A recovery boiler should be able to handle not only the design black liquor, but a range of typical black liquors. Normally actual design and performance estimation is done using actual black liquor elemental composition.



Figure 3-4, Black liquor air demand as a function of the lower heating value

Typical biofuels consist of carbon, hydrogen, nitrogen, sulfur and oxygen. Black liquor contains also a high amount of ash; sodium, potassium and chloride compounds. It is often impossible to define the individual chemical compounds that form the fuel. The stoichiometric air demand, I, can be calculated assuming that the fuel can be divided into three fractions

- Organic portion, which combusts fully
- Reactive inorganic portion, which reacts to predefined end products
- Inactive portion, which passes through combustion system unchanged

The basis for material calculations is typically one mass unit of black liquor. If mass balance values for one mass unit are known it is easy to formulate mass balance for a known load by multiplying all values with a single factor.

Example, Calculate required air flow for boiler in Table 3-2. Liquor dry solids analysis as mass percent is

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Element	Value
С	32,50
Н	3,30
Ν	0,09
S	6,10
Na	20,50
К	3,00
Cl	0,25
Inert	0,1
Oxygen (~difference)	34,16

Table 3-3,Example black liquor analysis for flows in Figure 3-3

In addition assume that the reduction degree is 96 % expressed as the mole ratio of sulfide to sum of sulfate and sulfide in smelt. The autocausticization degree is 80 % expressed as the mole ratio  $Na_3BO_3/(NaBO_2+Na_3BO_3)$ . Black liquor dry solids is 85 %. Air ratio is 1.1625 (~3 % O<sub>2</sub> in flue gas), SO<sub>2</sub> emissions are 13 mg/m<sup>3</sup>n in dry gas and dust emission is 0.2 g/kgds. Sootblowing steam consumption is 119 g/kgds. 10.8 g/kgds of sulphur and 21.6 g/kgds water enter the furnace with the concentrated gases. Moisture content of air is 22 g/kg dry air. The exiting ESP dust analysis is shown in Table 3-4. The recycle ash flow is 100 g/kgds and its analysis is shown in Table 3-5.

Table 3-4,Example dust for flows in Figure 3-3

Element	Flow, g/kgds
Na	0,1158
Κ	0,0260
Cl	0,0035
-CO <sub>3</sub>	0,0662
$-SO_4$	0,1682
-S	0,0004
-B	0,0000

Table 3-5, Example ash for flows in Figure 3-3

Element	Flow, g/kgds
Na	30,47
Κ	6,84
Cl	0,93
-CO <sub>3</sub>	17,41
$-SO_4$	44,25
-S	0,10
-B	0,00

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## **3.3.1** Reactions per 1 kg of as fired black liquor

Input flow of black liquor dry solids

	mass, g/kgds	mol/kgds	end product
Carbon	325	325/12,011=27,059	$CO_2$ , $Na_2CO_3$ , $K_2CO_3$
Hydrogen	33	33/2,016=16,369	$H_2O$ , $HCl$
Nitrogen	0,9	0,9/28,0134=0,032	$N_2$
Oxygen	341,6	341,6/31,999=10,675	$CO_2$ , $SO_2$ , $Na_2CO_3$ ,
			$Na_2SO_4$ , $K_2SO_4$ , $K_2CO_3$ ,
			H <sub>2</sub> O, NaBO <sub>2</sub> , Na <sub>3</sub> BO <sub>3</sub>
Chloride	2,5	2,5/35,453=0,071	NaCl, KCl, HCl
Potassium	30	30/78,204=0,384	$K_2S, K_2SO_4, K_2CO_{3}$
			KCl,
Sulfur	61	61/32,060=1,903	$SO_2$ , $K_2S$ , $Na_2S$ , $Na_2SO_4$
Sodium	200	200/45,980=4,350	Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> CO <sub>3</sub> ,
			NaCl, NaBO <sub>2</sub> , Na <sub>3</sub> BO <sub>3</sub>
Borates	5	5/10,811=0,463	NaBO <sub>2</sub> , Na <sub>3</sub> BO <sub>3</sub>
Water	1000*(1/0,85 - 1)	175,5/18,015=9,796	H <sub>2</sub> O
	= 175,5		

#### Sulfur balance

	molS/kgds	mass, gS/kgds	end product
	1,903	61,0	available sulfur
	0,333	10,7	in NCG
	-0,000	-0,0	SO <sub>2</sub>
	-0,002	-0,1	dust as -SO <sub>4</sub>
	-0,000	-0,0	dust as –S
	-0,461	-14,8	ash as –SO <sub>4</sub>
	-0,003	-0,1	ash as –S
Sum	1,770	56,7	S in smelt
	0,04*1,770=0,071	2,3	-SO <sub>4</sub> in smelt
	0,96*1,770=1,699	54,5	-S in smelt

Chloride balance

	molCl/kgds	mass, gCl/kgds	end product
	0,071	2,5	available chloride
	0,000	-0,0	NaCl and KCl in dust
	-0,026	-0,9	NaCl and KCl in ash
	-0,000	-0,0	HCl in flue gas
Sum	0,044	1,6	Cl in smelt

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	molB/kgds	mass, gB/kgds	end product
	0,462	5,0	available borate
	-0,000	-0,0	dust
	-0,000	-0,0	ash
Sum	0,462	5,0	borate in smelt
	0,370	4,0	Na <sub>3</sub> BO <sub>3</sub> in smelt
	0,092	1,0	NaBO <sub>2</sub> in smelt

Sodium and potassium balances need to be calculated together. It can be assumed that borate forms components only with sodium and other smelt compounds are formed in proportion of total sodium and potassium in smelt. The true distribution between e.g.  $Na_2S$  and  $K_2S$  in smelt is not known, but this does not affect the mass balance.

Sodium balance

	molNa <sub>2</sub> /kgds	mass, gNa/kgds	end product
	4,350	200,0	available sodium
	-0,003	-0,1	Na <sub>2</sub> SO <sub>4</sub> , NaCO <sub>3</sub> and NaCl in
			dust
	-0,663	-30,5	Na <sub>2</sub> SO <sub>4</sub> , NaCO <sub>3</sub> and NaCl in
			ash
Sum	3,684	169,4	sodium in smelt
	0,926*0,071=0,066	-3,0	$Na_2SO_4$ in smelt
	0,926*1,699=1,573	-72,3	$Na_2S$ in smelt
	0,555	-25,5	Na <sub>3</sub> BO <sub>3</sub> in smelt
	0,046	-2,1	NaBO <sub>2</sub> in smelt
	0,926*0,022=0,020	-0,9	NaCl in smelt
	3,684-Σ=1,425	65,5	Na <sub>2</sub> CO <sub>3</sub> in smelt

Potassium balance to smelt can be calculated by subtracting from incoming potassium the potassium in dust and ash.

	molK <sub>2</sub> /kgds	mass, gK/kgds	end product
	0,384	30,0	available potassium
	-0,000	-0,0	$K_2SO_4$ , $K_2CO_3$ and KCl in
			dust
	-0,087	-6,8	$K_2SO_4$ , $K_2CO_3$ and KCl in
			ash
Sum	0,296	23,1	potassium in smelt
	0,074*0,071=0,005	-0,4	$K_2SO_4$ in smelt
	0,074*1,699=0,126	-9,9	$K_2S$ in smelt
	0,074*0,022=0,002	-0,1	KCl in smelt
	0,296- Σ =0,163	12,7	$K_2CO_3$ in smelt

Other inorganic 1 g/kgds is assumed to pass through to smelt unreacted.

## Borate balance



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#### Carbon balance

	molC/kgds	mass, gC/kgds	end product
	27,059	325,0	available carbon
	-0,001	-0,0	Na <sub>2</sub> CO <sub>3</sub> and K <sub>2</sub> CO <sub>3</sub> in
			dust
	-0,290	-3,5	$Na_2CO_3$ and $K_2CO_3$ in
			ash
	-1,587	-19,1	Na <sub>2</sub> CO <sub>3</sub> in smelt
Sum	25,180	302,4	CO <sub>2</sub>

Oxygen balance

	molO <sub>2</sub> /kgds	mass, gO/kgds	end product	
	10,675	341,6	available oxygen	
	-25,184	-805,7	$CO_2$	
	-0,003	-0,1	CO <sub>3</sub> and SO <sub>4</sub> in dust	
	-1,357	-43,4	$CO_3$ and $SO_4$ in ash	
	-0,000	-0,0	$SO_2$	
	-0,142	-4,5	Na <sub>2</sub> SO <sub>4</sub> and K <sub>2</sub> SO <sub>4</sub> in smelt	
	-2,375	-76,0	$Na_2CO_3$ and $K_2 CO_3$ in	
			smelt	
	-0,555	-17,8	Na <sub>3</sub> BO <sub>3</sub> in smelt	
	-0,092	-3,0	NaBO <sub>2</sub> in smelt	
	-8,185	-261,9	H <sub>2</sub> O	
Sum	-27,220	-871,0		

The humid air demand is then 1.1625\*0,8711/0.22925= 4.537 kg/kgds

If we apply the carbon content versus higher heating value equation we get for LHV 12,6 MJ/kgds. From Figure 3-4 the air demand is from 3.2 to  $4 \text{ m}^3\text{n/kgds}$  or from 3.8 to 4.8 kg/kgds.

#### **3.3.2** Smelt balance

The smelt flow can be calculated if we add up all mass flows to smelt.

Example, Calculate smelt flow for the previous example.

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#### Smelt balance

	mol/kgds	mass, g/kgds	end product	
	0,127	14,0	$K_2S$ in smelt	
	1,577	123,1	Na <sub>2</sub> S in smelt	
	0,066	9,3	Na <sub>2</sub> SO <sub>4</sub> in smelt	
	0,005	0,9	$K_2SO_4$ in smelt	
	0,041	2,4	NaCl in smelt	
	0,003	0,2	KCl in smelt	
	1,421	150,6	Na <sub>2</sub> CO <sub>3</sub> in smelt	
	0,162	22,4	$K_2 CO_3$ in smelt	
	0,370	47,3	Na <sub>3</sub> BO <sub>3</sub> in smelt	
	0,092	6,1	NaBO <sub>2</sub> in smelt	
	-	1	Other inorganics	
Sum		377.4		

The smelt flow is then 0.3774 kg/kgds.

#### **3.3.3** Flue gas flow



# Figure 3-5, Black liquor flue gas production as function of the lower heating value.

Black liquor flue gas production depends on the black liquor heating value, Figure 3-5. For the simple analysis estimation based on predetermined mass ratio of flue gas to air can be done. An accurate flue gas flow can be calculated from simple mass balance if air flow, black liquor flow and smelt flow are known.

Example; Calculate flue gas flow for the previous example.

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	mass, g/kgds	product
	1000	dry black liquor
	176.5	water with black liquor
	4453.7	air
	118.7	sootblowing steam
	10.8	sulfur in NCG
	21.6	water in NCG
	-0.2	loss in dust
	-100.0	ash recycle
	-377.3	smelt
Sum	5308.8	flue gas

Mass balance

The flue gas flow is then 5.309 kg/kgds. For environmental reporting it is often useful to know the dry flue gas flow. The dry flue gas flow can be calculated by subtracting water with black liquor, sootblowing steam, water with air and water from hydrogen in black liquor from flue gas flow.

#### **3.3.4** Dry flue gas flow

Mass balance

	mass, g/kgds	product
	5308.8	wet flue gas flow
	-176.5	water with black liquor
	-118.8	sootblowing steam
	-21.6	water in NCG
	-0.022*4453.7	water with air
	-16.371*0.01802	water from hydrogen in black liquor
Sum	4820.9	dry flue gas

When calculating real recovery boiler air and flue gas flows leakage should be taken into account. Air flow through air fans is less than calculated as some of the air is infiltration air through various openings. Flue gas flow at stack can be significantly higher that through economizers because of the same reason.

#### 3.4 Useful heat output

Useful heat output includes all heats to all steam flows. This value depends on the boiler type and the boundaries with which we are calculating the boiler efficiency. Normally the useful heat output can be defined as

$$Q_{abs} = Q_{ms} + Q_{rh} + Q_{bd}$$

where

$Q_{ms}$	is the heat transferred to main steam
$Q_{rh}$	is the heat transferred to reheat steam
$Q_{bd}$	is the heat transferred to blow down

No credit is given of steam used to heat air or sootblow.

#### 3.5 Heat and energy input

The energy input has two components. One is proportional to the fuel flow, and the other does not depend on the fuel flow. Energy flows that depend on the fuel flow are

- Chemical energy in the main fuel,  $H_u$  (heat of combustion)
- Chemical energy in the auxiliary fuels,  $H_u$  (heat of combustion)
- Energy included in the fuel preheating,  $Q_f$
- Energy included in the air preheating,  $Q_a$

Examples of energy flows that are somewhat independent of the fuel flow are

- Shaft powers of the flue gas and air fans
- Shaft powers of circulation pumps
- Energy input by flue gas recirculation fan

It is customary to treat the useful heat input as a difference of input and output values. That is useful heat is the difference between enthalpies of output flows and input flows. Therefore it is logical that many energy flows are not considered input flows. Such input flows are

- Heat in feedwater
- Heat in desuperheating water flow
- Heat in incoming steam flow to reheater



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#### **3.6** Problems in determining efficiency with the direct method

Acceptance standard EN 12952-15:2003 "Water-tube boilers and auxiliary installations - Part 15: Acceptance tests" states that the efficiency can be calculated with direct method. When mass flows, specific heat values, and temperatures are known, the heat input with preheated air and fuel can be calculated using e.g. the following simplified formula

$$\eta = \frac{Q_{ms} + Q_{rh} + Q_{bd}}{H_{u} * m_{f} + Q_{f} + Q_{a} + \sum P}$$
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or with states of the flows as

$$\eta = \frac{\mathbf{m}_{ms}^{*}(h_{ms} - h_{fw}) + \mathbf{m}_{rh}^{*}(h_{rh,out} - h_{rh,in}) + \mathbf{m}_{bd}^{*}(h_{bd} - h_{fw})}{\mathbf{H}_{u}^{*}\mathbf{m}_{f} + \mathbf{m}_{f}^{*}(h_{f,out} - h_{f,in}) + \mathbf{m}_{a}^{*}(h_{a,out} - h_{a,in}) + \sum P}$$

$$4$$

where

$H_u$	is the heating value of fuel
$m_f$	is the fuel mass flow
$Q_f$	is the heat transferred to preheated fuel
$Q_a$	is the heat transferred to preheated air
ΣΡ	is the sum of mechanical end electrical energy input flows
$m_{ms}$	is the main steam mass flow
$m_{rh}$	is the reheat steam mass flow
$m_{bd}$	is the blow down mass flow
$m_a$	is the air mass flow
$h_{ms}$	is the enthalpy of main steam
$h_{fw}$	is the enthalpy of feedwater steam
$h_{bd}$	is the enthalpy of blowdown
h <sub>rh,out</sub>	is the outlet enthalpy of reheat steam
h <sub>rh,out</sub>	is the inlet enthalpy of reheat steam
h <sub>f,out</sub>	is the outlet enthalpy of fuel
h <sub>f,out</sub>	is the inlet enthalpy of fuel
h <sub>a,out</sub>	is the outlet enthalpy of air
h <sub>a,out</sub>	is the inlet enthalpy of air

The above presented formula is a very simple formula. It ignores most of the energy flows that cross the boundary. By looking at Figure 3-2 we note that at least the following streams typical for the recovery boiler have not been accounted for

- NCG-flows
- Methanol, turpentine flows
- Condensate
- Leakage air
- Sootblowing
- Other electricity flows

- Flows to and from flue gas cleaning
- Auxiliary fuels
- HVAC streams

It can be argued that these streams are minor and do not affect the calculation. It is difficult to assess their effect a priori without measuring them. So the need to measure many flows is the one of the main problems in direct efficiency measurement.

