Master Thesis

Development, Implementation, and Validation of a Kraft Recovery Boiler IPSEpro Simulation Model based on State-of-the-Art Calculation Methods

carried out for the purpose of obtaining the degree of Master of Science (MSc or Dipl.-Ing. or DI),
submitted at TU Wien, Faculty of Mechanical and Industrial Engineering, by

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Institute of Energy Systems and Thermodynamics, E302

Vienna, May 2023

Affidavit

I declare in lieu of oath that I wrote this thesis and performed the associated research myself, using only literature cited in this volume. If text passages from sources are used literally, they are marked as such.

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"I never lose. I either win or learn."

Table of Contents

I. Abstract

This master thesis describes the model development of an IPSEpro tool for the simulation of modern Kraft Recovery Boilers in pulp industry. The developed models are based on state-of-the-art calculation methods, they were compared and validated with recent literature. The implementation and simulation were carried out in commercial engineering software such as IPSEpro Model Development Kit and IPSEpro Process Simulation Environment. The purpose of the tool is to have quick and precise thermodynamic results in the design stage of the Kraft Recovery Boiler, as well as to give the user the possibility to integrate the units in a mill or plant and research the impacts when changing operating parameters.

The first chapter introduces the reader to Kraft Recovery Boilers and its state-of-the-art calculation approaches proposed by recent literature, the second chapter talks about the used software IPSEpro and its hierarchies. On that basis chapter three explains the general development process starting off with model V1 – the Base Model – and further evolving it, making it more user-friendly and complex by integrating the advantages of the software used. Chapters four and five talk about the modification, modeling and implementation of streams and the Kraft Recovery Boiler unit respectively. Chapter six, called User Manual aims to explain how to utilize the developed model in a practice-orientated manner. In chapter six firstly, the Base Model V1 is validated, giving identical results only varying in round-off errors. And secondly, testing the evolved Referenced Model V2's computations with four different cases all proven show results within tolerable discrepancies: the first one aim validates the developed model with the state-of-the-art calculation method it is based (Tran & Grace) on. The second case is a comparison with another calculation approach (Vakkilainen) pinpointing the discrepancies through their distinct assumptions. The third chapter researches and shows the model's precision of estimating the behavior of outputs when varying the black liquor dry solid content parameter. The fourth and last validation of the Referenced Model V2 was complicated due to the lack of insight into the study's exact calculation approach, assumptions made, etc.

Finally, chapter eight concludes that the obtained results given by the developed model are convincing and valid. Improvements in modeling black liquor and smelt as well as the inclusion of an internalized dust precipitator might enhance the model.

II. Deutsche Kurzfassung

In dieser Diplomarbeit wird die Modellentwicklung eines IPSEpro-Tools für die Simulation von modernen Kraftrückgewinnungskesseln der Zellstoffindustrie beschrieben. Die entwickelten Modelle basieren auf modernsten Berechnungsmethoden und wurden mit aktueller Literatur verglichen und validiert. Die Implementierung und Simulation wurde mit der Ingenieursoftware IPSEpro durchgeführt mit dem Zweck schnelle und präzise thermodynamische Ergebnisse in der Entwurfsphase zu erhalten ebenso wie die Auswirkungen von Änderung der Betriebsparameter in Bezug auf das Verhalten der Anlage zu untersuchen zu können.

Das erste Kapitel beschreibt Kraftwiedergewinnungskessel sowie die in der Literatur vorgeschlagenen modernen Berechnungsansätze. Das zweite Kapitel behandelt die verwendete Software IPSEpro und dessen Aufbau. In Kapitel drei wird der allgemeine Entwicklungsprozess erläutert, beginnend mit dem Basismodell V1 und dessen Weiterentwicklung, um von den Vorteilen der verwendeten Software zu profitieren mit dem Ziel es benutzerfreundlicher und komplexer zu machen. Kapitel vier und fünf befassen sich mit der Änderung, Modellierung und Implementierung von Strömen bzw. der Kraft-Wärme-Kessel-Einheit. Im sechsten Kapitel, dem Benutzerhandbuch, wird erläutert, wie das entwickelte Modell praxisorientiert eingesetzt werden kann. In Kapitel sechs wird zuerst das Basismodell V1 validiert, welches nur um geringe Rundungsfehler abweicht. Des Weiteren werden die Ergebnisse des Model V2 in vier verschiedenen Fällen getestet, in welchen sich die Abweichungen im Toleranzbereich bewegen: Der erste Fall dient der Validierung des entwickelten Modells mit der ihm zugrunde liegenden modernen Berechnungsmethode (Tran & Grace). Der zweite Fall vergleicht Model V2 mit einem anderen Berechnungsansatz (Vakkilainen), bei dem die Diskrepanzen durch die unterschiedlichen Annahmen begründet werden können. Die dritte Validierung bestätigt die Vorhersagekraft des Modells, wenn der Parameter Schwarzlaugen-Trockenmassegehalt variiert wird. Die vierte und letzte Validierung des Referenzmodells V2 war aufgrund des fehlenden Einblicks in den genauen Berechnungsansatz der Studie, die getroffenen Annahmen usw. schwierig. In Kapitel acht wird schlussgefolgert, dass die mit dem entwickelten Modell erzielten Ergebnisse überzeugend und gültig sind. Verbesserungen bei der Modellierung von Schwarzlauge und Schmelze sowie die Einbeziehung eines internalisierten Staubabscheiders könnten das Modell verbessern.

1 Introduction

Efficiency improvements in terms of minimizing losses throughout the whole process are the basis for sustainability enhancement, which are today - more than ever - in the focus of governments, industries, and human population. To achieve these previously mentioned advancements, simulations of processes are not only required, but of the essence to assure a deeper and more profound understanding of the potential. The obtained data acts as a tool in the decision-making process reaching from the pre-design to the realization of small changes in operating parameters of industrial plants such as in pulp and paper mills, where Kraft Recovery Boilers (KRB) are used for recovering chemicals originating from the pulp process and producing steam through the combustion of the byproduct of the paper-making process. Because of its complexity, due to various chemicals and parameters influencing the reactions in the process, a simulation tool for the mentioned KRB unit is of value, primarily to have quick and precise results in the design stage of the Kraft Recovery Boiler, as well as to enhance the efficiency of the entire plant by studying the impacts, as for instance, of back-end heat recovery systems.

This chapter is dedicated to Kraft Recovery Boilers especially in the application in a pulp and paper mill. Firstly, to give the reader a broad overview and understanding of the pulp and paper process, necessary equipment, mass flows entering and leaving the boiler, and state-of-the-art calculation models used and a comparison of these models.

1.1 Kraft Recovery Boilers -Short Overview

Kraft recovery boilers are used in the pulp and paper industry mainly to co-generate power and steam, minimizing the environmental impact of waste material (black liquor) as well of the recovery of pulping chemicals sodium hydroxide (NaOH) and sodium sulfide (Na_2S).

The produced steam is on the one hand used directly within the mill e.g., in the pulp process or on the other hand harnessed to power steam turbines and generators to produce electricity. The electricity can be either used onsite to reach the goal of a self-sustaining mill and a sustainable production cycle or can be further distributed and sold through the grid.

The recovery and reprocessing of the chemicals enable their reuse in the fiber line of the pulping process (Benda, 2020).

Since the pulp and paper industry is one of the largest global industrial sectors in terms of energy use the significance of recovery boilers is becoming clearer. Therefore, it is often referred to as the heart of the pulp mill underlining the necessity to improve its effectiveness, safety, reliability, and especially profitability and sustainability – to reduce the environmental impacts (Saari, et al., 2021). The Kraft Process or Sulfate Process accounts for more than 80 % of the worldwide pulp produced (Tomei, 2007).

Most of (the mill's) energy demand is supplied by the combustion of black liquor, which is a byproduct of the extraction of fibers from wood containing pulping chemicals which need to be regenerated. Even though being an energy-intensive process, requiring high amounts of heat and electricity, the energy originating from the mentioned black liquor combustion surpasses the required input typically making the pulp process a net-energy-producer. This fact can be illustrated by the example of Finland, a widely forested country with a well-established pulp and paper industry. The black liquor combustion in Finland can account for more than half of all renewable fuel sources in heat and power generation in reference to energy content (Saari, et al., 2021).

1.1.1. Kraft Pulping Process

The Kraft Process - also Sulfite Process- refers to the whole procedure from the preparation of wood to the production of paper as well as the generation of steam and electricity through the combustion of black liquor – the most important renewable biofuel, especially in Sweden and Finland. The high strength of kraft pulp, the process' high ability to operate with a wide variety of soft- as well as hardwood, and the high efficiency of chemical recovery – around 97 % - among other advantages explain its dominance over other pulping processes, accounting for over 90% of chemical pulp produced as well as for two-thirds of the world's virgin pulp production. For each ton of pulp produced 10 tons of weak black liquor or approximately 1.5 tons of black liquor dry solids are produced. Annually about 200 million tons of black liquor dry solids are burned globally in recovery boilers, recovering 50 million tons of cooking chemicals while producing 700 million tons of high-pressure steam and therefore being the fifth most important fuel worldwide after coal, oil, natural gas, and gasoline (Tran & Vakkilainen, 2007).

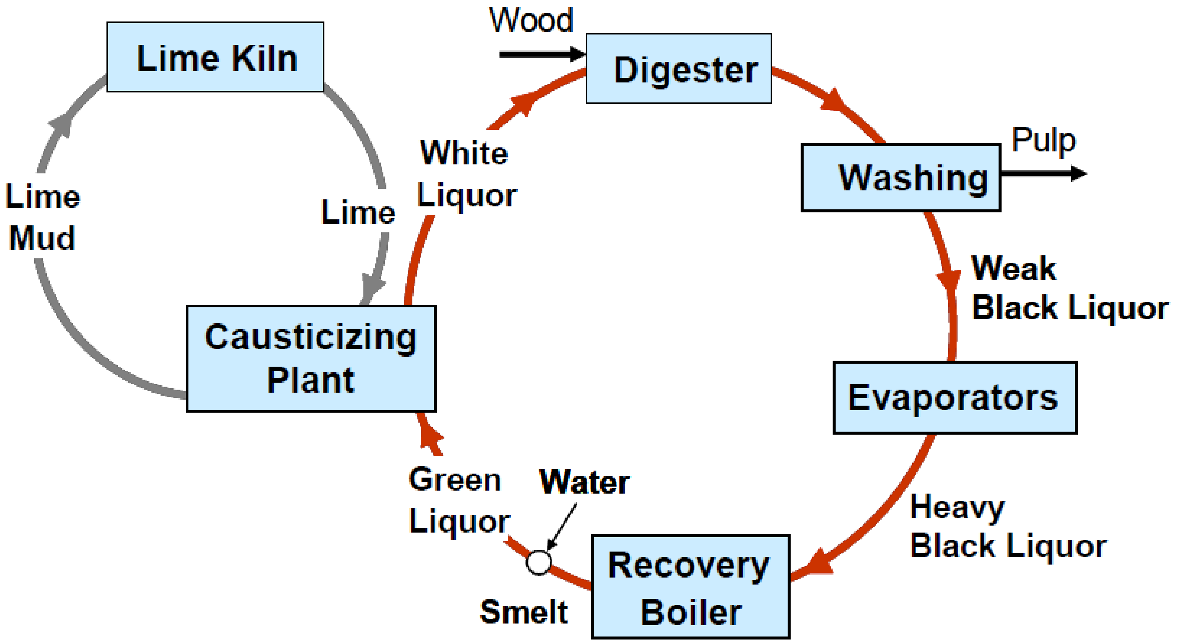


Fig. 1 Kraft Recovery Process (Tran & Vakkilainnen, 2007, p. 1)

Modern paper mills consist of four characteristic main areas, firstly, the wood yard and mechanical preparation area, where the wood is stored, debarked,

and chipped. Secondly, the fiber line, where pulp is produced through the cooking process in the digester, in which the wood chips are treated with white liquor consisting of chemicals sodium hydroxide (NaOH) and sodium sulfide (Na_2S).

Afterwards the pulp is bleached and transported to the third big area consisting of the paper machines, where the wet pulp is dried and manufactured into paper and other end products such as cardboard. The fourth main area is the recovery line, where inorganic chemicals originating from the fiber line of the pulp production are recovered so that they can be reused, while also producing steam and generating electricity through the combustion of the dissolved organics used as a fuel (Benda, 2020).

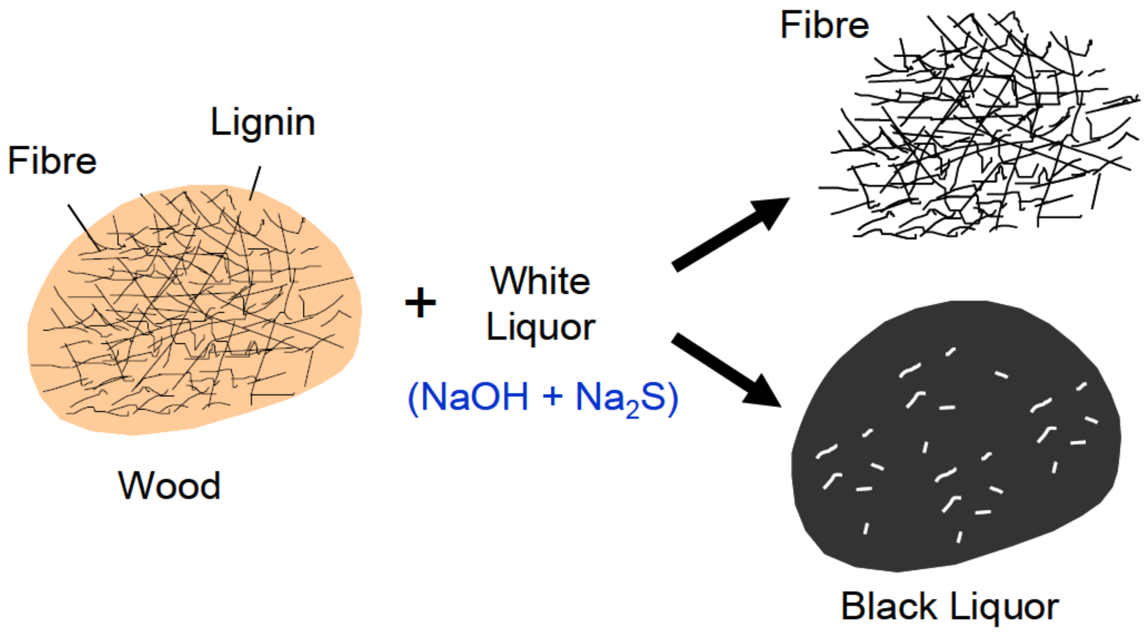


Fig. 2 Kraft Pulping Process (Tran & Vakkilainen, 2007, p. 1)

This is achieved through concentrating weak black liquor from the pulping process in multi-effect evaporators and concentrators at a dry solids rate of 65% or higher. This black liquor is then sprayed into the lower part of the recovery boiler (generating bank), where the combustion is taking place with a deficit of oxygen so that Na_2S is formed. The so-called reduction efficiency measures the sulfide formation and usually lies above 90% (Tran & Vakkilainen, 2007).

1.1.2 Kraft Recovery Boiler – General Design

Because of their size and complexity, recovery boilers are the costliest part of the kraft recovery process as well as one of the most essential criteria for the pulp and paper mills economic viability. This can be explained through recovery boilers' integral role in the mill's overall steam and power balance as well as the fact that the pulp and paper industry is one of the largest global industrial sectors in terms of energy use (Saari, et al., 2021).

The complexity and difficulty in the design process of recovery boilers are due to conflicting requirements such as complete oxidation of the organic matter in black liquor and the complete reduction of sulfur to sulfide, robust and practical design. Further constraints are char bed stability, convective section plugging, as well as chemical constraints such as reduction efficiency, and inorganic melting behavior needed to be taken into consideration in the general design process (Adams & Jones, 2018)

One can distinguish between the fire-side and the waterside in the balance of the recovery boiler. The fire-side includes input streams (combustion) air, black liquor and the exiting streams of flue gas and smelt, whereas the water-side consists of the entering feedwater and sootblowing steam and exiting super-heated steam, as well as blowdown stream.

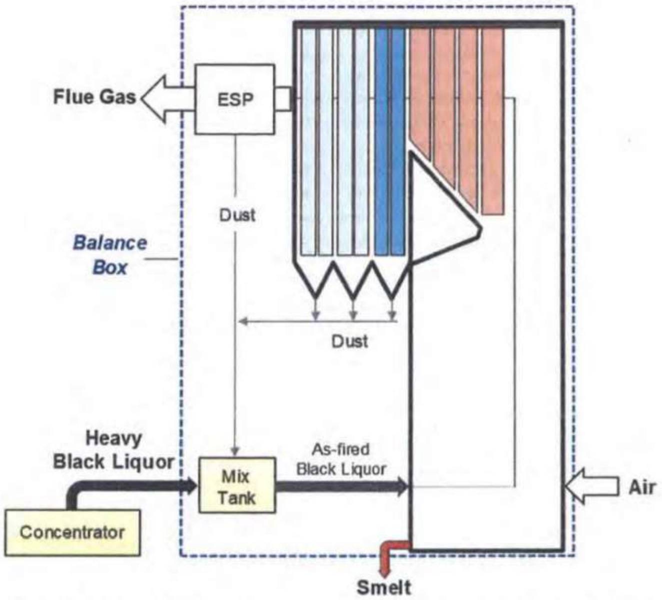


Fig. 3 KRB balance box (Tran & Grace, 2018, p. 328)

Depending on the chosen approach for sootblowing a distinction between external and internal sootblowing can be drawn which needs to be considered for the energy and mass balances as it can be seen in figure 4. Depending on if the steam used for sootblowing originates from inside the recovery boiler or from an external source, it is referred to as internal or external soot blowing respectively.

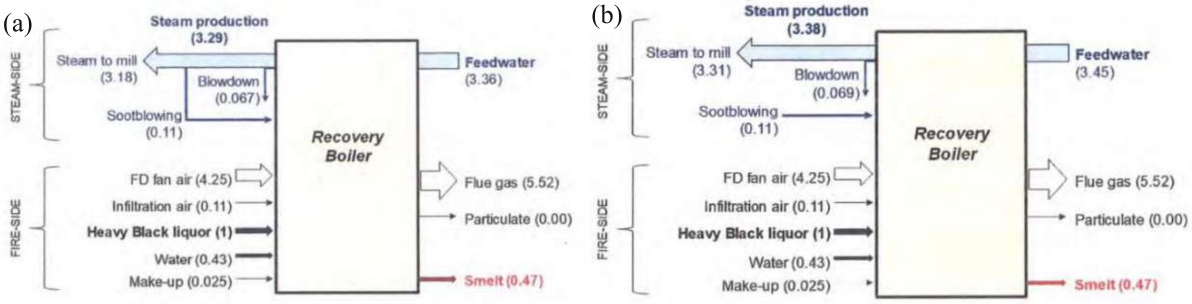


Fig. 4 (a) internal sootblowing steam source (b) external sootblowing steam source (Tran & Grace, 2018, p. 335)

A recovery boiler consists of a water-walled furnace, in which the combustion of black liquor is executed, followed by a series of heat traps to cool the flue gas-, and produce super-heated steam. All recovery boilers are top supported, which means all heat transfer surfaces and the furnace are suspended from the building steel instead of placing the boiler directly on the ground as shown in figure 5.

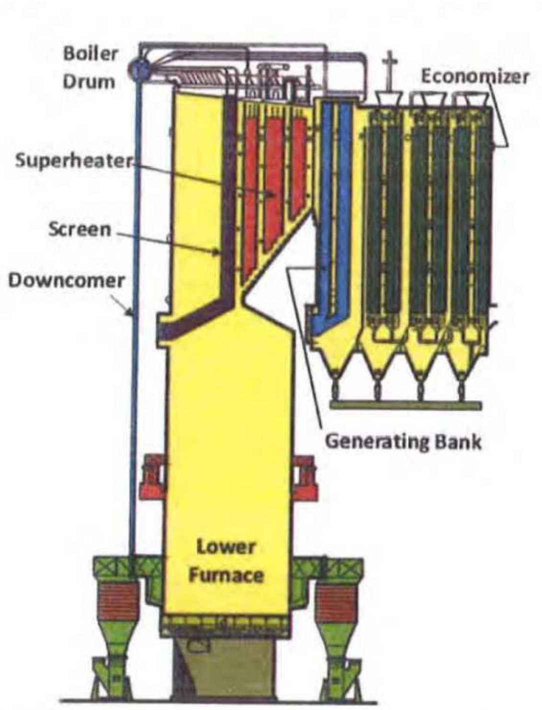


Fig. 5 Schematic diagram of a single-drum recovery boiler (Adams & Jones, 2018, p. 300)

In figure 5 a schematic diagram of a single-drum recovery boiler is illustrated. Originating from the lower furnace through the combustion of black liquor the hot combustion gases flow upwards towards the tube banks that form the screen section, the super-heater, the steam generating bank, and the economizer where the flue gas' heat is successively transferred to the feedwater.

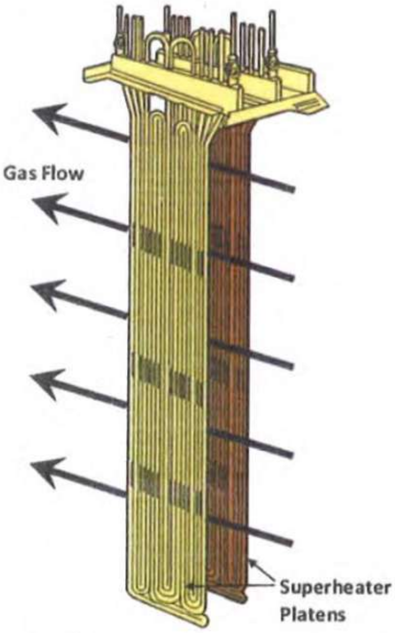
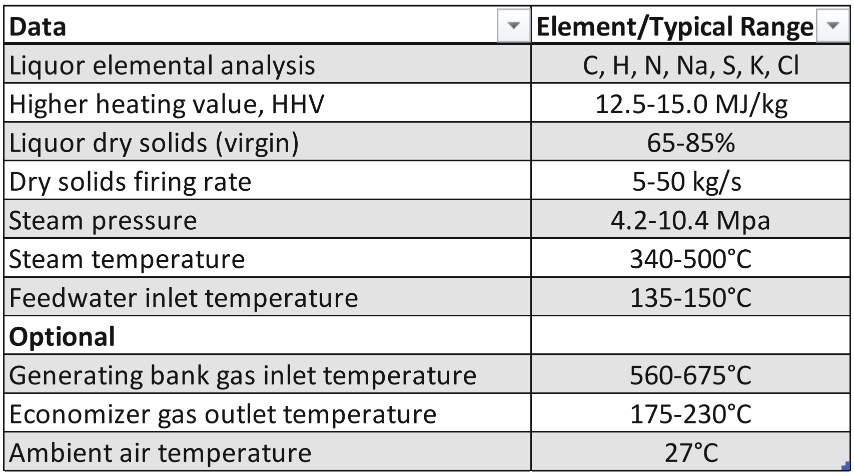


Fig. 6 Superheater platens (Adams & Jones, 2018, p. 303)

The water flows inside the tubes of the economizer to the steam drum, in which it is distributed to the tubes of the steam-generating bank and the tubes forming the walls of the furnace. In the boiler drum, the returned two-phase mixture of water and steam is separated and sent to the superheater where the steam temperature is increased from saturation temperature to the final superheated steam temperature.