Another problem arises from the theory of mathematical uncertainty associated with the measurements. As each and every stream needs to be measured the error in the efficiency becomes quickly very large. Therefore the direct method is very seldom used in practice.

#### 3.7 Determining efficiency with the indirect method

Recovery boiler efficiency is determined always by the indirect method. The efficiency equation can be arranged as

$$\eta = 1 - \frac{Q_{\text{in}} - Q_{\text{abs}}}{Q_{\text{in}}}$$

and even further as

$$\eta = 1 - \sum \frac{Q_{\text{loss,i}}}{Q_{\text{in}}}$$

where

Qloss.i is the i:th heat lost

The main losses in a recovery boiler steam generator are the following:

- Heat lost with the flue gases
- Losses of unburned combustible fuel
- Sensible heat in the smelt flow (ashes)
- Radiation and conduction losses.

Most of these losses can be estimated to a greater accuracy than the actual flows. The indirect method therefore gives a higher accuracy when estimating the efficiency of the steam generator.

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#### **3.7.1** Heat input to the boiler and other energy flows

Example; Calculate main steam flow and feedwater flow for the previous example. The main steam values are 9.1 MPa(a) and 490 °C. Feedwater process values are 11.0 MPa(a) and 115 °C. Flue gas flow exits at 155 °C. Air enters at 30 °C and is preheated as average to 108.8°C. The blowdown is 0.050 kg/kgds at drum pressure 10.36 MPa(a). Black liquor HHV is 13.00 MJ/kgds and it enters at 140 °C. Radiation and convection losses are 38 kJ/kgds. Unburned and others are 40 kJ/kgds. Manufactures margin is 67 kJ/kgds. Auxiliary fuel effect (CNCG) is 577 kJ/kgds.

Heat input with black liquor

In	massflow	enthalpy	
	kg/kgds	kJ/kg	kJ/kgds
Black liquor (HHV)	1,1765	13000,0	13000,0
Hydrogen correction	0,033	-2440/8,937*0,033	-719,6
Black liquor (LHV)	1,1765		12280,4
Water correction	0,1765	-2440*0,1785	-430,6
As-fired black liquor	1,1765		11849,8

#### Heat input

Input	mass flow	Enthalpy	
	kg/kgds	kJ/kg	kJ/kgds
As-fired black liquor	1,1765	11849,8	11849,8
Other fuel heat input			577,0
Sensible in black liquor	1,1765	140*2,64	434,8
Air	4,454	(30-0)*1,0336	131,2
Air preheat	4,454	(108,8-30)*1,0336	344,6
Infiltration air	0,223	(30-0)*1,0336	6,9
Outside sootblowing	0,1188	3054,8-2792,0	31,2
Sum			13375,6

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Figure 3-6, Example heat inputs to recovery boiler

As one can see from the Figure 3-6, most of the heat input comes from the heat that can be released in the combustion of black liquor. Other large sources are sensible heats in black liquor and air preheating.

#### 3.7.2 Useful heat

Useful heat can be calculated by subtracting from total heat input the sum of heat losses. Useful heat is the heat than can be used to generate steam and the heat that is used in reduction and autocausticizing reactions. Values for thermodynamic properties can be found in chapter 4.

Output	mass flow	Enthalpy		
•	kg/kgds	kJ/kg	kJ/kgds	
Na <sub>2</sub> S reduction	0,123	13092	1611,4	
$K_2S$ reduction	0,0139	9629	134,4	
SO <sub>2</sub> reduction	0,000052	5531	0,3	
Autocaustizicing Na <sub>3</sub> BO <sub>3</sub>	0,0473	1535	72,6	
Wet flue gas	5,309	155*1,107	910,4	
Loss as smelt sensible	0,377	0,377*1350	509,0	
Radiation and convection	-	0,283*12846,5	37,9	
Unburned and others	-	0,3*12846,5	40,1	
Margin	-	0,5*12846,5	66,9	
Sum			3382,9	

Heat available to steam generation is then

13375.6-3382,9 = 9992.2

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Figure 3-7 shows how the total heat input is used. Most of the heat input is converted to steam. Reduction reactions are responsible of almost half of the rest. Autocausticizing with borate takes quite little heat. The biggest actual losses are the heat lost with wet flue gases and the sensible heat in smelt.



Figure 3-7, Example heat outputs to recovery boiler

ing is used, then actual value is inserted into feedwater balance

### 3.7.3 Calculating feedwater flow and steam flow

Enthalpy of steam at 9.1 MPa(a) and 490 °C is 3360.7 kJ/kg. Enthalpy of water at 11.0 MPa(a) and 115 °C is 490.3 kJ/kg. Enthalpy of saturated water at 10.36 MPa(a) is 1423.3 kJ/kg. Enthalpy of sootblowing steam at flue gas exit temperature 155 °C is 2792.0 kJ/kg. Steam mass flow x can then be calculate from the simple balance x\*3360.7-0.050\*1423.3-(x+0.050)\*490.3-0.000\*2792.0 = 9992,2Steam mass flow, x is then 3.465 kg/kgds. Feedwater mass flow is 3.465+0.050+0.000 = 3.565 kg/kgds. It should be noted that outside sootblowing means 0 in the balance. If inside sootblow-

#### **3.8** Heat for reduction

Recovery boiler recovers heat from the combustion of organics in the black liquor. In addition it converts inorganic materials from their oxidized state to reduced state. All this is useful work and consumes usually about 10 % of heat input. It should be taken into account in the recovery boiler net efficiency.

$$\eta = 1 - \sum \frac{Q_{\text{loss,i}}}{Q_{\text{in}}} + \frac{Q_{\text{dR}}}{Q_{\text{in}}}$$

$$7$$

where

 $Q_{dR}$  is the sum of heats to reduction

Example; calculate the recovery boiler efficiency based on heat in incoming fuel for the previous example

$$\eta_{LHV} = 1 - \frac{\text{Losses}}{\text{Input}} - \frac{\text{Reduction}}{\text{Input}} = 1 - \frac{3382.9}{13375.6} + \frac{1818.7}{13375.6} = 88.3\%$$

The steam generation efficiency is

$$\eta_{LHV2} = \frac{\text{Net to steam}}{\text{Input}} = \frac{9992.6}{13375.6} = 74.7\%$$
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A recovery boiler is well in range of efficiencies of the modern biofuels boilers.

#### **3.9** High dry solids black liquor

One of the major trends of current years has been the increase of dry solids from evaporators. The data presented is for study of a 3000 tds/d recovery boiler. Even though this size of recovery boiler is chosen as example, the results should be applicable to most of the current recovery boilers.

The design parameters for the studied recovery boiler are shown in Table 3-6. Material balance data from low dry solids value of 65 % to high value of 90 % is presented in Table 3-7. In these calculations the black liquor elemental composition is assumed to remain constant. For same cases the corresponding energy balance values and steam flows are presented in Table 3-8.



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Parameter		
Maximum continuous firing rate	t dry solids/day	3000
Steam pressure	bar	90.0
Steam temperature	°C	490
Feedwater pressure	bar	110
Feedwater temperature	°C	115
Primary air percentage	%	35.0
Primary air temperature	°C	120
Secondary air percentage	%	50.0
Secondary air temperature	°C	120
Tertiary air percentage	%	15.0
Tertiary air temperature	°C	50
Flue gas temperature after economizer	°C	155
Black liquor analysis		
С	% weight	32.5
Na	% weight	20.5
S	% weight	6.1
$O_2$	% weight	34.16
$H_2$	% weight	3.3
K	% weight	3.0
Others	% weight	0.35
Higher heating value of dry solids	MJ/kg dry solids	13.0
Dry solids content before mixing tank	% weight	60 - 95
As-fired black liquor temperature	°C	140.0
Chemical loss to stack	g/kgds	0.2
Reduction	%	97
Sootblowing steam flow	g/kgds	119
Balance reference temperature	°C	0

### Table 3-6, 3000 tds/d recovery boiler main parameters

### Table 3-7, Material balance for the example boiler

Liquor dry solids, %	65	70	75	80	85	90
Liquor flow, kg/s	53.4	49.6	46.3	43.4	40.8	38.6
Air flow, kg/s	149.3	149.8	150.3	150.8	151.3	151.8
Sootblowing steam, kg/s	4.1	4.1	4.1	4.1	4.1	4.1
Ash and dust, kg/s	2.1	2.4	2.8	3.1	3.5	3.8
Smelt flow, kg/s	14.1	13.8	13.6	13.3	13.1	12.9
Flue gas flow, kg/s	195.1	191.7	188.8	186.3	184.2	182.3

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Dry solids, %	65	70	75	80	85	90
Heat in black liquor, kJ/kgds	10967	11235	11467	11670	11850	12009
Other fuel streams, kJ/kgds	577	577	577	577	577	577
Sensible heat in BL, kJ/kgds	569	528	493	462	435	411
Air preheating, kJ/kgds	476	478	480	481	483	484
Sootblowing, kJ/kgds	31	31	31	31	31	31
Total input, kJ/kgds	12620	12849	13048	13222	13376	13512
Smelt, kJ/kgds	547	537	528	518	509	499
Reduction+autocaust., kJ/kgds	2001	1956	1910	1864	1819	1773
Wet flue gas, kJ/kgds	965	948	933	921	910	901
Rad. and conv. + unburned +	137	139	141	143	145	146
margin, kJ/kgds						
Total losses, kJ/kgds	3650	3580	3513	3447	3383	3320
Net to steam, kJ/kgds	8970	9269	9535	9775	9993	10192
Steam, kg/kgds	3.093	3.197	3.2894	3.373	3.449	3.518
kg/s	107.4	111.0	114.2	117.1	119.8	122.2
Efficiency, %	86.9	87.4	87.7	88.0	88.3	88.5

#### Table 3-8, Energy balance for the example boiler

In the material balance the combustion air flow and black liquor dry solids flow remain constant. The flue gas flow decreases as less water enters the furnace with increasing black liquor dry solids content. The sum of smelt and ash remains almost constant. At higher dry solids more alkalis are vaporized. This means more dust and less smelt. Even though the steam flow increases with increasing black liquor dry solids content, the sootblowing can remain constant.

The total heat input with black liquor increases with increasing black liquor dry solids. This is because less water is evaporated per kilogram of dry solids.

Flue gas heat loss will decrease as the flue gas mass flow decreases. The heat available to steam production will increase as the heat losses decrease while the total heat input increases.



Figure 3-8, Effect of black liquor dry solids at boiler efficiency, steam flow and heat in black liquor

Steam generation increases with increasing dry solids. For a rise in dry solids content from 70 % to 80 % the main steam flow increases by 5.5 %. The increase is typically about 2.5 % per each 5 % raise in dry solids.

Steam generation efficiency improves with higher dry solids black liquor. For a rise in dry solids content from 70 % to 80 %, the steam generating efficiency improves about 0.8 %.



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#### **RECOVERY BOILER SPECIFIC QUESTIONS IN BALANCE**

Using European standard EN 12952-15:2003 "Water-tube boilers and auxiliary installations - Part 15: Acceptance tests" for recovery boiler balances, one needs to define some specific questions. Especially the following need to be specified when calculating the balance

- How to take NCG (DNCG and CNCG) into account
- How to take into account the dissolving tank vent gases
- How to take into account the methanol and turpentine
- How to take into account the ash pickup with evaporator liquor
- Determining the radiation and convection losses

#### 4.1 **DNCG** combustion in the balance

Combustion of dilute non condensable gases (HVLC) in recovery boilers should be treated like introducing wet additional air, if not otherwise agreed upon. If DNCG burning is allowed, their sulphur content needs to be very low. These gases do not typically contain combustibles. The error in the efficiency is small, Annex IV.

#### 4.2 CNCG combustion in the balance

Combustion of concentrated non condensable gases (LVHC) in recovery boilers should be treated like burning auxiliary fuel. In the performance test the heating value and the analysis in the contract corrected to actual conditions (water content) can be used. If contract has no specified values then the model analysis and heating value in the Annex can be used.

#### 4.3 Dissolving tank vent gas combustion in the balance

Combustion of dissolving tank vent gas in recovery boilers should be treated like combustion of dilute non condensable gases. Heating value for dissolving tank vent gas is zero and the analysis is a mixture of water vapour and dry air.

#### 4.4 Methanol and turpentine combustion in the balance

Combustion of methanol and turpentine in recovery boilers should be treated like burning auxiliary fuel. In the performance test the heating value and the analysis in the contract corrected to actual conditions (water content) can be used. If contract has no specified values then the model analysis and heating value in the Annex can be used.

#### 4.5 Ash pickup with evaporator liquor

The way boiler and ESP ash is mixed to the black liquor does not matter. Mixing tank is placed outside the boiler balance boundary. This way it does not matter for the boiler balance whether it has modern ash pickup with evaporator liquor or traditional ash mixing to incoming liquor.