The starting point of the general recovery boiler design is receiving the required data from the customer. Typical customer data are shown in the following table 1, which are either derived from current or expected operating conditions or from values characterizing similar operations.



Data	**Element/Typical Range**
Liquor elemental analysis	C, H, N, Na, S, K, Cl
Higher heating value, HHV	12.5-15.0 MJ/kg
Liquor dry solids (virgin)	65-85%
Dry solids firing rate	5-50 kg/s
Steam pressure	4.2-10.4 Mpa
Steam temperature	340-500°C
Feedwater inlet temperature	135-150°C
Optional	
Generating bank gas inlet temperature	560-675°C
Economizer gas outlet temperature	175-230°C
Ambient air temperature	27°C

Table 1 Customer supplied data (Tran & Grace, 2018, p. 301)

Three key factors influencing the determination of black liquor solids flow and heating value are the wood species used, expected pulping conditions, and pulp quality, which establish the heat input to the boiler.

Black liquor inorganic composition and dry solids firing rate are based on mill specific circumstances and operating strategies further resulting in different constraints for the melting and sintering behavior of the generating bank deposits (see figure 7).

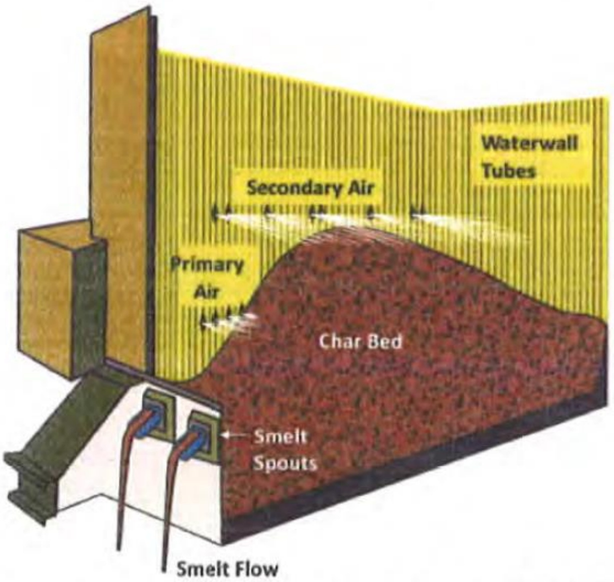


Fig. 7 Schematic diagram of a recovery furnace char bed (Adams & Jones, 2018, p. 302)

To limit plugging rate therefore, the generating bank gas inlet temperature needs to be below the temperature of rapid sintering. Through the elemental analysis of black liquor, the liquor dry solids percentage and experimental data the higher heating value can be estimated. Steam pressure and temperature, as well as feedwater inlet temperature, economizer gas outlet temperature and ambient air temperature are required to guarantee the completeness of the constraints and boundary conditions for the general design of the kraft recovery boiler (Adams & Jones, 2018).

Operational problems and environmental challenges:

The overall kraft recovery process is straightforward in theory, but the operation at high efficiency, safety and sustainably is a complex task. In multi-effect evaporators, problems like liquor side fouling, tube corrosion and foaming originate due to liquor concentration. These problems lead to evaporator boil outs, high steam consumption, and low solids in the product liquor. Furthermore, recovery boilers face operational problems reaching from fouling of heat transfer tubes and plugging of flue gas passages by fireside deposits to tube corrosion and cracking, poor water circulation, smelt-water explosions, unsteady smelt run-off, high dregs in smelt, poor smelt reduction, low steam production, blackouts, and air emissions.

The main environmental challenges of the pulp and paper industry include the control of the air emission of the recovery cycle, the water consumption, the decrease in wastewater discharge to minimize the overall impact on the aquatic ecosystem as well as the high energy consumption (Jiang, et al., 2021).

To solve the mentioned challenges modern research tendencies, focus on technologies such as carbon capture and storage, wastewater recycling, high solids firing (>75%) to lowering total reduced sulfur gas emissions and decrease boiler fouling and plugging, increase of steam temperature and pressure to maximize power generation and therefore efficiency. Additionally, improvements in scrubbers, cyclones, and precipitators enhance the sustainability of pulp and paper mills (Tran & Vakkilainen, 2007).

1.2. Models of Calculation

In this section, two state-of-the-art models of calculation in kraft recovery boilers are explained regarding mass and energy balances to show their similarities and differences to find a suitable approach for the implementation and development of the simulation model in the process simulation tool IPSEpro. In Benda 2020 a more detailed approach for modelling is proposed. It combines the advantages of estimating the setting parameters from CFD-simulations for further use in the advanced thermodynamic and heat engineering tools. To reach the target of developing a model that gives quick and comparable precise solutions of mass flows, compositions, energy balances and steam production, no further CFD-simulations are considered in this work.

1.2.1 Tran & Grace (2018)

The calculation approach is consistent with the developed short standard procedure by TAPPI (Technical Association of the Pulp and Paper Industry) reaching from required input and output information to formulation of energy and material balances and is derived from (Tran & Grace, 2018)

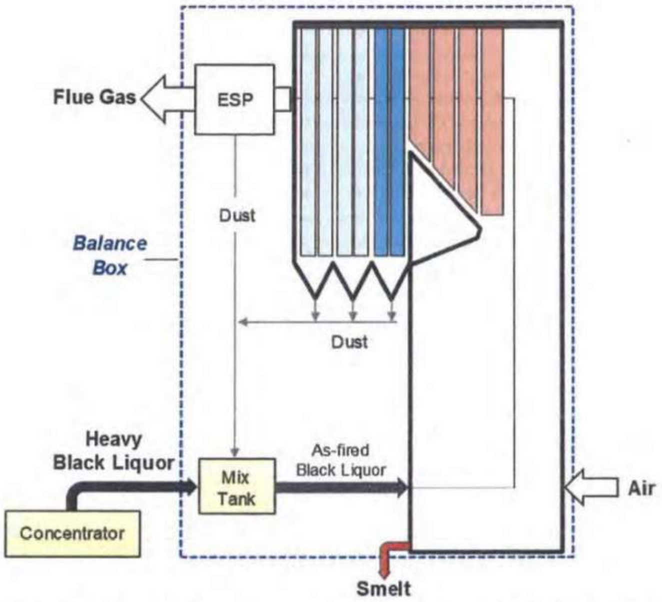


Fig. 8 KRB balance box (Tran & Grace, 2018, p. 328)

Firstly, the calculation boundaries need to be well defined with specified input and output streams. As shown in figure 8, the balance box is drawn in such a way that - on the fire side only air, flue gas, black liquor and smelt pass the balance box, mainly considering the dust not crossing the boundary to facilitate the balances and reduce unnecessary complexity.

The principles of mass and energy conservation are applied to relate the entering and exiting streams.

The Short Form TIP 0461-01 requires data on heavy black liquor such as elemental analysis, higher heating value (HHV), percent solids, as well as some data on smelt composition described through the reduction efficiency, and operating conditions like sootblowing steam consumption, excess air, etc. The complete list is shown in table 2 (Tran & Grace, 2018).

Items	Data
Heavy black liquor	Element analysis (C, H, O, S, Na, K, Cl, and inerts)
	Gross heating value (higher heating value, or HHV)
	Percent solids
	Flow rate
	Temperature
	Heating conditions (direct or indirect)
Smelt composition	Reduction efficiency (based on Na2S and Na2SO4)
	Unburned carbon in smelt
Combustion air and flue gas conditions	O2 concentration in flue gas (% excess O2)
	CO concentration in flue gas
	SO2 concentration in flue gas
	Air temperature to furnace
	Flue gas temperature at economizer exit or at direct contact evaporator (DCE) exit
Dilution flow to DCE (if applicable)	Amount
	Composition
Steam and feedwater conditions	Blowdown steam consumption
	Sootblowing steam consumption (whether this steam is internal or external to the recovery boiler)
Saltcake makeup	Amount (adjustments are needed for other types of makeup chemicals)
Assumed values	Infiltration air
	Heat capacity of heavy black liquor
	Radiation heat loss
	Unaccounted heat losses
	Recycled dust amount and composition (needed only for estimating as-fired black liquor properties)

Table 2 Main input data required for material and energy balance calculations (Adams & Jones, 2018, p. 334)

From the mentioned input parameters, the calculation of required air mass flows, composition and mass flows of flue gas and smelt are determined. Furthermore, amount of steam produced, steam generation efficiency, total heat inputs and losses are calculated.

Material balance:

The recovery boiler's formulation of material and energy balances is based on a unit mass of heavy black liquor dry solids (1 kg BLS) and its elemental composition, requiring a minimum of five elements: carbon (C), hydrogen (H), oxygen (O), sodium (Na) and sulfur (S).

Additionally, it is common to include potassium (K), chlorine (Cl), sometimes nitrogen (N) and inerts.

The impact of the water entering with black liquor also has a major impact on the energy balance, hence it needs to be considered in the mass balance significantly increasing the mass flow of flue gas leaving the boiler.

Neither full nor perfect combustion is taking place in a kraft recovery boiler, so the procedure of determining the air requirements of theoretical air needed for the combustion process is firstly calculated through the elemental analysis by:

1. Determining the amount of oxygen required to completely burn carbon according to the equation: C + O2 → CO2
2. Determining the amount of oxygen required to burn the hydrogen following the reaction: 2 H2 + ½ O2 → H2O
3. Adding (1) and (2) together and substracting it from the oxygen present in the fuel.

Additionally, elements such as sodium (Na), and sulfur (S) entering the boiler with the black liquor stream must be considered, as they react with oxygen in the combustion process, and mainly leaving the boiler as one of the three main constituents of the smelt which are sodium carbonate (Na2CO3), sodium sulfide (Na2S), and sodium sulfite (Na2SO4). The reduction efficiency is crucial since it describes how sulfur splits up into different entities because of decreasing the oxidation numbers of sulfur from +VI to -II as the following equation demonstrates (Benda, 2020, p. 28).

$$Na_2^{+I}\, S^{+VI}\, O_4^{-II} + 2\, C^0 \rightarrow Na_2^{+I}\, S^{-II} + 2\, C^{+IV}\, O_2^{-II}$$

Benda (2020) provides an in-depth explanation of the different reactions taking place, discussing the mentioned equations in a detailled manner.

In literature various different definitions of the reduction rate can be found. In this work it is defined as follows:

$$R = \frac{n_{Na2S}}{n_{Na2S} + n_{Na2SO4}}$$

Sulfur is either leaving the boiler as flue gas, being perfecty oxidized, or in the char bed, with the two possible end states: reduction taking place (reacting to Na2S in the oxidation state -II), and no reduction taking place, forming Na2SO4 (with an oxidation state of +VI), hence requiring different amounts of oxygen, which has to be accounted for in the air demand (Benda, 2020).

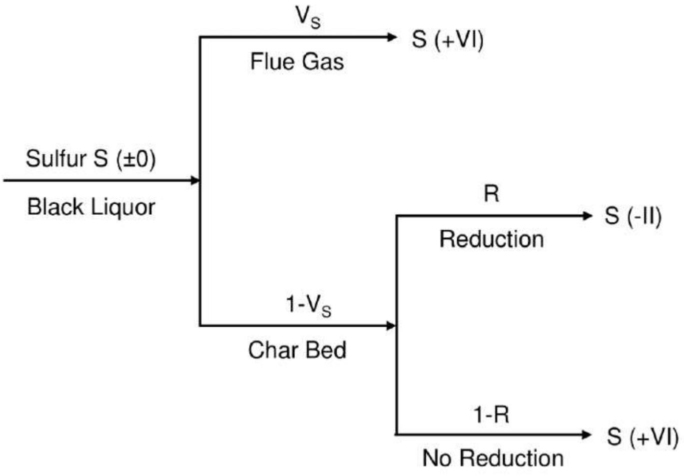


Fig. 9 Distribution structure sulfur (Benda, 2020, p. 29)

Additionally, excess air, being the amount of air entering the boiler beyond the theoretical air, is required to achieve complete combustion, since no perfect combustion is taking place in a real world recovery boiler. However, excess air increases the total gas mass flow, leading to lower gas temperature in the lower furnace, as well as an increased flue gas mass flue resulting in higher heat losses.

Furthermore, infiltration air, the air entering the furnace by other means than through forced draft fans and the furnace air ports, needs to be accounted for. Typically, the infiltration air is calculated as a percentage of the theoretical air input as 3 %.

Alkali, such as sodium (Na) and potassium (K), entering the boiler with black liquor and exiting with the smelt are the fundament for the calculation of the amount of mass flow of the smelt. As it was previously mentioned, the three main constituents of the smelt are sodium carbonate (Na2CO3), sodium sulfide (Na2S), and sodium sulfate (Na2SO4), as well as their analogous potassium salts (K2CO3, K2S, K2SO4). The smelt can contain Cl in the form of NaCl, KCl. Since Cl and K are minor components and CO3 is by far the largest component in the smelt, the assumption that Cl and K exist in the smelt as NaCl, and K2CO3 respectively, simplifies the mass balance calculation. Further simplifications include the neglection of other minor smelt components such as inerts, thiosulfate, unburnt smelt, or other miscansellous sulfur components.

For balancing the smelt, the sulfur reduction efficiency R is essential. It defines the relative amount of sulfide to sulfate, being measured or assumed.

The amount of alkali in the smelt is defined through Na and K of black liquor, whereas the sulfide and sulfate contents are obtained from the sulfur balance, from whose difference the carbonate content is calculated. The following equations describe chemical reactions taking place in this process.

$$4Na^{0} + O_2^{0} \rightarrow Na_2^{+I}O^{-II}$$

$$Na_2O + SO_3 \rightarrow Na_2SO_4$$

$$Na_2O + CO_2 \rightarrow Na_2CO_3$$

Due to the fact that certain components of the flue gas are only known in terms of volume contents, the flue gas' amount of moles has to be calculated first with the following formula giving FGmoles per kg BLS:

$$FG_{moles} = \frac{4.86\frac{C-Cu}{12} + 2.93\frac{H}{2} + \frac{H2O}{18} - 3.86\frac{O}{32} + 0.93\left(\frac{Na}{46} + \frac{K}{78} + \frac{Cl}{71}\right) + \left(6.79 - 7.72\frac{R}{100}\right)\frac{S}{32}}{1 - 4.76\frac{\%O2wvb}{100}}$$

Where:

- C, H, Na, K, Cl, S are inputs determined from the black liquor analysis in mass fractions (kg/kg),
- Cu (kg/kg BLS) is the unburnt carbon content in the smelt,
- H2O is the amount of water entering the boiler with black liquor and sootblowing steam (kg/kg BLS)
- R represents the smelt reduction efficiency (in %),
- %O2wvb stands for the percent excess oxygen on a wet volume basis.

From the moles of, for example H2O (water vapor), CO2, etc. in the flue gas the volume concentrations can be calculated as follows:

$$C_{H2O} = \frac{Moles\ of\ H_2O\ in\ Flue\ Gas}{Moles\ of\ Flue\ Gas} x100\%$$

$$C_{CO2} = \frac{Moles\ of\ CO_2\ in\ Flue\ Gas}{Moles\ of\ Flue\ Gas} x100\%$$

The main constituents of the flue gas are CO2, vapor of H2O, N2, O2. Through the previously obtained results from the smelt and the inputs of the black liquor analysis, the carbon balance computes the amount of CO2 in the flue gas as follows:

$$CO_2 = \frac{44}{12} C_{BL} - Equiv.CO_2\ in\ smlet$$

The hydrogen balance is executed like this:

$$H_2O = \frac{18}{2} H_{BL}$$

Where C_{BL}, and H_{BL} are the C and H content, respectively, in dry black liquor solids.

The oxygen of all the combustion products is determined by summing up the oxygen (O) content in carbonate and sulfate in the smelt as well as in H2O and CO2 in the flue gas.

$$O_{in\ Flue\ Gas} = FG_{moles}\ x\ \frac{O_{in\ BL}}{100x32}$$

Therefore, the following formulas are applied:

$$Theoretical\ Oxygen = O_{in\ Comb.Product} - O_{in\ BL}$$

$$Theoretical\ Air = \frac{Theoretical\ Oxygen}{0.232}$$

$$Total\ Air = Theoretical\ Air\ x\ (1 + \frac{Excess\ Air}{100})$$

$$N_{2\ in\ Flue\ Gas} = 0.768\ x\ Total\ Air$$

$$H_2O_{in\ Flue\ Gas} = H_2O_{from\ comb.} + H_2O_{in\ black\ liquor} + H_2O_{in\ air} + H_2O_{in\ sootblowing\ steam}$$

Since other components in air such as noble gases and CO2 form only a very small part, they can be neglected. High amount of SO2 has a small effect on the sulfur content of the smelt. Furthermore, a high CO content can influence the energy balance on a small scale and cannot be neglected.

Particulates leaving the boiler are normally only present in very small amounts and can be neglected in the majority mass balances. As already illustrated in figure 8 the balance box of the recovery boiler is drawn in such a way that the recollected dust from the dust precipitator is considered an internal stream and therefore does not have to be accounted for in the mass balances.

Energy Balance:

Even though various approaches exist to determine the energy balances of recovery boilers, the heat loss method is chosen due to advantageous characteristics. In the heat loss approach the steam production is calculated as the difference between the heat inputs and heat losses (outputs).

Three advantageous characteristics worth mentioning include the avoidance of inaccuracies originating mass flow rates measuring (which are not required), the relatively low number of needed measurements, and the illustration of where energy leaves the boiler, which can be used to pinpoint potentials for (operational) improvements.

The energy balances, as well as the previously described material balance is formulated based on 1 kg BLS.

Moreover, a reference temperature needs to be set, which most commonly is 25 °C.

Heat inputs:

The biggest fraction of the heat inputs (see figure 10 below) considered in the model is the higher heating value (HHV) of black liquor, normally making up about 93% total heat input, which emphasizes the importance of choosing / calculating it correctly.

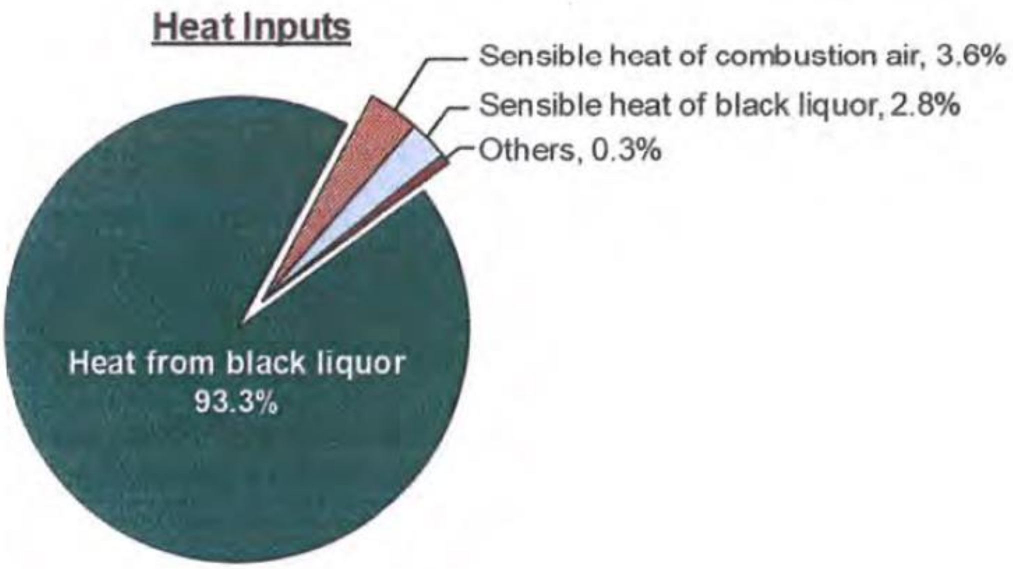


Fig. 10 Heat inputs distribution (Tran & Grace, 2018, p. 342)

In table 3 the different constituents of black liquor and their individual higher heating values are shown.

Component	Higher heating value kJ/kg BLS
Softwood lignin	26900
Hardwood lignin	25110
Carbohydrates	13555
Soap (resins, fatty acids)	37710
Sodium sulfide	12900
Sodium thiosulfate	5790
Sodium carbonate	0
Sodium sulfate	0

Table 3 Higher heating values of black liquor components (Adams & Jones, 2018, p. 337)

Softwood liquors usually have larger higher heating values than the ones from hardwood. The HHVs of black liquor commonly vary between 11600 kJ/kg and 15350 kJ/kg. Various factors influence the HHV, which are, for example, the black liquor's constituents and the chemical charge in the pulp used (Tran & Grace, 2018). Even though having limitations to its precision of estimation, considering the composition of black liquor is indispensable. A common approach is for the calculation of HHV of black liquor is using empirical equations such as:

$$HHV, kJ/kg = 25040\,C + 48920\,H + 177\,S - 2580\,Na + 4230$$

Where C, H, S, and Na are the carbon, hydrogen, sulfur, and sulfur contents in BLS, respectively. At this point, it is worth mentioning that empirical formulas are only estimates and if a more precise energy balance is required, accurate experimental measurements are of the essence.