The ash from recovery boiler increases with boiler load and black liquor dry solids. Figure 4-1 represents ash flows from modern recovery boiler.
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Figure 4-1, Effect of black liquor dry solids to dust flows; BB ash lowest line, ECO ash next higher line, ESP ash upper lines at different HHRR

Dust flow in Figure 4-1 is represented by the following equations

$q_{ESP} = 0.3509 \text{*ds} \cdot (2800 \text{-HHRR}) / 1000 \text{*} 5.6158 \text{-} 6.865 \pm 3$	10
$q_{ECO}=0.1*ds\text{-}4\pm2$	11

 $q_{BB} = 1 \pm 1$  12

#### where

<b>q</b> <sub>ESP</sub>	is the dust flow to electrostatic precipitator divided with dry flue gas flow at 3 % $O_2$ , g/m <sup>3</sup> n, dry
q <sub>ECO</sub>	is the dust flow from economizer hoppers divided with dry flue gas flow at $3\% \Omega_{-} q/m^{3}n dry$
q <sub>BB</sub>	is the dust flow from boiler bank hopper divided with dry flue gas flow at 3 $\% \Omega_{2}$ g/m <sup>3</sup> n dry
ds HHRR	is the heart heat release rate, $kJ/m^2$

# HHRR = $LHV*MCR/A_{bottom}$

#### where

LHV	is the as fired black liquor dry solids lower heating value, kJ/kgds
MCR	is the as fired black liquor dry solids flow, kgds/s
A <sub>bottom</sub>	is the recovery boiler furnace bottom area, m <sup>2</sup>

# 4.6 Sensible heat in black liquor

It is recommended that no separate determination of sensible heat of black liquor is done for the performance test. In the performance test the contract value corrected to actual conditions (dry solids, temperature) can be used. If contract has no specified values then the value in the Annex can be used.

# 4.7 Losses calculation

It is recommended that the thermodynamical properties in this document are used to calculate the losses. If this will not be the case, the matter needs to be specified in the contract.

# 4.7.1 Heat lost with the flue gases

The biggest heat loss from a steam generator is the heat lost with exiting flue gas. The flue gas loss depends on the final flue gas temperature and the amount of flue gases. Thus the higher the air ratio the higher the flue gas losses.

The flue gases should leave the boiler at a temperature as low as possible to minimize the flue gas losses. Usually either economics, equipment or corrosion issues limit the flue gas temperature between 150 and 200  $^{\circ}$ C.

# 4.7.2 Losses in the unburned combustibles

The fuels fired into the boiler will not combust totally. Thermodynamics limit the combustion process to some finite value. This means e.g. that there is always some CO, H2 and other hydrocarbons present in the flue gases.

When burning biofuels some carbon tends to remain unburned. This means that some carbon remains in the ash. Carbon in the ashes captured from the flue gases is mixed with black liquor. This means that no losses occur. Usually the carbon content in modern recovery boilers is extremely low.

Some unburned carbon exits with smelt. Heat lost with this stream is very low, Annex IV.

## 4.7.3 Losses of sensible heat of smelt

To know the loss in sensible heat of smelt the temperature, flow and enthalpy must be determined.

# 4.7.3.1 Enthalpy of smelt

The enthalpy of different smelt components (e.g. Na2S) can be expressed with the following equation:

$$h_{c} = h_{m} + c_{p}(T_{smelt} - T_{ref})$$
1

where

h <sub>c</sub>	is the specific enthalpy of component, J/kg
$h_m$	is the specific enthalpy of melting for component, J/kg
c <sub>p</sub>	is the specific heat capacity of component, J/kg $^{\circ}$ C
T <sub>smelt</sub>	is the smelt temperature, <sup>o</sup> C
T <sub>ref</sub>	is the reference temperature, °C

The enthalpy for a smelt with a given composition can then be calculated as;

$$H_{SMELT} = \sum_{i=1}^{n} m_i h_{c,i}$$
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where

H <sub>smelt</sub>	is the enthalpy of smelt, J
mi	is the mass of component i, kg
h <sub>c,i</sub>	is the specific enthalpy of component i, J/kg

Specific heats of melting and specific heat capacities for typical smelt compounds are shown in Table 4-1.

Table 4-1, Specific enthalpies of melting and specific heat capacities for typical smelt compounds with enthalpies for melt compounds at 850 °C

Compound	h <sub>m</sub> (25 °C)	с <sub>р</sub>	h <sub>c</sub> (850 °C)
	kJ/mol	kJ/mol °C	kJ/mol
Na <sub>2</sub> CO <sub>3</sub>	29.7	0.1586	164.5
$Na_2S$	19.2	0.1164	118.1
$Na_2SO_4$	23.8	0.1912	186.3
NaCl	28.3	0.0582	77.8
$Na_2S_2O_3$	29.7	0.1332	142.9
$K_2CO_3$	27.9	0.1596	163.6
$K_2S$	16.2	0.1052	105.6
$K_2SO_4$	34.4	0.1918	197.4
KCl	14.9	0.0735	77.4
NaBO <sub>2</sub>	33.5	0.1082	125.5
Na <sub>3</sub> BO <sub>3</sub>	35.5	0.1832	191.2

For other smelt compounds, the values  $h_m = 200 \text{ kJ/kg}$ ,  $c_p = 0.94 \text{ kJ/kg}$  °C and  $h_c = 1350 \text{ kJ/kg}$  can be used.

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# 4.7.3.2 Heat of formation

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The heat of formation is the energy required for the reaction of components in the base state to form that compound, Table 4-2. Heats of formation are important in proper calculation of energy balances.

Compound	Mole weight	$\mathbf{Dh}_{\mathbf{F}}$ (2)	25 °C)
	kg/kmol	MJ/kg	kJ/mol
Na <sub>2</sub> S	78.04	-4.691	-366.1
$Na_2SO_3$	126.05	-8.687	-1095.0
$Na_2SO_4$	142.04	-9.769	-1387.6
$Na_2S_2O_3$	158.11	-7.107	-1123.7
Na <sub>2</sub> CO <sub>3</sub>	105.99	-10.669	-1130.8
NaCl	58.443	-7.036	-411.2
$K_2S$	110.26	-3.416	-376.6
$K_2SO_4$	174.25	-8.251	-1437.7
$K_2CO_3$	138.2	-8.323	-1150.2
KCl	74.55	-5.858	-436.7
NaBO <sub>2</sub>	65.8	-14.828	-975.7
Na <sub>3</sub> BO <sub>3</sub>	127.78	-11.373	-1453.3
$H_2O_{(g)}$	18.0152	-13.422	-241.8
$SO_{2(g)}$	64.06	-4.633	-296.8
$CO_{2(g)}$	44.01	-8.941	-393.5

Table 4-2, Specific heats of formation for typical compounds in recovery boiler

# 4.7.3.3 Heat of reduction

Table 4.2	Specific reduction heats for typical smalt compounds
1 able 4-3,	specific reduction nears for typical smelt compounds

Compound	Dh <sub>R</sub> k.I/kg	Dh <sub>Rm</sub> kJ/mol
Na <sub>2</sub> S	13092	1021,5
NaCl	0	0
$Na_2SO_4$	0	0
Na <sub>2</sub> CO <sub>3</sub>	0	0
$Na_2SO_3$	2325	292,6
$Na_2S_2O_3$	5787	914,2
$K_2S$	9629	1061,1
KCl	0	0
$K_2SO_4$	0	0
$K_2CO_3$	0	0
NaBO <sub>2</sub>	0	0
Na <sub>3</sub> BO <sub>3</sub>	2033	259,8
SO <sub>2</sub>	5531	353.5



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# 4.7.4 Loss in elctrostatic precipitator ash

The heat loss in ash is usually small enough that even high inaccuracies in ash loss determination usually have a negligible effect on accuracy of overall efficiency, Annex IV.

ESP ash can be assumed to exit at flue gas temperature. We can assume the flow of ESP ash to be about 10 % of the black liquor flow. The ash temperature is the same as the flue gas and the ash  $c_p$  is 0.98 kJ/kgK. Then the magnitude of loss would be about 5 kJ/kgds. It is assumed that the loss in electrostatic precipitator as is included in other losses.

## 4.7.5 Radiation and convection heat losses

There are some losses from the hot boiler walls to the surroundings. Part of this energy increases the incoming air temperature. The amount of heat recovery does not affect the boiler efficiency but affects the amount of heat needed for air preheat. Radiation and convection heat losses do not depend on boiler load.

Radiation and convection heat losses from recovery boiler are hard to measure because there are many flows in and out to the space surrounding boiler proper inside the recovery boiler building. Radiation and convection heat loss can be estimated through equation 16. The coefficient 0.0257 is between coal (0.022) and lignite (0.0315) boiler values. This equation with Tappi loss function (Performance, 1996) is presented graphically in Figure 4-2.

$$\Phi_{RC} = 0.0257 * \Phi_s^{0.7}$$
 16

where

 $\Phi_{RC}$  is the radiation and convection heat loss, MW

 $\Phi_{\rm s}$ 

is the useful heat output at MCR load, MW



Figure 4-2, Radiation and convection losses equation 3-1, Tappi

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Most of the heat loss is from pipes (50 %). Ducts and tanks account for only a minor portion (10 %). Furnace accounts for roughly between fourth and fifth part (22 %). Almost as large portion as furnace of heat losses is from electrical equipment (18 %) (Ahtila, 1997).

Losses calculated from equation 16, losses from Tappi (Performance, 1996) and measured losses are compared in Table 4-4. Tappi loss function is not valid for boilers above 3500 tds/d.

Boiler	Capacity	Calculated	heat loss	Tappi loss	Measured
	tds/d	kJ/kgds	kW	kJ/kgds	kW
Sunila SK11	1000	63.3	734	72.9	870
Kaukopää, SK6	3000	45.6	1582	44.6	1590
Rauma, SK3	3200	44.7	1655	43.3	1600
Kaukas, SK3	3350	44.1	1709	42.6	2000

# Table 4-4,Calculated heat losses (equation 16, Tappi) compared to measuredheat losses from Finnish recovery boilers (Ahtiala, 1997)

# 4.8 Black liquor heating value and analysis

If not otherwise agreed on the determination of black liquor heating value and analysis during performance test is done at an accredited laboratory. The black liquor oxygen content can be analysed to determine the total analytical error.

Black liquor higher and lower heating value in dry black liquor are related with known equation

$$LHV = HHV - 2.443 * (M_{H20} / M_{H2}) * H$$
17

Where

H is the hydrogen mass fraction in black liquor, -

 $M_i$  is the mole weight of i, kg/kmol

Black liquor hydrogen to carbon ratio is practically constant and black liquor higher heating value is a function of carbon content. Therefore with a very good accuracy the lower heating value of black liquor can be presented as function of higher hrating value

$$LHV = 0.96454 * HHV - 0.25335 \pm 0.05$$
 18

Typically the lower heating value of dry black liquor is about 0.7 MJ/kgds less than the higher heating value. It should be noted that generally the analysis accuracy of heating value is about 0.1 MJ/kgka. The correlation shown in equation 18 is valid for all kinds of black liquors, Figure 4-3.





Figure 4-3, Black liquor higher heating value as function of lower heating value

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# 5 **PERFORMANCE TESTING**

When doing recovery boiler performance testing, the following needs to be noted

- Basis for determining guaranteed parameters
- Parameters subject to guarantee
- Basic test conditions
- Steady state
- Performance of tests
- Determining sampling need, frequency and location
- Determining reduction degree; weak wash/analysis green liquor, total sulfur

# 5.1 Basis for determining guaranteed parameters

Unless otherwise agreed, all guarantees relate to steady-state conditions. Guarantees that have absolute value and guarantees that have value that will be adjusted based on test conditions need to be specified in the contract. Typically e.g. emissions to air are absolute values.

Often guaranteed values are based on preconditions, such as flow values in boundaries. These values change as preconditions change.

The following factors shall always be considered when establishing the guaranteed parameters:

- Fuel properties (composition, lower heating value, ash properties) and pulping species;
- Feedwater and spray water characteristics (source, pressure, temperature);
- Cold reheat steam pressure, temperature and mass flow;
- Air temperature

parameters and thermodynamic properties relate to the envelope boundary

Any change in guarantee basis needs to be corrected to reflect the change in actual guaranteed properties. This change should be calculated using normal engineering practice.

If not otherwise agreed, the analysis are conducted using the recommended methods in chapter 2.

Usually there are number of smaller preconditions that typically differ from their base value. Any change in these preconditions need not to be taken into account when calculating guaranteed parameters for recovery boiler performance test. Such preconditions are

- Air pressure, moisture
- Heating steam values to auxiliary equipment
- Pressurized air pressure
- Cold, warm and hot water temperatures

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# 5.2 Parameters subject to guarantee

An acceptance and the performance test of a recovery boiler shall be carried out to verify compliance with the following guarantees.

The four main parameters that typically are guaranteed

- The maximum continuous rating (MCR); this preferably is expressed as tons of dry solids including ash per day. Alternatively this can be expressed as kilograms of main steam per second.
- The pressure and temperature of the generated steam
- Reduction ratio including in case of borate the autocausticization ratio
- The efficiency or losses, or the flue gas exit temperature from economizers

The following parameters are often subject to guarantee:

- The efficiency or losses for given fuels, their mixes and partial loads;
- The steam condition for all given fuels, their mixes and partial loads;
- The pressure drop across boiler high pressure (HP) system and reheater;
- The pressure loss in the combustion air and flue gas flows at agreed points;
- The air factor (ratio of actual to stoichiometric combustion air masses) at agreed points;
- The usage of sootblowing steam;
- The use of auxiliary energy;
- The unburned combustibles content of flue gases;
- Emission to air

# 5.2.1 Non measurable guarantees

Some guarantee values can not be measured during the guarantee tests. This is the case for long term guarantees

- Time between water washes
- Functioning of auxiliary equipment

The basis for validating these guarantees need to be agreed on separately.

## 5.2.2 Additional measurements

The following parameters may sometimes be measured by additional more accurate measurements when evaluating the recovery boiler:

- Pressure and temperature of water and steam at different points (boiling in economizers, superheating);
- Stability of char bed
- Combustion air pressure, temperature and velocity (flow rate) at different points along the ducting system (symmetry and stability);
- Flue gas composition, pressure, temperature and velocity (flow rate) at different points along the ducting system.

The use of additional measurements during the performance test needs to be agreed upon in the contract.

# 5.2.3 Supply of steam generator components by several manufacturers

If steam generator components are supplied by several manufacturers, additional measurements may be necessary in order to provide proof that the guarantees have been complied with.

# 5.3 Basic test conditions

During acceptance and performance testing the process values need to be recorded. It is recommended that major differences between process values during and before testing are highlighted.

## 5.3.1 Sootblowing and other cleaning equipment

Recovery boiler needs to be designed so that guaranteed performance refers to a fouled heat transfer surfaces. Normal fouling is typically reached after the boiler has operated for a few weeks following a water wash. Where the steam generator has been supplied with cleaning equipment (e.g. sootblowers or a shot cleaning plant), such equipment should be continuously employed for cleaning before the acceptance test.

The operation of the sootblowing and possible other cleaning equipment should be comparable to the period before and after the tests. The sootblowing steam requirement is based on the ability to keep the boiler long term fouling at minimum, so any guarantee should reflect at least the monthly average consumption. Note that the sootblowing steam consumption does not depend on the boiler load.

# 5.3.2 General conditions

The validity of all of the parameters listed in 5.1 should be determined before carrying out performance and acceptance tests. If the operating conditions do not allow the boiler to operate at predetermined operating conditions, the tests may, subject to prior agreement, be performed under different conditions. However, deviations should be kept to a minimum. It will then be necessary to correct the efficiency to the guaranteed conditions.

# 5.3.3 Preliminary test runs

Prior to the regular performance test, the supplier shall be given the opportunity to conduct preliminary test runs which seek to train test personnel as well as to check the accuracy of test equipment and methods.

It is recommended that during these preliminary runs all values related to performance test be recorded. If a preliminary test yields satisfactory results, it may be declared an acceptance test, subject to agreement of all parties involved.



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# 5.4 Steady-state conditions

All guarantees refer to steady state conditions. Guarantees can not be met if the boiler is not fired stably.

# 5.4.1 Attaining steady-state conditions

As the guaranteed values refer to steady-state conditions only, it shall be ensured that the steam generator has reached equilibrium. The time required to attain equilibrium will vary widely with the boiler design. Normally, the steam generator shall have been in continuous operation for several days prior to the test. Steady state means normally that the test load has been run for the test duration prior to the commencement of the test. Steady-state operation shall be confirmed by all parties prior to the test.

# 5.4.2 Monitoring the steady-state condition

During the test all operating values shall be recorded. It is recommended that trends of particularly characteristic and significant measured values such as temperatures, pressures and flows of main steam, black liquor and other flue gas flows are printed. These values are used to verify that steady-state conditions have been maintained.

# 5.4.3 Adjustment of firing system

The test fuel shall be made available well in advance so that the supplier has sufficient time to adjust the fuel burning equipment and to ensure that steady-state conditions with respect to the fuel are reached.

## 5.5 **Performance of test**

## 5.5.1 Test duration

The duration of testing should be long enough so that reaching steady state conditions can be established. Recovery boiler performance test contains several measurements and samplings, which all contain a margin of error. As a guideline, it is recommended that the test duration for each guarantee load is six (6) hours.

## 5.5.2 Conditions at beginning and end of test

At the beginning and end of the test, values for the following should be as close as practicable:

- Water level and steam pressure;
- Steam and feed water flows
- Within reason the air distribution and temperature
- Recovery boiler char bed shape as seen from observations
- Excess air.

For recovery boilers the quantity of char bed on the furnace floor shall be the same at the beginning and end of the test.

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The time for which measurements are taken should be longer than the actual duration of the test. It is recommended that the above-mentioned values be monitored before commencement and after completion of the test in order to reliably establish that steady-state conditions have been attained.

# 5.5.3 Frequency of readings

All readings shall be taken as often as necessary to minimize the integration error. This can be achieved by using automatic data recording equipment. When data are recorded manually, the following frequency of readings shall be observed:

- 3 min; flow measurements
- 5 min; flue gas analyses
- pressure and temperature measurements 10 min;
- 120 min. sampling

From recorded measurements hourly mean values are formed for every hour of the test as well as two hours before and after test.

# 5.5.4 **Permissible fluctuations**

Operationally induced fluctuations of steam mass flow (throughput) shall not exceed 3 to 10 % of the average test results; for details refer to figure 5-1 (EN 12952-15:2003). See figure 5-2 (EN 12952-15:2003) for the maximum permissible pressure fluctuations. Flue gas temperature shall be in steady state conditions. The fluctuations of the difference between the temperature of flue gas at the recovery boiler outlet and the temperature of cold fluid (water or air) at the last exchanger inlet shall not exceed  $\pm 3$  %.

If the contract does not stipulate otherwise the black liquor is suitable for guarantee tests if its heating value deviates no more than 0.8 MJ/kgds from the guarantee value and the dry solids deviates no more than 3 % from the guarantee value. Guarantee values need to be adjusted to possible deviations. Guarantee test run must be rejected if suitable black liquor was not available.







Figure 5-1, Maximum permissible main steam flow fluctuations (EN 12952-15:2003)



# Figure 5-2, Maximum permissible main steam pressure fluctuations (EN 12952-15:2003)

If the limit values specified in figures 5-1 and 5-2 are exceeded, the test may be rejected.

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# 5.6 Test plan

Sample test plan is as follows

		PERFORMANCE TEST PLAN	
Monday	8 - 12	<b>Startup meeting</b> verification of the test plan, agreement on target loads, agreement on sampling and measurement plan	
	12 - 16	<b>Verification of measurement accuracy</b> emission measurement places and control, temperature and flow measurement control, placement of possible auxiliary measurement devices	
	22	100 % load firing started tuning	
Tuesday	9 – 15	<b>100% load</b> testing of boiler at design load, emission measurements, recording of operating values, sampling of black liquor, smelt and dust	
	22	60 % load firing started tuning	
Wednesday	9 – 15	<b>60% load</b> testing of boiler at minimum load, emission measurements, recording of operating values, sampling of black liquor, smelt and dust.	
	22	70 % load firing started tuning	
Thursday	9 – 15	<b>70% load</b> testing of boiler at low load, emission measurements, recording of operating values, sampling of black liquor, smelt and dust	
Friday	8-17	<b>Spare day</b> To be used if mill conditions do not permit running at one of the earlier days	
	9 - 11	<b>Conclusion meeting</b> Conclusion of boiler performance tests, agreement on performance test review schedule	

# 5.7 Sampling

During the performance testing sampling of relevant streams needs to be done. The aim is to find proper thermodynamic coefficients and relevant chemical compositions. Usually all samples are collected as doubles. One set is used for analysis and the second set is stored in case the first set has problems.

Sampling frequencies are recommended for the typically sampled streams. Doing more frequent samples is possible, but normally it does not improve accuracy and results in unnecessary cost.

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# 5.7.1 As fired black liquor

As fired black liquor sampling can be done from several locations

- As fired black liquor to the guns
- Black liquor from strong black liquor tank
- Black liquor from pressurized black liquor tank

The sampling location is usually chosen to be the most relevant to the as fired black liquor. The time lag of the black liquor flow between the sampling point and the liquor guns should not be more than 15 min.

High dry solids liquor will flash when the pressure decreases, so sampling location needs to have liquor cooler installed. If not then correction for dry solids needs to be done. High dry solids black liquor is hot. Sample vessels need to be able to handle high temperature.

The sampling should be done so that no more than four hours passes between subsequent samples. Typically black liquor sampling is done

- At the beginning of the test period
- At two hour intervals during the test period
- At the end of the test period

Elementary analysis of as fired liquor is done typically only from one mixed sample that is formed by mixing equal amounts of black liquor from each stream sample together. Dry solids analysis is typically done from each sample. Heating value is done by dividing as fired samples to at least two equal length time periods and doing the analysis for all. If the black liquor properties vary during the test the amount of analysis should be higher.

Only Kjehldal analysis is recommended as basis for black liquor nitrogen content analysis. LECO analysis of nitrogen in black liquor can not be trusted. Care should be taken to ensure reliable sodium analysis.

## 5.7.2 Ash recycle rate

To find ash recycle rate it is recommended that ash content in the flue gas to the ESP is measured and the material balance flue gas flow representative of the test period is used to multiply to arrive to ESP ash flow. Boiler bank ash flow and economizer ash flow are taken from the relevant equations in 4.5. Ash flow is then the sum of ESP ash flow, BB ash flow and the economizer ash flow.

An alternative method to determine ash recycle rate is to determine the sulfur balance for ash mixing tank with flows to and from ash mixing tank and their sulfur contents. Then black liquor sampling needs to be done for two streams

- Black liquor to ash mixing
- Black liquor from ash mixing



The sampling location is usually the pumps to and from the mixing tanks. The time lag of the black liquor flow between the sampling point and the mixing tank should not be more than 15 min.

If sampling is done from high dry solids liquor (> 65 %), it will flash when the pressure decreases, so sampling location needs to have liquor cooler installed. If not then correction for dry solids needs to be done. Black liquor is hot. Sample vessels need to be able to handle high temperature.

To find ash recycle ratio the samples to and from ash mixing are divided to two equal length time periods. All four samples are then analyzed. It is recommended that dry solids and total sulfur are analysed from each sample. Ash recycle ratio can be calculated from the increase in sulfur flow. The dry solids is used to check whether the sampling has succeeded.

# 5.7.3 Sampling ash

Ash sampling is done to find ash recycle ratio and to determine K and Cl in ash. Because there are several ash streams all of them need to be sampled. Typically ash is sampled

- At the ESP conveyor (represents fume)
- At the boiler bank conveyor (represents mixture of carryover and fume)
- At the economizer conveyor (represents mixture of carryover and fume)

Often several samples need to be taken and then combined to make a relevant sample that represents that stream. It might be so that samples need to be taken from each economizer and combined if combined economizer sample is not available. Similarly if ESP ash from each chamber is directly conveyed to mix tank then each stream should be sampled and combined sample used to represent ESP ash.

The ash sampling is typically done at two hour intervals. It should be done so that no more than three hours but at least one hour passes between subsequent samples. Typically ash sampling is done

- At the beginning of the test period
- At two hour intervals during the test period
- At the end of the test period

It is recommended that from each stream a combined sample is done and analysed for Na, K, Cl,  $CO_3$  and  $SO_4$  (or total S). If borate autocausticizing is done then B should be analysed.

To find sulfur in the ash a combined sample for each stream that represent about the same time length is prepared. From each combined sample the total sulfur is analysed and the average is used to represent the sample. Ash sulfur is then the mass flow averaged sulfur content to mix tank. If all mass flows have not been measured, then values from 4.5 can be used to calculate the average sulfur content.

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# 5.7.4 Sampling smelt

Smelt is sampled to determine the reduction rate. Reduction rate is determined from all smelt streams to dissolving tank.

The smelt sampling is typically done at two hour intervals. It should be done so that no more than three hours but at least one hour passes between subsequent samples. Typically smelt sampling for reduction determination is done

- At the beginning of the test period
- At two hour intervals during the test period
- At the end of the test period

Reduction degree is the average of successful analysis after at least 10 % of the highest and 10 % of the lowest values have been removed.

## 5.7.5 Sampling water and steam

Water and steam samples are needed to determine the efficiency of gas removal in the feed water and the efficiency of droplet separation in the steam drum.

Water and steam samples should be taken using installed sampling stations.

For analysis two samples taken at least two hours apart is normally enough.

# 5.7.6 Emission measurements

Emission measurements are recommended to be done by the mill's installed on-line equipment. Outside emission measurement firms should be employed to calibrate the mills emission measurement equipment.

Reliable flue gas dust content measurement is very difficult with on-line equipment. Flue gas dust content measurement should be done by a reliable emission measurement firm using agreed upon methods.

## 5.8 Determining reduction degree

The main process property of the smelt is the reduction. Reduction is usually expressed as the molar ratio of sulfide (-S) to sum of sulfide and sulfate (-SO4),

$$Reduction = \frac{-S}{-S + -SO_4}$$
19

The higher the reduction the lower the amount of sodium that reaches the cook unusable. Reduction rates of 95 ... 98 % are not uncommon in well operated recovery boilers. Usually the reduction efficiency increases as the char bed temperature increases. From thermodynamical equilibrium calculations we note that there should be very little of sodium oxides and thiosulfate.

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Smelt sampling should be done according to the "ETY-soodakattila valiokunta, Suositus sulan and viherlipeän reduktioasteen määrittämiseksi" VK-15 394V-02. This method can be used if reduction analysis is done at the mill.

Glass tube sampling of smelt is recommended if reduction analysis is done at independent laboratory.



# Figure 5-3, Effect of weak white liquor composition on reduction in green liquor, reduction is smelt 95 %, sulfidity 35 %

Often the typical mill analysis of reduction rate is done for green liquor. Alkali in the weak white liquor will typically result in lower values that what is measured in smelt, Figure 5-3. Typically in modern mills the reduction in green liquor is 2 ... 3 percent points lower that in smelt.

Reduction degree can also be defined as the ratio of sulfide to total sulfur

$$Reduction = \frac{-S}{S_{tot}}$$
 20

The reduction degree as anlysed by the two methods is not the same. It is not uncommon to see two percentage point difference between the two. It is not possible to convert reliably reduction degree measured with one method to reduction degree at the other method.

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# 6 ERROR ANALYSIS

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Errors associated with measuring equipment and analysis methods will affect the result of performance test. All used measuring equipment should be calibrated before the performance test. If the result of an individual measurement has not been subjected to closer error analysis the error in efficiency can be assumed to be according to Table 6-1.

Measured property	Error		Efficiency
	%	Unit	%
Temperature at nose (pyrometer)	$\pm 5$	±50 °C	-
Temperature before bb (calibrated probe)	$\pm 5$	±30 °C	-
Temperature before bb (net, calibrated probe)	±2	±12 °C	-
Temperature after eco (calibrated probe)	±2	±3 °C	0.2
Temperature after eco (net, calibrated probe)	$\pm 0.5$	±1 °C	0.05
Air temperature (calibrated probe)	±0.5	±0.2 °C	0.00
Black liquor HV (KCL)	±0.6	±0.1 MJ/kgka	1.0
Carbon in black liquor (LECO)	$\pm 1.4$	±0.5 %-unit	0.05
Hydrogen in black liquor (LECO)	±0.2	±0.01 %-unit	0.03
Sulfur in black liquor (KCL)	$\pm 5$	±0.2 %-unit	0.6
Reduction (1 sample, KCL)	±1	±1.0 %	0.1
Reduction (10 samples aver., KCL)	±0.2	±0.2 %	0.03
Dry-solids (calibrated refraktometer)	±2.5	±2 %	0.7
Dry-solids (1 sample, KCL)	±0.5	±0.4 %	0.1
NOx (calibrated mill measurement 0-200)	$\pm 3$	±6 ppm	-
NOx (outside accredited firm)	±3	±2 ppm	-
SO <sub>2</sub> (calibrated mill measurement 0-500)	$\pm 3$	±15 ppm	-
SO <sub>2</sub> (outside accredited firm)	±3	±2 ppm	-

# Table 6-1, Error in efficiency caused by error in measurement



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# **ANNEX I**

Typical analysis for additional streams

#### APPENDIX I.1

|--|--|

Name:

Temperature before heating 60 oC

Mass fractions

Gas:	mol	kg	m3n	Fuel gas.	mol	mol -%	vol -%	kg	wt-%			%	
CH4	12.00	0.193	0.27	CO2	224.91	8.163	8.117	9.898	12.97		С	27.74	
C2H2	0.00	0.000	0.00	H2O	539.75	19.589	19.600	9.726	12.74		Н	8.82	
C2H4	0.00	0.000	0.00	SO2	19.00	0.690	0.674	1.217	1.59	1	0	27.98	
C2H6	6.81	0.205	0.15	N2	1907.79	69.240	69.290	53.437	70.02		Ν	17.26	
C3H6	0.00	0.000	0.00	O2	63.87	2.318	2.319	2.043	2.68		S	6.24	
C3H8	1.16	0.051	0.03	Total	2755.33	100.000	100.000	76.322	100.000		H2O	11.96	
C4H8	0.00	0.000	0.00								Ash	0.00	
C4H10	1.03	0.060	0.02								Sum	100.00	
C6H6	0.00	0.000	0.00										
C7H8	0.00	0.000	0.00	Stoch.O2	425.83	mol	dry-O2	2.884	vol -%		HHV	544.50	MJ/kmol
H2	0.00	0.000	0.00	Stoch.air	142.14	m3n/kmol						18.30	MJ/kg
H2S	1.00	0.034	0.02	Comb.air	163.46	m3n/kmol	5.49	m3n/kg fue			LHV	471.60	MJ/kmol
CH3SH	0.00	0.000	0.00		209.50	kg/kmol	7.04	kg/kg fuel				15.85	MJ/kg
CH3SCH3	4.00	0.249	0.09	Flue gas.	188.43	m3n/kmol	6.33	m3n/kg fue	1		HHV	24.31	MJ/m3n
CH3SSCH3	7.00	0.659	0.16		233.17	kg/kmol	7.84	kg/kg fuel			LHV	21.06	MJ/m3n
CH3OH	169.00	5.415	3.79	Air ratio	1.150								
HCN	0.00	0.000	0.00	kgH20/kgA	0.0130								
NH3	0.00	0.000	0.00					0.19762					
O2	0.00	0.000	0.00	FLUE GAS	ELEMENT	ARY W%							
CO	0.00	0.000	0.00			С	H2	02	N2	S			
CO2	0.69	0.030	0.02		[%]	[12.011]	[2.016]	[31.99]	[28.013]	[32.06]			
N2	60.00	1.681	1.34	CO2	8.117	0.975	i	2.597					
H2O	64.68	1.165	1.45	H2O	19.600		0.395	3.135					
TOTAL	327.37	9.741	7.33	SO2	0.674					0.000	)		
TOTAL dry	262.69	8.576	5.88	N2	69.290				19.410	1			
Density		1.329 kg/	m3n	O2	2.319			0.742					

#### **APPENDIX I.2**

#### Methanol

Temperature b	efore heatir	ng	52	оС							Mass fr	actions	
Gas:	mol	kg	m3n	Fuel gas.	mol	mol -%	vol -%	kg	wt-%			%	
CH4	0.00	0.000	0.00	CO2	77.20	8.679	8.630	3.398	13.87	7	С	32.82	
C2H2	0.00	0.000	0.00	H2O	182.24	20.489	20.499	3.284	13.41		Н	10.98	
C2H4	0.00	0.000	0.00	SO2	2.30	0.259	0.253	0.147	0.60	)	0	42.12	
C2H6	0.00	0.000	0.00	N2	606.87	68.229	68.273	16.998	69.40	)	Ν	3.57	
C3H6	0.00	0.000	0.00	O2	20.85	2.345	2.345	0.667	2.72	2	S	2.61	
C3H8	0.00	0.000	0.00	Total	889.46	100.000	100.000	24.494	100.000		H2O	7.90	
C4H8	0.00	0.000	0.00								Ash	0.00	
C4H10	0.00	0.000	0.00								Sum	100.00	
C6H6	0.00	0.000	0.00										
C7H8	0.00	0.000	0.00	Stoch.O2	139.03	mol	dry-O2	2.950	vol -%		HHV	620.77	MJ/kmol
H2	0.00	0.000	0.00	Stoch.air	163.90	m3n/kmol						20.36	MJ/kg
H2S	0.40	0.014	0.01	Comb.air	188.48	m3n/kmol	6.18	m3n/kg fue	el		LHV	533.83	MJ/kmol
CH3SH	1.00	0.048	0.02		241.57	kg/kmol	7.92	kg/kg fuel				17.51	MJ/kg
CH3SCH3	0.90	0.056	0.02	Flue gas.	214.85	m3n/kmol	7.05	m3n/kg fue	el		HHV	27.71	MJ/m3n
CH3SSCH3	0.00	0.000	0.00		264.29	kg/kmol	8.67	kg/kg fuel			LHV	23.83	MJ/m3n
CH3OH	74.40	2.384	1.67	Air ratio	1.150								
HCN	0.00	0.000	0.00	kgH20/kgA	0.0130								
NH3	0.00	0.000	0.00					0.13366					
02	0.00	0.000	0.00	FLUE GAS	6 ELEMENT	FARY W%							
CO	0.00	0.000	0.00			C	H2	02	N2	S			
CO2	0.00	0.000	0.00		[%]	[12.011]	[2.016]	[31.99]	[28.013]	[32.06]			
N2	3.60	0.101	0.08	CO2	8.630	1.037	,	2.761					
H2O	12.39	0.223	0.28	H2O	20.499		0.413	3.279					
TOTAL	92.69	2.826	2.08	SO2	0.253					0.000			
TOTAL dry	80.30	2.602	1.80	N2	68.273				19.125	5			
Density		1.361	l kg/m3n	02	2.345			0.750					

#### **APPENDIX I.3**

#### Turpentine

Temperature b	pefore heat	ing	72	оС							Mass fra	actions	
Gas:	mol	kg	m3n	Fuel gas.	mol	mol -%	vol -%	kg	wt-%			%	
CH4	0.00	0.000	0.00	CO2	1001.90	13.508	13.435	44.094	20.56		С	80.77	
C2H2	0.20	0.005	0.00	H2O	1006.88	13.575	13.584	18.144	8.46		Н	10.86	
C2H4	0.00	0.000	0.00	SO2	0.80	0.011	0.011	0.051	0.02		0	0.00	
C2H6	0.00	0.000	0.00	N2	5226.99	70.471	70.534	146.408	68.26		Ν	0.19	
C3H6	0.20	0.008	0.00	O2	180.65	2.436	2.437	5.779	2.69		S	0.17	
C3H8	0.00	0.000	0.00	Total	7417.22	100.000	100.000	214.476	100.000		H2O	8.01	
C4H8	0.00	0.000	0.00								Ash	0.00	
C4H10	0.00	0.000	0.00								Sum	100.00	
C6H6	0.00	0.000	0.00										
C10H16	100.00	13.623	2.90	Stoch.O2	1204.35	mol	dry-O2	2.820	vol -%		HHV	3385.93	MJ/kmo
H2	0.00	0.000	0.00	Stoch.air	781.48	m3n/kmol						38.28	MJ/kg
H2S	0.10	0.003	0.00	Comb.air	898.70	m3n/kmol	10.16	m3n/kg fue	el		LHV	3121.56	MJ/kmo
CH3SH	0.50	0.024	0.01		1151.80	kg/kmol	13.02	kg/kg fuel				35.29	MJ/kg
CH3SCH3	0.20	0.012	0.00	Flue gas.	985.88	m3n/kmol	11.14	m3n/kg fue	el		HHV	128.51	MJ/m3n
CH3SSCH3	0.00	0.000	0.00		1273.73	kg/kmol	14.40	kg/kg fuel			LHV	118.48	MJ/m3n
CH3OH	0.00	0.000	0.00	Air ratio	1.150								
HCN	0.00	0.000	0.00	kgH20/kgA	0.0130								
NH3	0.00	0.000	0.00					0.33424					
O2	0.00	0.000	0.00	FLUE GAS	ELEMENT	ARY W%							
CO	0.00	0.000	0.00			С	H2	02	N2	S			
CO2	0.00	0.000	0.00		[%]	[12.011]	[2.016]	[31.99]	[28.013]	[32.06]			
N2	1.00	0.028	0.02	CO2	13.435	1.614	Ļ	4.298					
H2O	66.21	1.193	1.48	H2O	13.584		0.274	2.173					
TOTAL	168.41	14.898	4.44	SO2	0.011					0.000			
TOTAL dry	102.20	13.705	2.95	N2	70.534				19.759				
Density		3.358	kg/m3n	02	2.437			0.779					

ANNEX II

Typical material balance

#### ANNEX II

	Appendix II
Finnish Recovery Boiler Committee	27.6.2006
Mass balance	ESV
Model balance, short calculation	

#### Basic data

	Black liquor analysis				
(1)	High heating value (HHV)		13.0	MJ/kgds	
(2)	Carbon		32.5	weight-%	
(3)	Hydrogen		3.30	weight-%	
(4)	Nitrogen		0.09	weight-%	
(5)	Sulfur		6.1	weight-%	
(6)	Sodium		20.0	weight-%	
(7)	Potassium		3.00	weight-%	
(8)	Chloride		0.25	weight-%	
(9)	Borate		0.50	weight-%	
(10)	Oxygen		34.16	weight-%	
(11)	NPE		0.10	weight-%	
(12)	Sum		100.00	weight-%	
(13)	Reduction degree for S		96.00	mole-%	S/(SO4+S)
(14)	Autocausticization degree for B		80.00	mole-%	Na3BO3/(Na
(15)	Dry solids		85.00	%	
(16)	SO2		0.000052	g/kgds	
		~	13.00	mg/m3n	
(17)	HCI		0.000010	g/kgds	
		~	3.00	mg/m3n	
(18)	K in dust		0.0000609	kg/kgds	
(19)	Na in dust		0.0000137	kg/kgds	
(20)	CI in dust		0.0000019	kg/kgds	
(21)	CO3 in dust		0.0000348	kg/kgds	
(22)	SO4 in dust		0.0000885	kg/kgds	
(23)	S in dust		0.0000002	kg/kgds	
(24)	B in dust		0.0000000	kg/kgds	
(25)	Dust		0.0002000	kg/kgds	
		~	50.00	mg/m3n	
(26)	Ash recycle		0.1000000	kg/kgds	
(27)	Sulfur in NCG		0.0108000	kg/kgds	
(28)	Water in NCG		0.0216000	kg/kgds	
(29)	Air coefficient		1.1625000	-	
(30)	Water in air		0.0220000	kg/kgda	
(31)	Direct preheating		0.0000000	kg/kgds	
(32)	Sootblowing steam		0.1188000	kg/kgds	
		~	3.45	%	

#### Input flow of black liquor dry solids

			mass, g/kgds	kg/kmol		mol/kgds	end product
(33)	Carbon	С	325.0	1	12.011	27.059	CO2, Na2CO3, KCO3
(34)	Hydrogen	H2	33.0		2.016	16.371	H2O
(35)	Nitrogen	Ν	0.9		28.013	0.032	N2
(36)	Sulfur	S	61.0		32.060	1.903	SO2, K2S, Na2S, Na2SO4, K2SO4
(37)	Sodium	Na2	200.0		45.980	4.350	Na2S, Na2SO4, Na2CO3, NaCl
(38)	Potassium	K2	30.0		78.197	0.384	K2S, K2SO4, K2CO3, KCI
(39)	Chloride	CI	2.5		35.453	0.071	NaCl, KCl
(40)	Borate	В	5.0		10.811	0.462	NaBO2, Na3BO3
(41)	Oxygen	0	341.6	i	31.999	10.675	CO2, SO2, Na2CO3, Na2SO4, K2SO4
(42)	Water	H2O	176.5		18.015	9.796	H2O
(43)	Inert		1.0		-	-	
(44)	Sum		1176.5			71.101	

molS/kgds

## Sulfur balance

	ounu	Dalance		
			mass, gS/kgds	
(45)		(36)		61.0
(46)		(27)		10.8
(47)		(16)		0.0
(48)		(22)		0.0
(49)		(23)		0.0
(50)		(22)*(27)/(25)		-14.8
(51)		(23)*(27)/(25)		-0.1
(52)	Sum			56.9
(53)		(52)*(13)		54.6
(54)		(52)*(1-(13))		2.3

#### Chloride balance

	GIIIOI			
			mass, gCl/kgds	
(55)		(39)		2.5
(56)		(20)		0.0
(57)		(20)*(27)/(25)		-0.9
(58)		(17)		0.0
(59)	Sum			1.6

#### Borate balance

			mass, gB/kgds	
(60)		(40)		5.0
(61)		(24)		0.0
(62)		(24)*(27)/(25)		0.0
(63)	Sum			5.0
(64)		(63)*(14)		4.0
(65)		(63)*(1-(14))		1.0

#### Sodium balance

		mass, gNa/kgds
(66)	(37)	200.0
(67)	(18)	-0.1
(68)	(18)*(27)/(25)	-30.5
(69)	Sum	169.5
(70)	(53)*(69)/((69)+(79))	-3.0
(71)	(54)*(69)/((69)+(79))	-72.5
(72)	(59)*(69)/((69)+(79))	-0.9
(73)		-25.5
(74)		-2.1
(75)	Residue	65.3

#### Potassium balance

	mass, gK/kgds
(37)	30.0
(19)	0.0
(19)*(27)/(25)	-6.8
Sum	23.1
(53)*(79)/((69)+(79))	-0.4
(54)*(79)/((69)+(79))	-9.9
(59)*(79)/((69)+(79))	-0.1
Residue	12.7
Potassium in smelt	7.4 %
Sodium in smelt	92.6 %
	(37) (19) (19)*(27)/(25) Sum (53)*(79)/((69)+(79)) (54)*(79)/((69)+(79)) (59)*(79)/((69)+(79)) Residue Potassium in smelt Sodium in smelt

#### Carbon balance

		mass, gC/kgds
(84)	(32)	325.0
(85)	(21)	0.0
(86)	(21)*(27)/(25)	-3.5
(87)	(75)+(83)	-19.0
(88)	Residue	302.5