The other heat input accounted for is the sensible heat of black liquor, calculated as the following:

$$H_{BL} = \frac{C_p(T_{BL} - T_{ref})}{1 - s}$$

Where:

- C_p is black liquor’s specific heat capacity (kJ/kg/C),
- (T_{BL} - T_{ref}) is th the difference between black liquor temperature and its reference temperature (commonly 25°C),
- and s is the black liquor dry solids content

Furthermore, the sensible heat of air entering the boiler is calculated through its two parts: the enthalpy of dry air and the one of moisture in air accounted for as follows:

$$H_{Comb.Air} = (Dry\ Air\ x\ C_{p\ dry\ air} + Moisture\ x\ C_{p\ moisture})(T_{air} - T_{ref})$$

Most commonly, auxiliary fuel is used for startup and shutdown of kraft recovery boilers. If considered in the energy balances, here being mentioned for the sake of completeness, the following equation is applied:

$$H_{Auxiliary\ Fuel} = \frac{Auxiliary\ fuel}{Black\ liquor\ solids} x\ HHV_{Auxiliary\ fuel}$$

Some makeup chemicals' heating values cannot be neglected such as sodium hydrogen sulfide (NaSH) and sodium organic chemicals and therefore need to be considered in the energy balance if they are fired in the recovery boiler as shown:

$$H_{Makeup} = \frac{Makeup}{Black\ liquor\ solids} x\ HHV_{Makeup}$$

Other makeup chemicals such as Na2SO4 and Na2CO3, do not have any heating value and can be neglected.

When using external sootblowing steam, its heat needs to be accounted for as a heat input. If using internal sootblowing steam, the heat used originates from inside the balance box and therefore must not be seen as a heat input.

In table 4 an overview of heat inputs is illustrated underlining the three main heat inputs such as the heating value of black liquor (~93%), the sensible heat of black liquor, and the sensible heat of air.

Input term	**kJ/kg BLS**
Heating value of black liquor	14000
sensible heat of black liquor	421
Sensible heat from black liquor heating	21
Sensible heat of air	544
Heat in feedwater for blowdown steam	26
Total	15012

Table 4 Example heat inputs (Tran & Grace, 2018, p. 339)

Heat Outputs (Losses):

A significant amount of heat is lost through the sensible heat of the (dry) flue gas leaving the boiler is calculated as shown in the following equation:

$$H_{Flue\ Gas} = \frac{Dry\ flue\ gas}{Black\ liquor\ solids} x\ C_{P\ dry\ flue\ gas}(T_{flue\ gas} - T_{ref})$$

Furthermore, the heat lost in the flue gas that comes from the heat of evaporation of water vapor in the (wet) flue gas needs to be applied:

$$H_{Moist.\ in\ FG} = \frac{Water\ vapor\ from\ all\ sources}{Black\ liquor\ solids} x\ C_{P\ FG}(T_{FG} - T_{ref})$$

Where $C_{p\ FG}$ is the specific heat capacity of (wet) flue gas (1.9 kJ/kg/C), $T_{flue\ gas}$ is the exit temperature of the flue gas and T_{ref} is the set reference temperature.

Another heat loss that needs to be accounted for originates from the latent heat of water produced by the combustion of hydrogen (heat of evaporation of water is 2442 kJ/kg). The heat loss is determined as shown:

$$H_{H2O\ from\ H\ comb.} = \frac{Water\ from\ H\ comb.}{Black\ liquor\ solids} x\ 2442$$

As the black liquor does not only consist of solids but also of water that is evaporated (heat of evaporation of water is 2442 kJ/kg) in the combustion process it needs to be accounted for as a heat loss as in the following equation:

$$H_{H2O\ in\ BL} = \frac{100\ - \%\ solids}{\%\ solids} x\ 2442$$

If the source of the water (vapor) for soot blowing is internal, the heat in the moisture of the sootblowing steam must be accounted for since it is generated within the boiler and leaving the balance boundaries.

$$H_{SB\ Steam} = Water\ from\ sootblowing\ x\ [\ 2442\ + C_P\ (T_{FG} - T_{ref})]$$

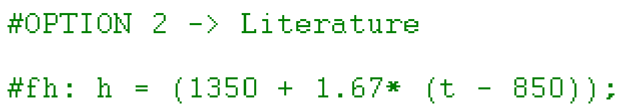
Where 2442 kJ/kg is again the heat of evaporation, C_p is the specific heat capacity of water vapor (4.18 kJ/kg/C), $T_{flue\ gas}$ is the exit temperature of the flue gas and T_{ref} is the set reference temperature.

To determine the heat loss through the sensible heat of the smelt leaving the boiler the smelt mass flow is multiplied with its enthalpy.

In the proposed literature smelt enthalpy’s reference state is 1350 kJ/kg and 850 °C (Tran & Grace, 2018, p. 340).

$$H_{Smelt} = Smelt\ Flow\ Rate\ x\ Smelt\ Enthalpy$$

Following this equation with the referenced enthalpy of 1350 kJ/kg at 850°C and interpolating from that state to smelt temperature t using 1.67 kJ/kg°C as smelt specific heat capacity $C_{p,smelt}$ the following is obtained:



```
#OPTION 2 -> Literature
#fh: h = (1350 + 1.67* (t - 850));
```

Fig. 11 Implementation smelt enthalpy option 2

A further big fraction of the heat output in the recovery boiler is due to the sulfide formation reaction of 12900 kJ/kg in the smelt. This endotherm applies to all Na2S leaving in the smelt exiting the boiler regardless of the sulfide's initial origin (black liquor solids or makeup chemicals). This is reasoned because all heat input terms are based Na2SO4 as the combustion product (Tran & Grace, 2018, p. 340). The heat loss term is calculated through the multiplication of the smelt mass flow, the Na2S content in the smelt, and the previously mentioned heat of sulfide formation reaction (12900 kJ/kg) as shown in the following equation:

$$H_{Sulfide\ formation} = Smelt\ Flow\ Rate\ x\ Na_2S\ content\ in\ smelt\ x\ Heat\ of\ Reaction$$

Incomplete combustion also contributes to heat losses and is accounted for through the unburned carbon leaving the boiler in the smelt (32.800 kJ/kg), and carbon monoxide (CO, 10100 kJ/kg). Another heat loss originates from the heat of formation of SO2 (5450 kJ/kg), leaving the boiler with the flue gas (Tran & Grace, 2018, p. 340).

Further losses like radiation losses and unaccountable losses are calculated as a percentage of the total heat input, normally being around 0.15 % to 0.5% and 1% to 2% respectively, depending on size and age of the operated recovery boiler.

A broad overview of the heat outputs can be gained from figure 12 and table 5 below.

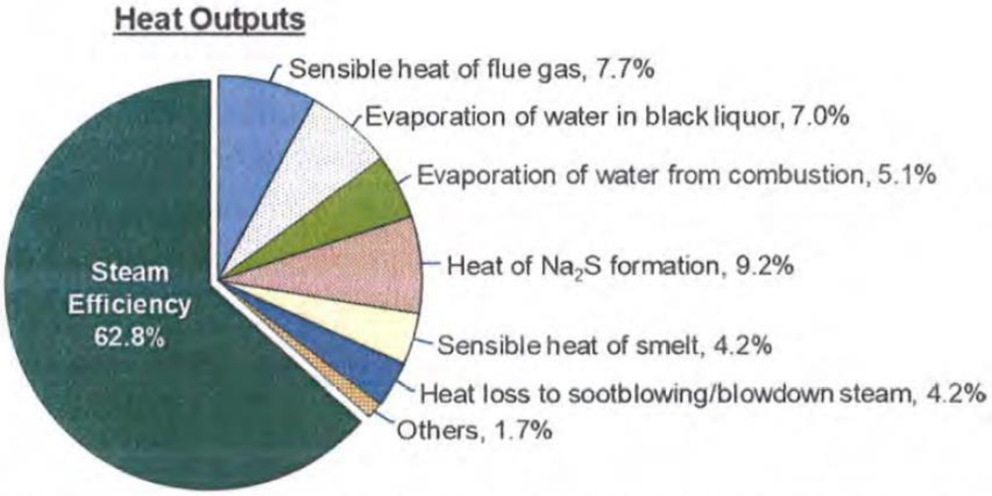


Fig. 12 Heat outputs distribution (Tran & Grace, 2018, p. 342)

Term	**kJ/kg BLS**
Sensible heat of dry flue gas	859
Sensible heat of moisture in flue gas	277
Latent heat of water formed by combustion	747
Latent heat of water in black liquor	1047
Heat out with sooblowing steam	446
Heat content of molten smelt	616
Heat to form sulfide in smelt	1330
Heat of combustion of unburned carbon in smelt	75
Heat loss due to CO and SO2 in flue gas	6
Radiation loss	38
Unaccountables	151
Heat to steam (by difference)	9483

Table 5 Example of heat outputs (Tran & Grace, 2018, p. 342)

1.2.2 Vakkilainen (2005)

The whole following chapter is in reference to Vakkilainen (2005).

There is only one standard that covers mass and energy balances in recovery boilers which is called TAPPI standard (Performance, 1996) (Vakkilainen, 2005).

The balance box in this approach is identical with the boiler house of the recovery boiler as illustrated in figure 13 the same as the system boundary in the previous calculation approach discussed.

The assumptions made are:

- The ratio of sodium sulfide to potassium sulfide equals the ratio of sodium to potassium in smelt
- All chloride reacts to form sodium and potassium chloride
- All sulfur that is not escaping with flue gas reacts either to sulfide or sulfate
- Boron is present only as sodium borate due to the lack of thermodynamical data
- The ESP ash to recycle and the dust to stack have the same analysis

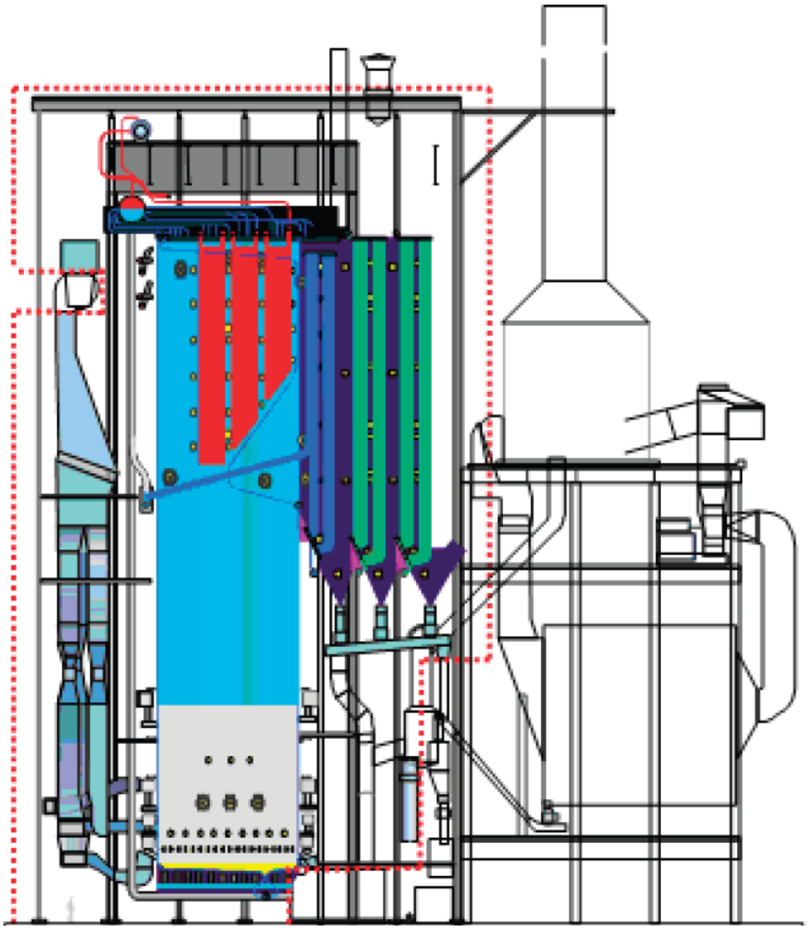


Fig. 13 Modern recovery boiler with balance boundaries shown (Vakkilainen, 2005, p. 2)

To better explain the proposed approach a brief example from Vakkilainen (2005) is presented below.

Input parameters required are shown in table 6 and black liquor elemental analysis in table 7, respectively.

Input parameter	**Value**	**Unit**
Reduction degree	96	%
Black liquor dry solids	85	%
Air ratio	1.1625	1
SO2 emissions	0.052	mg/kgds
HCl emissions	0.01	mg/kgds
Sootblowing steam consumption	150	g/kgds
Dust loss	380	mg/kgds
Recycled ash	100	g/kgds

Table 6 Required input parameters (Vakkilainen, 2005, p. 2)

Element	**Value in %**
C	32.5
H	3.3
N	0.09
S	6.1
Na	20
K	3
Cl	0.25
B	0.5
Inert (NPE)	0.1
Oxygen (by difference)	34.16

Table 7 Black liquor analysis (Vakkilainen, 2005, p. 2)

Mass balance

The elemental analysis of black liquor (table 7) gives the basis for the (elemental) mass balance. The material balances are calculated in moles of the element or compound. For each element in black liquor the amount of substance is calculated as the given mass by the molar mass (see figure 14).

	mass, g/kgds	mol/kgds	end product
Carbon	325	325/12,011 =27,059	CO_2, Na_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_2O, $NaBO_2$, Na_3BO_3
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	NaCl, Na_2S, Na_2SO_4, Na_2CO_3, $NaBO_2$, Na_3BO_3
Boron	5	5/10,811 =0,462	$NaBO_2$, Na_3BO_3
Water	1000* (1/0,85 - 1) =175,5	175,5/18,015 =9,796	H_2O

Fig. 14 Example input flows (Vakkilainen, 2005, p. 3)

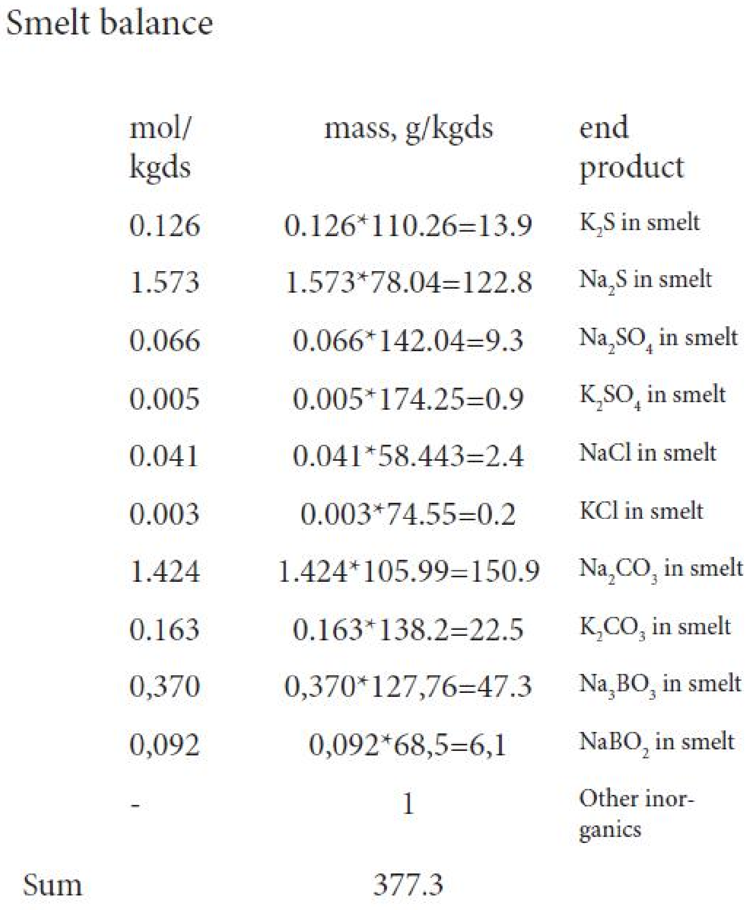
An example of such an elemental balance for sulfur can be seen in figure 15.

	molS/kgds	mass, gS/kgds	end product
	1,903	61,0	available sulfur
	0,333	10,7	in NCG
	-0,000	-0,0	SO_2
	-0,002	-0,1	dust as $-SO_4$
	-0,000	-0,0	dust as -S
	-0,461	-14,8	ash as $-SO_4$
	-0,003	-0,1	ash as -S
Sum	1,770	56,7	S in smelt
	0,04*1,770=0,071	2,3	$-SO_4$ in smelt
	0,96*1,770=1,699	54,5	-S in smelt

Fig. 15 Example sulfur balance (Vakkilainen, 2005, p. 3)

All entering streams accounted for with a positive sign and leaving streams with a negative sign. Finally, all components are summed giving a total of 1.770 molS/kgds in smelt from which, using the reduction degree given as 0.96, the -S content in smelt can be calculated (0.96*1.770 molS/kgds = 1.699 molS/kgds).
This procedure is executed for each of the following elements: sulfur, chlorine, boron, carbon, oxygen and for sodium and potassium together. Nitrogen only reacts to N2 so there is no need for a balance as for the other elements. The calculations for those elements can be found in Vakkilainen (2005).

Afterwards a balance for each stream is done by summing each of its compounds as illustrated for the smelt in figure 16.



Smelt balance

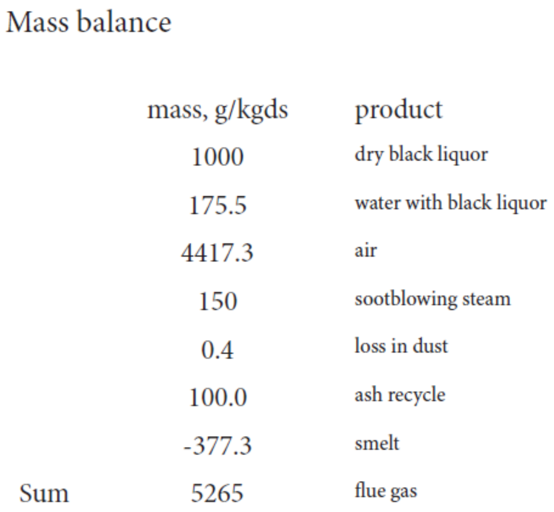
	mol/ kgds	mass, g/kgds	end product
	0.126	0.126*110.26=13.9	K_2S in smelt
	1.573	1.573*78.04=122.8	Na_2S in smelt
	0.066	0.066*142.04=9.3	Na_2SO_4 in smelt
	0.005	0.005*174.25=0.9	K_2SO_4 in smelt
	0.041	0.041*58.443=2.4	NaCl in smelt
	0.003	0.003*74.55=0.2	KCl in smelt
	1.424	1.424*105.99=150.9	Na_2CO_3 in smelt
	0.163	0.163*138.2=22.5	K_2CO_3 in smelt
	0,370	0,370*127,76=47.3	Na_3BO_3 in smelt
	0,092	0,092*68,5=6,1	$NaBO_2$ in smelt
	-	1	Other inorganics
Sum		377.3	

Fig. 16 Example summing of compounds smelt (Vakkilainen, 2005, p. 4)

From the oxygen balance the humid air demand can be calculated as follows:

$$\text{humid air demand} = \frac{\text{Air ratio x mass flow (in } gO_2/kgds\text{)}}{mass\ fraction\ of\ O_2\ in\ air}$$

Finally, the overall mass balance of each mass flow stream entering and leaving the boiler helps to eventually determine the flue gas mass flow as shown below (figure 17).



Mass balance

	mass, g/kgds	product
	1000	dry black liquor
	175.5	water with black liquor
	4417.3	air
	150	sootblowing steam
	0.4	loss in dust
	100.0	ash recycle
	-377.3	smelt
Sum	5265	flue gas

Fig. 17 Example mass balance (Vakkilainen, 2005, p. 5)

Energy Balance

As in the mass balance it is essential to have a well-defined balance box for the energy balances. The previously executed mass balance resulted in calculating all unknown mass flows, which are required for the energy balance. The approach proposed in Vakkilainen (2005) is called a heat loss method, in which firstly, the sum of all input energy flows is calculated. By subtracting the heat losses, the net heat available for steam generation is obtained.

Inputs

Most of the heat input originates from the heat released during black liquor combustion, as can be seen in figure 18. Further amounts of heat inputs come from sensible heat in black liquor, and air preheating. Other inputs are the sensible heat from the unheated air and infiltration air entering the recovery boiler.

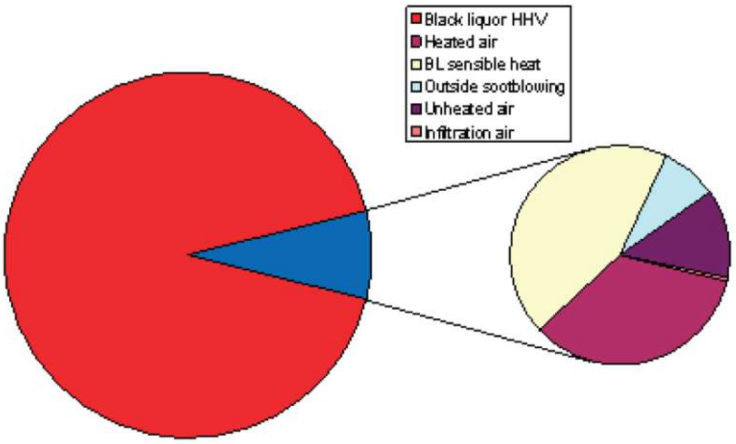
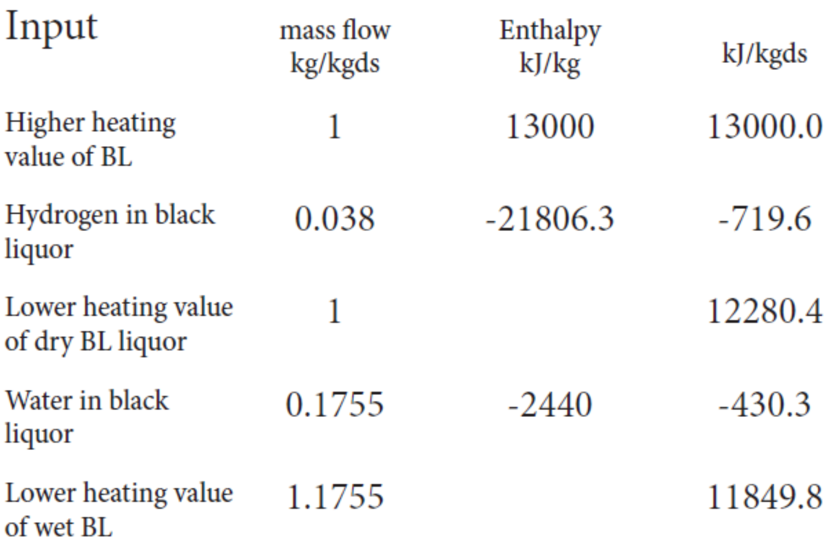


Fig. 18 Example heat inputs to recovery boiler (Vakkilainen, 2005, p. 6)

Instead of the most used HHV (higher heating value) as a heat input, Vakkilainen (2005) uses the lower heating value of wet black liquor. It is by correcting the higher heating value of black liquor with hydrogen and water in fuel loss. The following figure 19 illustrates this procedure.