1.903	available sulfur
0.337	s in NCG
0.000	SO2
-0.001	dust as -SO4
0.000	dust as -S
-0.461	ash as -SO4
-0.003	ash as -S
1.775	S in smelt
1.704	(-S) in smelt
0.071	(-SO4) in smelt
<i>molCl/kgds</i>	<i>end product</i>
0.071	available chloride
0.000	NaCl and KCl in dust
-0.026	NaCl and KCl in ash
0.000	HCl in flue gas
0.044	Cl in smelt
molB/kgds	end product
0.462	available borate
0.000	dust
0.000	ash
0.462	borate in smelt
0.370	Na3BO3 in smelt
0.092	NaBO2 in smelt
molNa/kgds	end product
4.350	available sodium
-0.001	Na2SO4, NaCO3 and NaCl in dust
-0.663	Na2SO4, NaCO3 and NaCl in ash
3.686	sodium in smelt
-0.066	Na2SO4 in smelt
-1.577	Na2S in smelt
-0.021	NaCl in smelt
-0.555	Na3BO3 in smelt
-0.046	NaBO2 in smelt
1.421	Na2CO3 in smelt
molK/kads	end product

end product

moirvkgas	ena product
0.384	available potassium
0.000	K2SO4, K2CO3 and KCl in dust
-0.087	K2SO4, K2CO3 and KCl in ash
0.296	potassium in smelt
-0.005	K2SO4 in smelt
-0.127	K2S in smelt
-0.002	KCI in smelt
0.162	K2CO3 in smelt

molC/kgds	end product
27.059	available carbon
-0.001	Na2CO3 and K2CO3 in dust
-0.290	Na2CO3 and K2CO3 in ash
-1.583	Na2CO3 in smelt
25.184	CO2