Input	mass flow kg/kgds	Enthalpy kJ/kg	kJ/kgds
Higher heating value of BL	1	13000	13000.0
Hydrogen in black liquor	0.038	-21806.3	-719.6
Lower heating value of dry BL liquor	1		12280.4
Water in black liquor	0.1755	-2440	-430.3
Lower heating value of wet BL	1.1755		11849.8

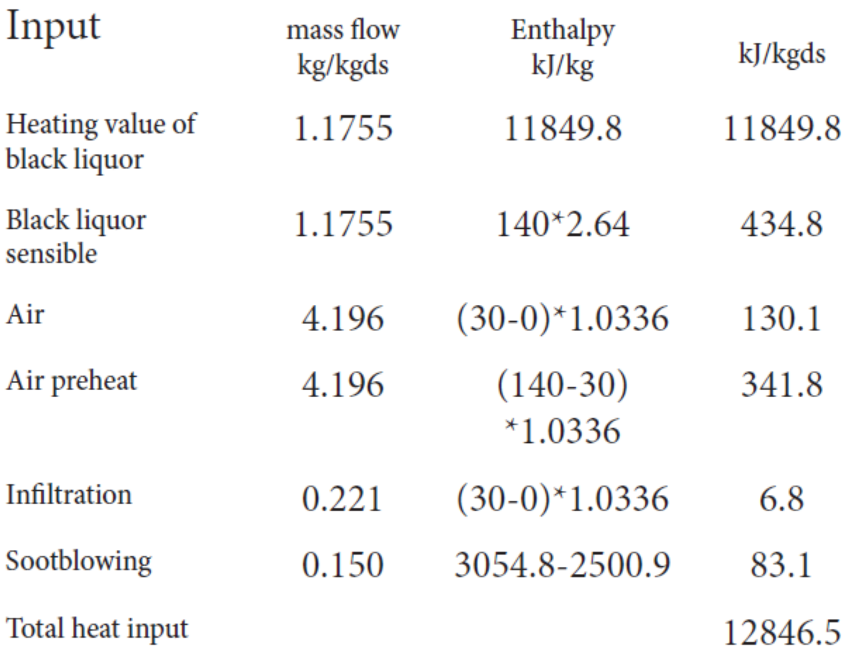
Fig. 19 Correction HHV (Vakkilainen, 2005, p. 7)

The total heat inputs accounted for are the lower heating value of wet black liquor, black liquor sensible heat, heat entering with air above ambient temperature, air preheating, air infiltration, and external sootblowing. Sensible heats are calculated by multiplying the specific heat capacity with the temperature difference and the mass flow as in:

$$\dot{Q}_i = \dot{m}_i \, C_P (T_i - T_{ref})$$

It should be noted that T_{ref} can be the ambient temperature – in the example explained here it is 0°C- or as in the air preheating, T_{ref} is the air temperature at which it enters the preheater (30°C).

The sum of the heat inputs in the example of calculation from Vakkilainen (2005) amounts to 12846.5 kJ/kgds.



Input	mass flow kg/kgds	Enthalpy kJ/kg	kJ/kgds
Heating value of black liquor	1.1755	11849.8	11849.8
Black liquor sensible	1.1755	140*2.64	434.8
Air	4.196	(30-0)*1.0336	130.1
Air preheat	4.196	(140-30) *1.0336	341.8
Infiltration	0.221	(30-0)*1.0336	6.8
Sootblowing	0.150	3054.8-2500.9	83.1
Total heat input			12846.5

Fig. 20 Example heat inputs (Vakkilainen, 2005, p. 7)

Outputs

As can be seen in figure 21, most of the heat loss in recovery boilers is due to sulfide reduction (Na2S, K2S, SO2) and losses of sensible heat leaving the boiler with wet flue gas and smelt. Other losses are autocausticizing (of Na3BO3), radiation & convection losses, as well as due to incomplete combustion (unburned). The difference between the heat input and the heat loss is called net to steam, the heat used to generate steam.

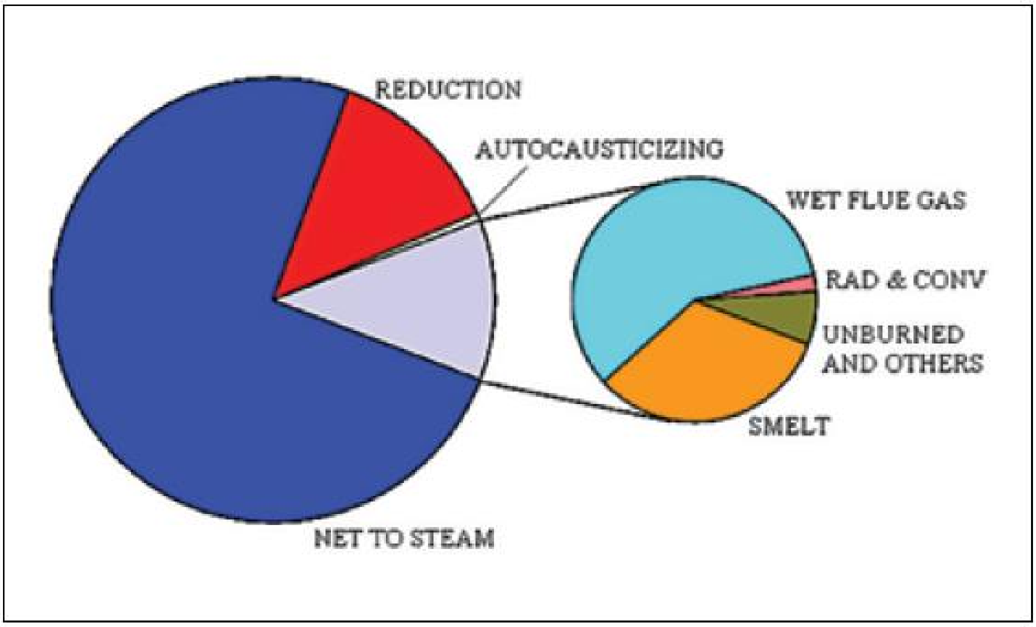
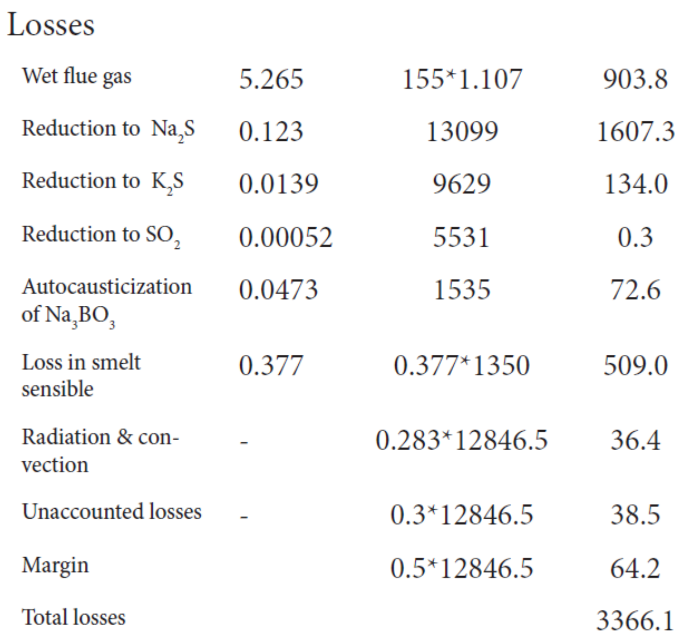


Fig. 21 Example heat outputs of a recovery boiler (Vakkilainen & Ahtila, 2011, p. 61)



Losses

Wet flue gas	5.265	155*1.107	903.8
Reduction to Na_2S	0.123	13099	1607.3
Reduction to K_2S	0.0139	9629	134.0
Reduction to SO_2	0.00052	5531	0.3
Autocausticization of Na_3BO_3	0.0473	1535	72.6
Loss in smelt sensible	0.377	0.377*1350	509.0
Radiation & convection	-	0.283*12846.5	36.4
Unaccounted losses	-	0.3*12846.5	38.5
Margin		0.5*12846.5	64.2
Total losses			3366.1

Fig. 22 Example heat losses (Vakkilainen, 2005, p. 7)

Like the heat inputs, the heat losses are calculated as shown in figure 22. Sensible heat losses follow the equation:

$$\dot{Q}_i = \dot{m}_i \, C_P (T_i - T_{ref})$$

Where T_i is the temperature at which the mass flow $\dot{m}_i$ leaves the boiler and T_{ref}, again, is the ambient or reference temperature (here as 0°C).

Reduction losses are calculated through multiplying the mass fraction flow of the compound to its heat of reaction (see equation below).

$$\dot{Q}_i = \dot{m}_i \; h_{reaction}$$

Radiation, unaccounted convection, and margin losses are calculated as a percentage of the total heat input, here being 0.283 %, 0.3 %, and 0.5 %, respectively.

The net heat available can then be computed as the difference between the heat input and the heat loss:

$$Net\ Heat\ Available = Heat\ Input - Heat\ Loss$$

In the example, the net heat available is 9480.4 kJ/kgds. (12846.5-3366.1= 9480.4)

Next, the steam mass flow can be obtained by balancing the enthalpy flows on the water side of the boiler as follows:

$$\dot{m}_{steam} h_{steam} + \dot{m}_{blowdown}\ h_{sat.water} - (\dot{m}_{steam} + \dot{m}_{blowdown})\, h_{water} + \dot{m}_{int.sootblowing}\ h_{sootblowing} = Net\ Heat\ Available$$

Resulting in a steam mass flow of 3.270 kg/kgds, from which the feedwater mass flow can be calculated using a mass balance as follows:

$$\dot{m}_{steam} + \dot{m}_{blowdown} + \dot{m}_{int.sootbowing} = \dot{m}_{feedwater}$$

It is noted that contrary to external sootblowing steam, only internal sootblowing increases the feedwater mass flow because external sootblowing steam – as the name implies – originates from an external source and not from the feedwater stream to the boiler.

1.2.3 Differences

For the development of a model for the simulation based on the two proposed state-of-the-art calculation models both approaches need to be compared. Both are based on the standards given TAPPI with different alternations. The basis for this comparison is the calculation approaches from the previous two subsections (Tran & Grace, 2018) and (Vakkilainen, 2005).

Mass balances:

One major difference in the calculations of the two examples is that in Vakkilainen (2005) further components and therefore compounds are considered such as the element Boron is used in the autocausticization of Na3BO3, and other compounds like K2S, K2SO4 are considered. This difference originates from the assumption proposed in Tran & Grace (2018) that Cl and K exist in the smelt as NaCl, or K2CO3 respectively. This greatly simplifies the calculation method.