mass, g0/kgds         molOkgds         end product           (90)         (68) $+305.9$ $-25.184$ CO2           (91)         (21)+(22) $-0.1$ $-0.003$ CO3 and SO4 in dust           (92)         ((21)+(22))^{(27)/(25)} $-4.34$ $-1.357$ CO3 and SO4 in ash           (93)         ((53)+(60) $-4.5$ $-0.142$ Na2SO4 and K2SO4 in smelt           (95)         ((75)+(63) $-7.6.0$ $-2.375$ Na2CO3 and K2SO4 in smelt           (96)         (73) $-7.7.8$ $-0.092$ NaBO2 in smelt           (97)         (74) $-3.0$ $-0.092$ NaBO2 in smelt           (98)         (34).(17) $-261.3$ $-8.185$ H2O           (100)         (20)*(99)^{**}C $4357.8$ dry air           (101)         (100)*(30) $95.9$ wrater in air           (102)         (100)+(101) $4453.7$ humid air           Simet balance           mass, g/kgds         end product           (103)         (81)         14.0         110.26         0.127 K25 in smelt           (104)         (71)         123.1         72.00 and SO4 in smelt           (105) <t< th=""><th></th><th>Oxygen balance</th><th></th><th></th><th></th><th></th><th></th><th></th></t<>		Oxygen balance						
(89)       (40)       341.6       10.675 available oxygen         (90)       (88)       -905.9       -25.184 CO2         (91)       (21)+(22)       -0.1       -0.03 CO3 and SO4 in dust         (92)       ((21)+(22))'(27)/(25)       -43.4       -1.375 CO3 and SO4 in dust         (93)       (16)       0.0       -0.001 SO2         (94)       (68)+(80)       -4.5       -0.142 Na2SO4 and K2SO4 in smelt         (95)       (773)       -17.8       -0.555 Na3BO3 in smelt         (96)       (773)       -17.8       -0.555 Na3BO3 in smelt         (97)       (74)       -3.0       -0.028 NaBO2 in smelt         (98)       (34),(17)       -261.9       -8.185 H2O         (99) Sum       -871.0       -27.220 Oxygen demand         Humid air demand         mass, g/kgds       end product         (100)       (29)'(9)*c       4357.8       dfy air         (101)       (100)*(100)       4453.7       humid air         Size for available avail			mass, g0/kgds			molO/kgds	end product	
(90)         (88)         -905.9         -25.184 CO2         use           (91)         (21)+(22)         -0.1         -0.03 CO3 and SO4 in dist           (92)         (21)+(22)+(27)(25)         -43.4         -1.357 CO3 and SO4 in dist           (93)         (16)         0.0         -0.001 SO2           (94)         (69)+(80)         -4.5         -0.142 Na2SO4 and K22O4 in smelt           (95)         (75)+(83)         -76.0         -2.375 Na2GO3 and K2 CO3 in smelt           (98)         (71)         -261.9         -8.185 H2O           (98)         (71)         -261.9         -8.185 H2O           (99)         Sum         -871.0         -27.220 Oxygen demand           Humid air demand           mass. g/kgds         end product           (100)         (29)*(99)*c         4357.8         dry air           (101)         (100)*(101)         4453.7         humid air           Sum         mass. g/kgds         end product           (103)         (81)         14.0         110.26         0.127 K25 in smelt           (104)         (71)         122.1         78.04         1.577 Na25 is smelt           (105)	(89)	(40)	341.6			10.675	available oxygen	
(91)       (21)+(22)'(27)/(25)       -0.1       -0.003 CO3 and SO4 in dust         (93)       ((21)+(22)'(27)/(25)       -4.3.4       -1.357 CO3 and SO4 in such         (93)       ((6)+(80)       -4.5       -0.01 SO2         (94)       (6)+(80)       -4.5       -0.142 Na2CO3 and K2 CO3 in smelt         (95)       (77)       -17.8       -0.55 Na3BO3 in smelt         (96)       (73)       -17.8       -0.022 Na2O2 in smelt         (98)       (34)(17)       -261.9       -8.185 H2O         (99)       Sum       -871.0       -27.220 Oxygen demand         Municipal Action of the second	(90)	(88)	-805.9			-25.184	CO2	
(2)       ((21)+(22))'(27)(25)       -43.4       -1.357 CO3 and SO4 in ash         (3)       (6)       0.0       -0.001 SO2         (94)       (68)+(80)       -4.5       -0.142 Na2SO4 and K2CO3 in smelt         (95)       (73)       -17.8       -0.555 Na3EO3 in smelt         (96)       (73)       -17.8       -0.555 Na3EO3 in smelt         (98)       (31/7)       -261.9       -8.185 H2O         (99)       Sum       -871.0       -27.220 Oxygen demand <b>Humid air demand</b> mass. g/kgds       end product         (100)       (29)'(99)'c       4357.8       dry air         tomass. g/kgds       end product         (100)-(100)'(30)       95.9         water in air         tomass. g/kgds       end product         (100)-(101)       445.7         tomass. g/kgds       end product         (101)       (217) K25 in smelt         tomass. g/kgds       end product         (102)       (101/2)       60       1.27 K25 in smelt         (102)       (21)       (22) in smelt       110.26       0.127 K25 in smelt <td>(91)</td> <td>(21)+(22)</td> <td>-0.1</td> <td></td> <td></td> <td>-0.003</td> <td>CO3 and SO4 in dust</td> <td></td>	(91)	(21)+(22)	-0.1			-0.003	CO3 and SO4 in dust	
(3)         (16)         0.0         -0.01 SO2           (94)         (69)+(80)         -4.5         -0.142 Na2SO4 and K2SO4 in smelt           (95)         (77)         -17.8         -0.55 Na3BO3 in smelt           (96)         (73)         -17.8         -0.55 Na3BO3 in smelt           (97)         (74)         -3.0         -0.032 NaBO2 in smelt           (98)         (34),(17)         -261.9         -8.185 H2O           (99)         Sum         -871.0         -27.220 Oxygen demand           Humid air demand           mass, g/kgds         end product           (100)         (29)*(99)*c         4357.8         dry air           (101)         (100)+(101)         4453.7         humid air           Smeit balance           mass, g/kgds         end product           (102)         (100)+(101)         4453.7         humid air           Smeit balance           mass, g/kgds (b         0.012 K25 in smelt           (103)         (81)         14.0         10.26         0.127 K25 in smelt           (104)         (71)         123.1         78.04         1.577 Na25 in smelt	(92)	((21)+(22))*(27)/(25)	-43.4			-1.357	CO3 and SO4 in ash	
(a4)         (68)-(60)         -4.5         -0.142         Na2CO3 and K2SO4 in smelt           (95)         (75)+(63)         -76.0         -2.375         Na2CO3 and K2 CO3 in smelt           (97)         (74)         -3.0         -0.092         NaBO2 in smelt           (98)         (34),(17)         -261.9         -8.185         HzD           (99)         Sum         -871.0         -27.220         Oxygen demand           mass, g/kgds         ond product           (100)         (29)*(99)*c         4357.8         dy air           (101)         (100)+(101)         4453.7         humid air           (103)         (61)         110.26         0.127         K2S in smelt           (104)         (71)         123.1         78.04         1.577         Na2SO4 in smelt           (105)         (60)         0.9         174.25         0.005         K2SO4 in smelt           (107)         (72)         2.4         58.443         0.041         Na2SO4 in smelt           (106)         (60)         0.2         74.55         0.005         K2SO4 in smelt           (107)         (72)         2.4         58.443         0.041         Na2SO4 in smelt	(93)	(16)	0.0			-0.001	SO2	
(a5)       (75)-(63)       -76.0       -2.375 Na2CO3 and K2 CO3 in smelt         (96)       (73)       -17.8       -0.555 Na3BO3 in smelt         (97)       (74)       -3.0       -0.092 NaBO2 in smelt         (98)       (34).(17)       -261.9       -8.185 H2O         (99)       Sum       -87.10       -27.220 Oxygen demand         Humid air demand         mass. g/kgds       end product         (100)       (29)'(99)'c       4357.8       dry air         (101)       (100)'(100)'(100)       95.9       water in air         (102)       (100)+(101)       4453.7       humid air         Simet balance         mass. g/kgds       end product         (103)       (81)       14.0       110.26       0.127 K2S in smelt         (104)       (71)       123.1       78.04       0.066 Na2SO4 in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.003 KCl in smelt         (107)       (72)       2.4       58.43       0.41 Na2CO3 in smelt         (109)       (75)       150.6       105.9       1.421 Na2	(94)	(68)+(80)	-4.5			-0.142	Na2SO4 and K2SO4 in smelt	
(96)       (73)       -17.8       -0.555       Na3BO2 in smelt         (97)       (74)       -3.0       -0.092       NaBO2 in smelt         (98)       (34)(17)       -261.9       -8.185       H2D         (99)       Sum       -871.0       -27.220       Oxygen demand         Humid air demand         mass, g/kgds       end product         (100)       (29)*(99)*c       4357.8       dry air         molkgds       end product         (101)       (100)+(101)       4453.7       humid air         Smelt balance         molkgds       end product         (103)       (81)       14.0       110.26       0.127 K2S in smelt         (104)       (71)       123.1       78.04       1.577 Ma2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.003 K2SO4 in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (110) <td>(95)</td> <td>(75)+(83)</td> <td>-76.0</td> <td></td> <td></td> <td>-2.375</td> <td>Na2CO3 and K2 CO3 in smel</td> <td>t</td>	(95)	(75)+(83)	-76.0			-2.375	Na2CO3 and K2 CO3 in smel	t
(97)       (74)       -3.0       -0.032 NaBO2 in smeth         (98)       (34),(17)       -261.9       -8.185 H2O         (99)       Sum       -871.0       -27.220 Oxygen demand         Hunid air demand         mass, g/kgds       end product         (100)       (29)'(99)'C       4357.8       dry air         (101)       (100)+(101)       4453.7       humid air         Samet balance         mass, g/kgds       mol/kgds       end product         (103)       (61)       14.0       110.26       0.127 K25 in smelt         (104)       (71)       123.1       78.04       1.677 M282 in smelt         (105)       (70)       9.3       142.04       0.066 Na2504 in smelt         (106)       (80)       0.9       174.25       0.005 K2S04 in smelt         (107)       (72)       2.4       58.43       0.041 M2C03 in smelt         (109)       (75)       150.6       105.99       1.421 M2C03 in smelt         (110)       (63)       22.4       138.2       0.162 K2 C03 in smelt         (111)       (10       63.8       0.092 NaBO2 in smelt         (111)	(96)	(73)	-17.8			-0.555	Na3BO3 in smelt	
(98)         (34).(17)         -261.9         -8.185         H2O           (99)         Sum         -871.0         -27.220         Oxygen demand           Humid air demand         mass, g/kgds         end product         dry air           (100)         (29)*(99)*c         4357.8         dry air         dry air           (101)         (100)*(10)         95.9         water in air         humid air           Smelt balance         mass, g/kgds         end product         frage of the conduct           (103)         (81)         14.0         110.26         0.127         K2S in smelt           (104)         (71)         123.1         78.04         1.577         Na2S in smelt           (105)         (70)         9.3         142.04         0.066         Na2S Val in smelt           (105)         (70)         9.3         142.04         0.066         Na2S Val in smelt           (106)         (80)         0.2         74.55         0.003         KCI in smelt           (106)         (83)         22.4         138.2         0.162 K2 CO3 in smelt           (110)         (83)         22.4         138.2         0.162 K2 CO3 in smelt           (111)         (11)         1.0	(97)	(74)	-3.0			-0.092	NaBO2 in smelt	
(9)         Sum         -871.0         -27.220         Oxygen demand           Humid air demand         mass, g/kgds         end product           (100)         (29)*(99)*c         4357.8         dry air           (101)         (100)+(101)         4453.7         humid air           Smelt balance         mass, g/kgds         kg/kmol         mol/kgds         end product           (103)         (81)         14.0         110.26         0.127         K28 in smelt           (105)         (70)         9.3         142.04         0.066         Na2SO4 in smelt           (105)         (70)         9.3         142.04         0.066         Na2SO4 in smelt           (106)         (80)         0.9         174.25         0.005         K2SO4 in smelt           (107)         (72)         2.4         58.43         0.041         Na2CO3 in smelt           (109)         (75)         150.6         105.99         1.421         Na2CO3 in smelt           (110)         (83)         22.4         138.2         0.162 K2 CO3 in smelt           (111)         (73)         47.3         127.78         0.370         Na3BO2 in smelt           (112)         (74)         6.1	(98)	(34).(17)	-261.9			-8,185	H2O	
Humid air demand         mass, g/kgds         end product           (100)         (29)*(99)*c         4357.8         dry air           (102)         (100)+(101)         4453.7         humid air           Smelt balance         mass, g/kgds         end product           (103)         (81)         14.0         110.2           (104)         (71)         123.1         78.04         1.577           (105)         (70)         9.3         142.04         0.066 Na2SO4 in smelt           (106)         (80)         0.9         174.25         0.005 K2SO4 in smelt           (107)         (72)         2.4         58.443         0.041 NaCl in smelt           (108)         (82)         0.2         74.55         0.003 KCl in smelt           (109)         (75)         150.6         105.99         1.421 Na2CO3 in smelt           (111)         (73)         47.7         N.370 Na3BO3 in smelt           (112)         (74)         6.1         65.8         0.092 NaBO2 in smelt           (111)         (73)         47.7         Arnount of smelt           (114)         1.577         0.370 Na3BO3 in smelt         1114           (114)         0.0         direct proheating	(99)	Sum	-871.0			-27.220	Oxygen demand	
Humid air demand         mass, g/kgds         end product           (100)         (29) (99)*c         4357.8         dry air           (101)         (100)+(101)         4453.7         humid air           Smelt balance           mass, g/kgds         kg/kmol         mol/kgds         end product           (103)         (81)         14.0         110.26         0.127 K25 in smelt         1           (104)         (71)         123.1         78.04         1.577 Na25 in smelt         1           (104)         (71)         123.1         78.04         0.066 Na2504 in smelt         1           (105)         (70)         9.3         142.04         0.066 Na2504 in smelt         1           (106)         (80)         0.9         174.25         0.003 KC1 in smelt         1           (109)         (75)         150.6         105.99         1.421 Na2CO3 in smelt         1           (110)         (83)         22.4         138.2         0.162 K2 C30 in smelt         1           (111)         (73)         47.3         127.78         0.370 Na3BO3 in smelt         1           (112)	. ,							
Image         grkgds         end product           (100)         (29)*(99)*C         4357.8         dry air           (101)         (100)+(101)         4453.7         humid air           Smelt balance         mass, grkgds         kg/kmol         molkgds         end product           (103)         (81)         14.0         110.26         0.127 K2S in smelt         1           (104)         (71)         123.1         78.04         1.577 Na2S in smelt         1           (105)         (70)         9.3         142.04         0.066 Na2SO4 in smelt         1           (107)         (72)         2.4         58.443         0.041 NaCl in smelt         1           (108)         (82)         0.2         74.55         0.003 K20 in smelt         1           (110)         (83)         22.4         138.2         0.162 K2 CO3 in smelt         1           (111)         (73)         47.3         127.78         0.370 Na3BO3 in smelt         1           (111)         (73)         47.3         127.78         0.370 Na3BO3 in smelt         1           (112)         (74)         6.1         65.8         0.029 MaD2 in smelt         1           (112)         (74)		Humid air demand	<i>"</i>					
(100)       (29)*(99)*C       4357.8       dry ar         (101)       (100)*(100)*(30)       95.9       water in air         (102)       (100)+(101)       4453.7       humid air         Smelt balance         mass, g/kgds       kg/kmol       mol/kgds       end product         (103)       (81)       110.26       0.127 K2S in smelt         (104)       (71)       123.1       78.04       1.577 Na2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.005 K2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 K2I in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.022 NaBO2 in smelt         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)		<i>(</i> ) <i>(</i> ) <i>(</i>	mass, g/kgds				end product	
(101)       (100)*(30)       95.9       water in air         (102)       (100)+(101)       4453.7       humid air         Smett balance         (103)       (81)       14.0       110.26       0.127 K2S in smelt         (104)       (71)       123.1       78.04       1.577 Na2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.005 K2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 KCl in smelt         (110)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.092 NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass. g/kgds       end product         (115)       (44)       1176.5       black liquor         (114) <t< td=""><td>(100)</td><td>(29)*(99)*c</td><td>4357.8</td><td></td><td></td><td></td><td>dry air</td><td></td></t<>	(100)	(29)*(99)*c	4357.8				dry air	
(102)       (100)+(101)       4453.7       humid air         Smelt balance         mass, g/kgds       mol/kgds       end product         (103)       (81)       14.0       110.26       0.127 K25 in smelt         (104)       (71)       123.1       78.04       1.577 Na2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.005 K2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 KCl in smelt         (119)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO2 in smelt         (112)       (74)       6.1       6.5.8       0.92 NaBO2 in smelt         (113)       (11)       1.0       Other organics         Immunot air         mass, g/kgds       end product         Immunot air         Mass, g/kgds       end product         Immunot air         Immunot	(101)	(100)*(30)	95.9				water in air	
Smelt balance           mass, g/kgds         kg/kmol         mol/kgds         end product           (103)         (81)         14.0         110.26         0.127 K2S in smelt           (104)         (71)         123.1         78.04         1.577 Na2S in smelt           (105)         (70)         9.3         142.04         0.066 Na2SO4 in smelt           (106)         (80)         0.9         174.25         0.005 K2SO4 in smelt           (107)         (72)         2.4         58.443         0.041 NaCl in smelt           (109)         (75)         150.6         105.99         1.421 Na2CO3 in smelt           (110)         (83)         22.4         138.2         0.370 Na3BO3 in smelt           (111)         (73)         47.3         127.78         0.370 Na3BO3 in smelt           (113)         (11)         1.0         Other organics           (114)         Samount of smelt         377.4         Amount of smelt           (115)         (44)         1176.5         black liquor           (116)         (102)         4453.7         air           (117)         (25)         -0.2         loss in dust           (118)         (27)         -100.0	(102)	(100)+(101)	4453.7				humid air	
mass, g/kgds         kg/kmol         mol/kgds         end product           (103)         (81)         14.0         110.26         0.127 K2S in smelt           (104)         (71)         123.1         78.04         1.577 Na2S in smelt           (105)         (70)         9.3         142.04         0.066 Na2SO4 in smelt           (106)         (80)         0.9         174.25         0.005 K2SO4 in smelt           (108)         (82)         0.2         74.55         0.003 KCI in smelt           (109)         (75)         150.6         105.99         1.421 Na2CO3 in smelt           (110)         (83)         22.4         138.2         0.162 K2 CO3 in smelt           (111)         (73)         47.3         127.78         0.370 Na3BO3 in smelt           (111)         (73)         47.3         127.78         0.370 Na3BO2 in smelt           (113)         (11)         1.0         Other organics           (114)         Sampt         air           (115)         (44)         1176.5         black liquor           (115)         (44)         1176.5         olas in dust           (117)         (25)         -0.2         loss in dust           (118)		Smelt balance						
(103)       (81)       14.0       110.26       0.127 K2S in smelt         (104)       (71)       123.1       78.04       1.577 Na2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.005 K2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 KCl in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.092 NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, $g/kgds       end product         (115)       (44)       1176.5       black liquor         (114)       0.0       asir       in dust         (115)       (44)       1176.5       black liquor         (118)       (27)       -100.0       ash recycle      <$			mass. a/kads	ka/kmol		mol/kads	end product	
(104)       (71)       123.1       78.04       1.577 Na2S in smelt         (105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.005 K2SO4 in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (122)       (28)       21.6       water in NCG         (123)<	(103)	(81)	14.0	<b>J</b>	110.26	0.127	K2S in smelt	
(105)       (70)       9.3       142.04       0.066 Na2SO4 in smelt         (106)       (80)       0.9       174.25       0.005 K2SO4 in smelt         (107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 KCl in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (111)       (73)       47.3       127.74       0.370 Na3BO3 in smelt         (113)       (11)       1.0       Other organics         (114) Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       soutblowing steam         (121)       (27)       10.8       suffur in NCG         <	(104)	(71)	123.1		78.04	1.577	Na2S in smelt	
Implement         Implement <thimplement< th=""> <thimplement< th=""> <thi< td=""><td>(105)</td><td>(70)</td><td></td><td></td><td>142 04</td><td>0.066</td><td>Na2SO4 in smelt</td><td></td></thi<></thimplement<></thimplement<>	(105)	(70)			142 04	0.066	Na2SO4 in smelt	
(107)       (72)       2.4       58.443       0.041 NaCl in smelt         (108)       (82)       0.2       74.55       0.003 KCl in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.092 NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       Smelt       0.2         (124) Sum       5303.8       flue gas       0.2         (125) Black liquor       1176.5	(100)	(80)	0.0		174 25	0.000	K2SO4 in smelt	
(108)       (12)       1.1       34.55       0.003 KCl in smelt         (109)       (75)       150.6       105.99       1.421 Na2CO3 in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.092 NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       soutblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       Smelt       377.4<	(107)	(72)	2.4		58 443	0.041	NaCl in smelt	
(109)       (75)       150.6       105.99       1.4.21       Na2CO3 in smelt         (110)       (83)       22.4       138.2       0.162 K2 CO3 in smelt         (111)       (73)       47.3       127.78       0.370 Na3BO3 in smelt         (112)       (74)       6.1       65.8       0.092 NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       southowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       Smelt         (124) Sum       5303.8       flue gas         (125) Black liquor       1176.5       Dust       0.2         (124) Sum       5303.8       flue gas       5303.8	(108)	(82)	0.2		74 55	0.011	KCl in smelt	
(10)       (13)       100.0       100.30	(100)	(02)	0.2 150 6		105.00	1 /21	Na2CO3 in smalt	
(110)       (03)       22.4       130.2       0.102       102 COS in smelt         (111)       (73)       47.3       127.78       0.370       Na3BO2 in smelt         (112)       (74)       6.1       65.8       0.092       NaBO2 in smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         (125)       Black liquor       1176.5       Dust       0.2         (124)       Sum       5303.8       flue gas       5303.8         (125)       Black liquor       1176.5	(103)	(13)	22.4		128.2	0.162	K2 CO3 in smalt	
(111)       (13)       (14)       127.73       0.370       NabO2 in Smelt         (112)       (74)       6.1       65.8       0.092       NabO2 in Smelt         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ashrecycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (124)       Sum       5303.8       flue gas         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       10.8       Sublack liquor       0.2         (128)	(110)	(03)	22.4		100.2	0.102	No3BO3 in smolt	
(112)       (14)       0.1       0.35       0.052       Nab02 Nab02 Nab02 Nab02 Nab04         (113)       (11)       1.0       Other organics         (114)       Sum       377.4       Amount of smelt         Flue gas flow         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air       air         (117)       (25)       -0.2       loss in dust       ash recycle         (118)       (27)       -100.0       ash recycle       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (124)       Sum       5303.8       flue gas         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Airs       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (125)       Black liquor       118.8       Flue gas       5303.8 <t< td=""><td>(112)</td><td>(73)</td><td>-17.5 6.1</td><td></td><td>65.8</td><td>0.010</td><td>NaBO2 in smalt</td><td></td></t<>	(112)	(73)	-17.5 6.1		65.8	0.010	NaBO2 in smalt	
Instruction       Instruction       Output mass, g/kgds       Other organics         Flue gas flow       mass, g/kgds       end product         Instruction       black liquor       air         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124) Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8	(112)	(14)	0.1		05.0	0.092	Other organics	
Flue gas flow       end product         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (124) Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       10.8       10.8         (130) Water in NCG       21.6       5781.4       Sum	(113) (114)	Sum	377.4				Amount of smelt	
Flue gas flow         end product           (115)         (44)         1176.5         black liquor           (116)         (102)         4453.7         air           (117)         (25)         -0.2         loss in dust           (118)         (27)         -100.0         ash recycle           (119)         (31)         0.0         direct preheating           (120)         (32)         118.8         sootblowing steam           (121)         (27)         10.8         sulfur in NCG           (122)         (28)         21.6         water in NCG           (124)         Sum         5303.8         flue gas           Input mass, g/kgds         Output mass, g/kgds           (125)         Black liquor         1176.5         Dust         0.2           (126)         Air         4453.7         Ash         100.0           (127)         Air preheat         0.0         Smelt         377.4           (128)         Sootblowing steam         118.8         Flue gas         5303.8           (129)         Sulfur in NCG         10.8         10.9         10.8           (130)         Water in NCG         21.6	(,							
Instruction       mass, g/kgds       end product         (115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (124) Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       102.0       103.8         (130) Water in NCG       21.6       10.8       103.3         (131) Sum       5781.4       Sum       5781.4		Flue gas flow	, ,					
(115)       (44)       1176.5       black liquor         (116)       (102)       4453.7       air         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         Input mass, g/kgds       Output mass, g/kgds         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Air preheat       0.0       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (129)       Sulfur in NCG       10.8       103.8       100.0         (130)       Water in NCG       21.6       10.8       10.3         (131)       Sum       5781.4	(445)		mass, g/kgas				ena product	
(116)       (102)       4453.7       ar         (117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124) Sum       5303.8       flue gas         Input mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       100.0       10.8         (130) Water in NCG       21.6       10.8       10.8         (131) Sum       5781.4       Sum       5781.4	(115)	(44)	1176.5				black liquor	
(117)       (25)       -0.2       loss in dust         (118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124) Sum       5303.8       flue gas         Input mass, g/kgds         125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       102.0       103.8         (130) Water in NCG       21.6       103.8       103.8         (131) Sum       5781.4       Sum       5781.4	(116)	(102)	4453.7				air	
(118)       (27)       -100.0       ash recycle         (119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (124)       Sum       5303.8       flue gas         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Air preheat       0.0       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (129)       Sulfur in NCG       10.8       10.0       10.8         (130)       Water in NCG       21.6       10.8       10.1         (131)       Sum       5781.4       Sum       5781.4	(117)	(25)	-0.2					
(119)       (31)       0.0       direct preheating         (120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Air preheat       0.0       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (129)       Sulfur in NCG       10.8       10.8       100.0         (130)       Water in NCG       21.6       10.8       10.3         (131)       Sum       5781.4       Sum       5781.4	(118)	(27)	-100.0				ash recycle	
(120)       (32)       118.8       sootblowing steam         (121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124) Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       5303.8       5303.8         (130) Water in NCG       21.6       5781.4       Sum       5781.4	(119)	(31)	0.0				direct preheating	
(121)       (27)       10.8       sulfur in NCG         (122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124) Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds         (125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       5781.4       Sum       5781.4	(120)	(32)	118.8				sootblowing steam	
(122)       (28)       21.6       water in NCG         (123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Air preheat       0.0       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (129)       Sulfur in NCG       10.8       5303.8       5303.8         (130)       Water in NCG       21.6       5781.4       Sum       5781.4	(121)	(27)	10.8				sulfur in NCG	
(123)       (114)       -377.4       smelt         (124)       Sum       5303.8       flue gas         Input       mass, g/kgds       Output       mass, g/kgds       0.2         (125)       Black liquor       1176.5       Dust       0.2         (126)       Air       4453.7       Ash       100.0         (127)       Air preheat       0.0       Smelt       377.4         (128)       Sootblowing steam       118.8       Flue gas       5303.8         (129)       Sulfur in NCG       10.8       5303.8       5303.8         (130)       Water in NCG       21.6       5781.4       Sum       5781.4	(122)	(28)	21.6				water in NCG	
Input         mass, g/kgds         Output         mass, g/kgds           (125) Black liquor         1176.5         Dust         0.2           (126) Air         4453.7         Ash         100.0           (127) Air preheat         0.0         Smelt         377.4           (128) Sootblowing steam         118.8         Flue gas         5303.8           (129) Sulfur in NCG         10.8         5781.4         Sum         5781.4	(123)	(114)	-377.4				smelt	
Inputmass, g/kgdsOutputmass, g/kgds(125) Black liquor1176.5Dust0.2(126) Air4453.7Ash100.0(127) Air preheat0.0Smelt377.4(128) Sootblowing steam118.8Flue gas5303.8(129) Sulfur in NCG10.810.810.0(130) Water in NCG21.65781.4Sum	(124)	Sum	5303.8				flue gas	
Input         mass, g/kgds         Output         mass, g/kgds           (125) Black liquor         1176.5         Dust         0.2           (126) Air         4453.7         Ash         100.0           (127) Air preheat         0.0         Smelt         377.4           (128) Sootblowing steam         118.8         Flue gas         5303.8           (129) Sulfur in NCG         10.8         10.3         10.3           (130) Water in NCG         21.6         5781.4         Sum         5781.4								
(125) Black liquor       1176.5       Dust       0.2         (126) Air       4453.7       Ash       100.0         (127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       10.3       10.3         (130) Water in NCG       21.6       5781.4       Sum       5781.4		Input	mass, g/kgds			Output	mass, g/kgds	
(126) Air4453.7Ash100.0(127) Air preheat0.0Smelt377.4(128) Sootblowing steam118.8Flue gas5303.8(129) Sulfur in NCG10.810.810.3(130) Water in NCG21.65781.4Sum(131) Sum5781.4Sum5781.4	(125)	Black liquor	1176.5			Dust	0.2	
(127) Air preheat       0.0       Smelt       377.4         (128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       10.8       10.3         (130) Water in NCG       21.6       5781.4       Sum       5781.4	(126)	Air	4453.7			Ash	100.0	
(128) Sootblowing steam       118.8       Flue gas       5303.8         (129) Sulfur in NCG       10.8       10.8       10.8         (130) Water in NCG       21.6       5781.4       Sum       5781.4	(127)	Air preheat	0.0			Smelt	377.4	
(129) Sulfur in NCG     10.8       (130) Water in NCG     21.6       (131) Sum     5781.4     Sum     5781.4	(128)	Sootblowing steam	118.8			Flue gas	5303.8	
(130) Water in NCG         21.6           (131) Sum         5781.4         Sum         5781.4	(129)	Sulfur in NCG	10.8			•		
(131) Sum 5781.4 Sum 5781.4	(130)	Water in NCG	21.6					
	(131)	Sum	5781.4			Sum	5781.4	

ANNEX III

Typical energy balance

			ŀ	Appendix III		
	Finnish Recovery Boiler Committee Energy balance Model balance, short calculation				ESV	27.6.2006
	Basic data					
					%	
(1)	Balance reference temperature	0	°C			
(2)	Higher heating value of dry solids	13000.0	kJ/kgds		97.2	
(3)	Dry solids content	85.0	%			
(4)	After direct preheating	85.0	%			
(5)	Hydrogen	3.30	mass-%			
(6)	Black liquor cp	2.64	kJ/kg°C			
(7)	Black liquor temperature	140.0	°C			
(8)	Heat in auxiliary fuel	577.0	kJ/kgds			
(9)	Air temperature	30.0	°C			
(10)	Combustion air temperature	108.8	°C			
(11)	Infiltration air	5.00	mass-%			
(12)	Air cp	1.03	kJ/kg°C			
(13)	Sootblowing steam	0	(0=outside,1=ir	nside)		
(14)	Enthalpy of sootblowing steam	3054.8	kJ/kg	,		
(15)	Heat of evaporation in ref. state	2500.9	kJ/kg			
(16)	Smelt temperature	851.6	°Č			
(17)	Flue gas temperature	155.0	°C			
(18)	Flue gas cp	1.11	kJ/kg			
(19)	Steam of flue gas	2792.0	kJ/kg			
(20)	Radiation and convection	0.283	%			
(21)	Unburned and other	0.300	%			
(22)	Marginal	0.500	%			
(23)	Enthalpy in feed water flow	490.3	kJ/kg			
(24)	Enthalpy in steam flow	3360.7	kJ/kg			
(25)	Enthalpy in blow out	1423.3	kJ/ka			
(26)	Blow out flow	0.0500	kg/kgds			
. ,			0.0			

#### Input

	kJ/kgds	%
12280.4		91.8
0		0.0
-430.6		-3.2
	11849.8	88.6
	577.0	4.3
	434.8	3.3
	131.2	1.0
	344.6	2.6
	6.9	0.1
	31.2	0.2
	13375.6	100.0
	12280.4 0 -430.6	kJ/kgds 12280.4 0 -430.6 11849.8 577.0 434.8 131.2 344.6 6.9 31.2 13375.6

#### Losses

			kJ/kgds	%	
(39)	In smelt	(Na2+K2)S	199.9	1.5	
(40)		(Na2+K2)SO4	13.3	0.1	
(41)		(Na2+K2)CO3	260.7	1.9	
(42)		(Na+K)Cl	3.5	0.0	
(43)		Na3BO3+NaBO2	82.5	0.6	
(44)		Inert	1.4	0.0	
(45)	Reduction	Na2S	1611.1	12.0	
(46)		SO2	0.3	0.0	
(47)		K2S	134.4	1.0	
(48)	Autocausticizing	Na3BO3	96.1	0.7	
(49)	Smelt+reduction+autocausticizisin	g	2403.2	18.0	
(50)					
(51)	Wet flue gas		910.4	6.8	
(52)	Radiation and convection		37.9	0.3	
(53)	Unburned and other		40.1	0.3	
(54)	Marginal		66.9	0.5	
(55)	Sum		3458.5	25.9	
(56)	Net to steam		9917.1	74.1	
(57)	Efficiency (HHV)	%	68.3		
(58)	Efficiency (LHV)	%	74.1		
(59)	Efficiency (LHV, reduction, autoc.)	%	87.9		
(60)	Efficiency (NHV)	%	88.6		
	Steam production				
	-				

kg/kgds	
3.4888	161.5181
0.0500	2.3148
0.1188	5.5000
3.4388	159.2033
	kg/kgds 3.4888 0.0500 0.1188 <b>3.4388</b>

	Heat Input	mass, g/kgds	Out	mass, g/kgds
(65)	As-fired black liquor	11849.8	Net to steam	9917.1
(66)	Other fuel heat input	577.0	Reduction	1745.8
(67)	Sensible in black liquor	434.8	Autocausticizing	96.1
(68)	Air	131.2	In smelt	561.3
(69)	Air preheat	344.6	Wet flue gas flow	910.4
(70)	Infiltration air	6.9	Radiation and conve	cti 37.9
(71)	Outside sootblowing	31.2	Unburned and others	s 107.0
(72)	Sum	13375.6		13375.6

ANNEX IV

Magnitude of losses

16A0913-E0078 1/2

Appendix IV Finnish Recovery Boiler Committee 27.6.2006 Energy balance ESV Losses calculation Miscellaneous losses 14.32 kJ Unburned in combustibles Unburned in smelt 0.03 kJ Unburned in ash 1.28 kJ Heat in electrostatic precipitation ash 15.22 kJ Heat value correction to ref. temperature -77.65 kJ Shaft power 86.40 kJ 39.61 kJ Sum 0.30 % Unburned in flue gas flow Flue gas flow (dry) 4.558 kg/kgds Density of flue gas flow 1.376 kg/m3n CO 200 ppm v CO +0.5\*O2 -> CO2 283 MJ/kmol Loss in CO 8.37 kJ H2 100 ppm v H2 + 0,5\*O2 -> H2O 241.8 MJ/kmol Loss in H2 3.58 kJ VOC 20 ppm v CH4 + 2\*O2 -> 2H2O + CO2 802.3 MJ/kmol Loss in VOC 2.37 kJ Sum of losses 14.32 kJ 0.11 % Unburned in smelt Smelt flow 0.38 kg/kgds Carbon cotent in smelt 2.54 mg/kg smelt Carbon cotent in green liquor 400 mg/m3 Green liguor 2.40 l/kgds Loss in carbon 32.00 MJ/kg carbon Sum of losses 0.03 kJ 0.00 % Unburned in ash Ash flow 0.10 kg/kgds Carbon content in ash 400 mg/kg ash Carbon loss 32.00 MJ/kg carbon Sum of losses 1.28 kJ

0.01 %

# Heat loss in elctrostatic precipitator ash

Ash flow	0.100 kg/kgds
Flue gas flow (dry)	3.313 m3/kgds
Ash flow	30.2 g/m3n
Temperature	155 oC
Ash cp	0.982 kJ/kgK
Loss in heat of ash	15.22 kJ
	0.11 %

#### Heat value correction to balance reference temperature

Fuel flow	1.176 kg/kgds
Specific heat capacity	2.640 kJ/kgK
Loss in heat of ash	-78 kJ
	-0.58 %

#### Consideration of shaft power

Shaft power

86 kJ/kgds 0.65 %

ANNEX V

Calculation of flue gas properties for a mixture

#### Appendix V

#### Calculation of flue gas properties for a mixture

	CO2	H2O	SO2	N2	02	со	H2	Mixture
E1	-8.4952	-9.0771	-9.8553	-7.4596	-7.2367	-7.9112	-7.2956	-7.8825
E2	24.74	33.22	31.21	26.57	24.62	28.97	24.45	27.11
E3	24.875	1.328	17.321	3.275	7.926	0.071	9.955	7.276
E4	-6.752	1.768	-3.725	-0.176	-1.860	0.108	-6.242	-1.213
E5	-8.3957	7.4312	-8.0402	5.2744	3.1092	2.1630	-24.4049	2.4422
E6	0.08415	0.00968	0.06845	0.07161	0.07479	0.09700	1.03473	0.06715
E7	3.327E-06	0.0001103	-3.239E-05	-1.3E-05	1.635E-05	-6E-05	-0.0015319	6.071E-06
E8	-8.453E-09	-3.025E-08	1.836E-08	2.08E-09	-1.459E-08	2.257E-08	1.402E-06	-4.447E-09
E9	-1.47366	-1.60121	-0.11323	2.44488	2.07235	2.89722	1.29196	1.06544
E10	0.0618969	0.0333459	0.0438088	0.0583692	0.0712374	0.0579242	0.0323359	0.0568142
E11	-2.454E-05	1.214E-05	8.726E-07	-2.574E-05	-3.417E-05	-3.018E-05	-2.813E-05	-2.15E-05
E12	5.383E-09	-6.27E-09	-5.237E-09	6.55E-09	1.001E-08	9.73E-09	1.824E-08	4.957E-09
E13	0.5059	1.2438	0.3417	0.7997	0.6998	0.7999	11.1273	0.7505
E14	22.263	22.408	21.887	22.403	22.394	22.404	22.432	22.376
E15	188.9	461.5	129.8	296.8	259.8	296.8	4124.3	278.8
E16	44.010	18.016	64.060	28.016	31.999	28.010	2.016	29.817

Enthalpy coefficient Enthalpy coefficient Enthalpy coefficient Enthalpy coefficient Conductivity coefficient Conductivity coefficient Onductivity coefficient Viscocity coefficient Viscocity coefficient Viscocity coefficient Viscocity coefficient Viscocity coefficient Conversion kg-> m3n Volume Rm Mole veight

#### Composition, mol - %

	<b>CO2</b> 19.071	<b>H2O</b> 14.123	<b>SO2</b> 0.123	<b>N2</b> 63.305	<b>O2</b> 3.125	<b>CO</b> 0.230	<b>H2</b> 0.023	<b>Sum</b> 100.000	Input
Composi	tion, vol	-%							
	<b>CO2</b> 18.975	<b>H2O</b> 14.143	<b>SO2</b> 0.120	<b>N2</b> 63.381	<b>02</b> 3.127	<b>CO</b> 0.230	<b>H2</b> 0.023	<b>Sum</b> 100.000	

#### **Isobaric Properties for flue gas**

Isobaric Data for P = 0.10130 MPa

Temperat ure (K)	Pressure (MPa)	Density (mol/l)	Density (kg/m3)	Volume (I/mol)	Volume (m3/kg)	Enthalpy (kJ/mol)	Enthalpy (kJ/kg)	Enthalpy (kJ/m3n)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
200	0.1013	0.06092	1.816	16.4153	0.5505	-2.180	-73.1	-97.4	11.6077	0.016079	vapor
250	0.1013	0.04874	1.453	20.5191	0.6882	-0.670	-22.5	-29.9	14.0024	0.019540	vapor
273.15	0.1013	0.04460	1.330	22.4191	0.7519	0.040	1.3	1.8	15.0808	0.021147	vapor
300	0.1013	0.04061	1.211	24.6229	0.8258	0.872	29.2	39.0	16.3081	0.023014	vapor
350	0.1013	0.03481	1.038	28.7267	0.9634	2.445	82.0	109.3	18.5286	0.026498	vapor
400	0.1013	0.03046	0.908	32.8305	1.1011	4.047	135.7	180.9	20.6676	0.029989	vapor
450	0.1013	0.02708	0.807	36.9343	1.2387	5.679	190.5	253.8	22.7288	0.033484	vapor
500	0.1013	0.02437	0.727	41.0382	1.3763	7.339	246.1	328.0	24.7160	0.036979	vapor
550	0.1013	0.02215	0.661	45.1420	1.5140	9.026	302.7	403.4	26.6328	0.040471	vapor
600	0.1013	0.02031	0.605	49.2458	1.6516	10.740	360.2	480.0	28.4830	0.043957	vapor
650	0.1013	0.01874	0.559	53.3496	1.7893	12.479	418.5	557.7	30.2703	0.047434	vapor
700	0.1013	0.01741	0.519	57.4534	1.9269	14.242	477.7	636.5	31.9983	0.050897	vapor
750	0.1013	0.01625	0.484	61.5572	2.0645	16.030	537.6	716.4	33.6709	0.054344	vapor
800	0.1013	0.01523	0.454	65.6610	2.2022	17.840	598.3	797.3	35.2918	0.057771	vapor
850	0.1013	0.01433	0.427	69.7649	2.3398	19.671	659.7	879.1	36.8646	0.061175	vapor
900	0.1013	0.01354	0.404	73.8687	2.4774	21.524	721.9	961.9	38.3931	0.064553	vapor
950	0.1013	0.01283	0.382	77.9725	2.6151	23.397	784.7	1045.6	39.8810	0.067901	vapor
1000	0.1013	0.01218	0.363	82.0763	2.7527	25.289	848.1	1130.2	41.3320	0.071216	vapor
1050	0.1013	0.01160	0.346	86.1801	2.8903	27.199	912.2	1215.5	42.7498	0.074495	vapor
1100	0.1013	0.01108	0.330	90.2839	3.0280	29.126	976.8	1301.7	44.1382	0.077734	vapor
1150	0.1013	0.01059	0.316	94.3878	3.1656	31.070	1042.0	1388.5	45.5009	0.080931	vapor
1200	0.1013	0.01015	0.303	98.4916	3.3032	33.029	1107.7	1476.1	46.8415	0.084080	vapor
1250	0.1013	0.00975	0.291	102.5954	3.4409	35.002	1173.9	1564.3	48.1639	0.087180	vapor
1300	0.1013	0.00937	0.279	106.6992	3.5785	36.989	1240.6	1653.1	49.4717	0.090228	vapor
1350	0.1013	0.00903	0.269	110.8030	3.7161	38.989	1307.6	1742.5	50.7686	0.093218	vapor
1400	0.1013	0.00870	0.259	114.9068	3.8538	41.001	1375.1	1832.4	52.0583	0.096149	vapor
1450	0.1013	0.00840	0.251	119.0106	3.9914	43.024	1442.9	1922.8	53.3447	0.099017	vapor
1500	0.1013	0.00812	0.242	123.1145	4.1290	45.056	1511.1	2013.6	54.6313	0.101819	vapor

Data fitted to NIST equations

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