In Tran & Grace (2018) the flue gas mass flow is calculated through firstly computing the entire mole weight of the flue gas per kgBLS. Through given inputs such as SO2, CO in flue gas, percentage of O2 in flue gas, theoretical air, excess air, and combustion air composition, the composition of the flue gas, and flue gas mass flow can be obtained. In the calculation approach proposed in Vakkilainen (2005), the flue gas mass flow is computed by a mass balance of every stream, entering and leaving the boiler (black liquor, sootblowing steam, combustion air, loss in dust, recycled ash, smelt and flue gas) as balanced in figure 17.

Energy balances

In the given two examples of calculation by Tran & Grace (2018) and Vakkilainen (2005) the mayor differences are that in Tran & Grace (2018) the heating value is used as a heat input and the correction of hydrogen and water evaporation is accounted for as a heat loss, whereas in Vakkilainen (2005) the higher heating value of black liquor is already corrected by using the lower heating value of wet black liquor. Furthermore, in the examples given by Vakkilainen (2005) and Tran & Grace (2018) various heat inputs and losses are accounted for, which table 4 and table 5 illustrate. Additionally, to the heating value and sensible heat of black liquor, the sensible heat of air (= air + air preheat) in Vakkilainen (2005) infiltration air is considered as a source of heat input, whereas Tran & Grace (2018) accounts for the heat transferred from the blowdown steam to feedwater. In the calculations in Vakkilainen (2005) sootblowing steam is considered as a heat input because of its external source. In the calculation example in Tran & Grace (2018) it is not accounted for in the energy balance. This is because of the use of an internal sootblowing source.

In terms of different heat losses accounted for in the two different models, through the previously mentioned additional chemicals / compounds in the system (e.g., boron, Na3BO3, and K2S), additional heat losses due to heat of formation / reduction needs to be considered. In figure 22 can be seen that reduction to K2S and Autocausticization of Na3BO3, as well as margin losses are mentioned in Vakkilainen (2005). In Tran & Grace 2018 on the other hand, the non-complete combustion and oxidation of carbon (C in smelt or CO in flue gas) is considered. Heat losses accounted for in Tran & Grace (2018) but not in Vakkilainen (2005) are heat out with sootblowing steam, sensible heat of moisture in flue gas, and latent heat of water in black liquor, which is consider in Vakkilainen (2005) through the correction of the higher heating value (a correction in the input instead of an additional heat loss).

2 IPSEpro

2.1 Overview & general application

IPSEpro (Integrated Process and System Engineering) is a state-of-the-art software tool applied to model, analyze, and optimize processes in energy engineering, chemical engineering, and other areas. IPSEpro is developed by SimTech Simulation Technology, an Austrian company based in Graz. The focus of the software is to model a wide range of different applications such as in power plants, heating and cooling networks, and renewable energy systems – just to mention a few.

The software tool consists of two main modules called PSE (Process Systems Engineering) and MDK (Model Development Kit). PSE is used to build, simulate, and analyze energy plants. Due to its wide range of built-in models for energy plant components like heat-exchangers, turbines, and boilers it is easy to handle, and modifications can be implemented using the MDK toolkit to obtain customized models (SimTech Simulation Technology, n.d.).

IPSEpro's models are used to calculate heat and energy balances, predict design and off-design performance, verification purposes, monitoring, and optimization of processes.

For this thesis IPSEpro was chosen due to the advantageous possibility to easily implement and edit equations in MDK's Model Description Language (MDL), which is an equation orientated language in which a model is defined by writing blocks of equations and is solved in the sequence based on the context of the underlying equations. The translation of the implementation in MDK is compiled into a binary format guaranteeing high performance (SimTech Simulation Technology, 2014).

SimTech's IPSEpro offers eight different model libraries, including Advanced Power Plant Library, Gas Turbine Library, Concentrating Power Library, Refrigeration Process Library, Desalination Process Library, Low Temperature Process Library, Flue Gas Cleaning Library, Pyrolysis and Gasification Library. The basis for the developed Kraft Recovery Boiler Library is the Advanced Power Plant Library (APP). The three main concepts edited in the process of the developing Kraft Recovery Boiler Library (KRB) are Connections, Units and Globals. All these mentioned features allow the user to fully define physical properties, mass, and energy flows, as well as operation conditions and performance characteristics of each component required in the simulation (SimTech Simulation Technology, n.d.). Figure 23 illustrates the hierarchy of the model classes.

2.2 Default Streams / Connections used for KRB Library

Streams / connections in IPSEpro are used to model and specify mass and energy flows between units, as well as define its physical properties like temperature, pressure, and chemical composition.

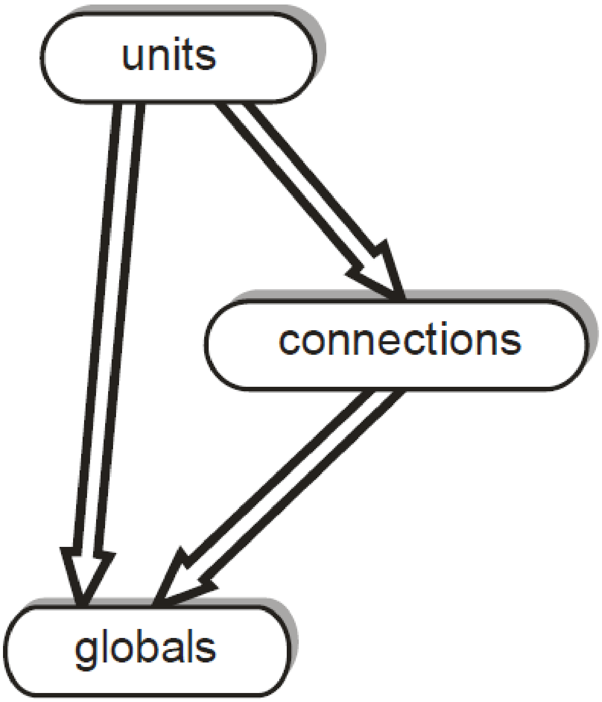


Fig. 23 Hierarch of the model classes (SimTech Simulation Technology, 2014, p. 2.4)

In the developed Kraft Recovery Boiler Library new streams are implemented based on the default connections of SimTech's Advanced Power Plant Library, including fuel Stream (fuel_stream), stream (stream), and water (stream) (originating from Refrigeration Process Library). The required new connections customized in MDK are used for modeling black liquor (fuel), smelt (stream), and mass flows on the water side of the Kraft Recovery Boiler model (water).

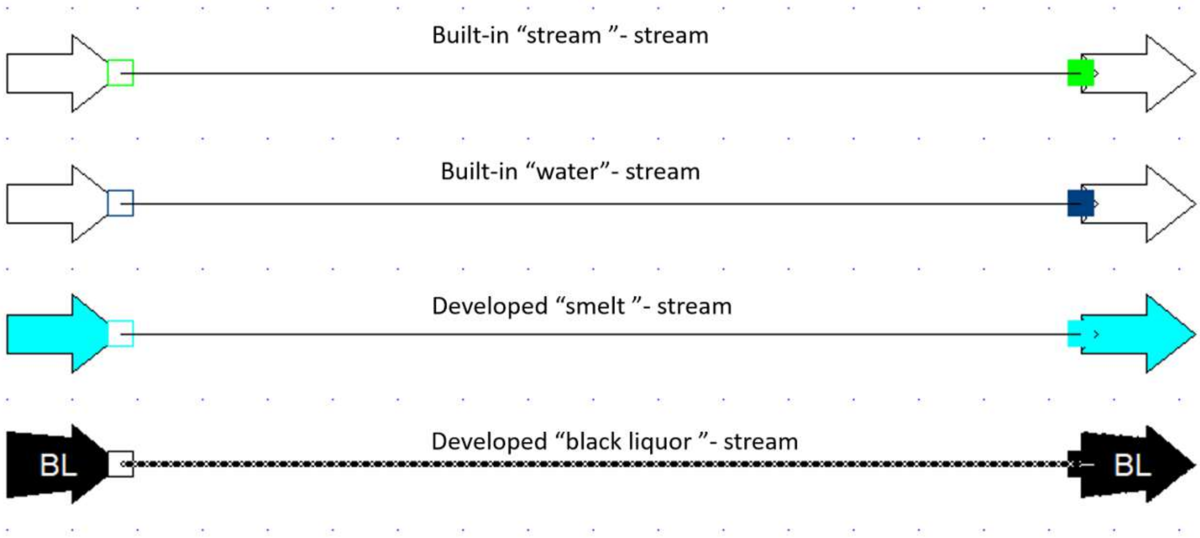


Fig. 24 Overview streams in KRB Lib.

2.3 Default Unit used for KRB Library

In IPSEpro units are the representation of physical parts of plants, such as heat-exchangers, turbines, reactors, and boilers. A set of input and output streams are required to fully define mass and energy flows used for calculations of mass and energy balances. Furthermore, various specifications of operational conditions, efficiencies, etc. are needed.

Starting from the built-in unit solution called combustor (see figure 25) the heart of KRB Library – Kraft Recovery Boiler Unit – is developed due to idea that the fire-side of the recovery boiler follows the same fundamental principle of a combustor. Black liquor enters the recovery boiler as fuel (red terminal), is mixed with combustion air (green terminal on the left), burnt, and leaves the boiler as flue gas (white-green terminal on the right). The in chapter one discussed state-of-the-art models will build the basis for the reactions in the combustor and will be implemented using MDK's Model Descriptive Language.

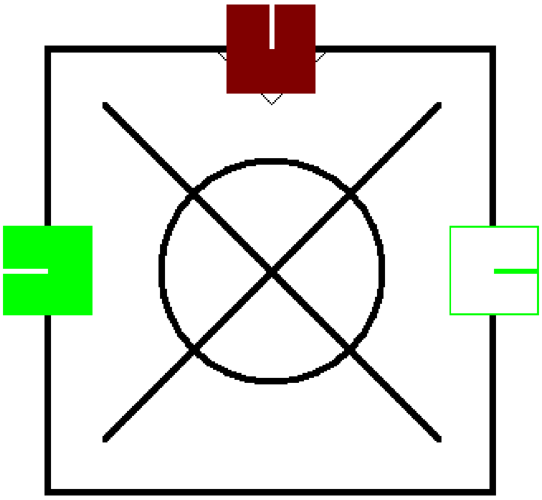


Fig. 25 Default unit used for KRB

2.4 Default globals used for KRB Library

In IPSEpro globals do not directly relate to the network structure. They are used to represent the information which is shared by an undefined number of other objects. A typical example of such a global is a chemical composition because it is very likely to be shared by many streams that use this composition. Even though globals can be referenced by objects of all other model types, globals themselves cannot reference any other objects as illustrated in figure 23 representing the hierarchy of model classes.

In Kraft Recovery Boiler Library customized globals needed for black liquor stream (BL_composition) and smelt stream (KRB_composition) originate from the globals fuel_composition and composition respectively.

3 General Model Development

3.1 Process / idea

The main objective of this thesis is to develop an IPSEpro Library dedicated to recovery boiler simulations in SimTech's Model Development Kit to extend its functionality. The developed Kraft Recovery Boiler Library therefore must include new streams, connections, units and globals as mentioned in chapter 2 based on the proposed state-of-the-art models described in a detailed manner in chapter 1.

The process of the development was the following: after gaining a profound understanding of the calculation approaches and technical information on recovery boilers from literature as well as understanding IPSEpro's functionalities and methods, the general development and implementation of Kraft Recovery Boiler Library was started. One of the main concerns ad priori was establishing a functioning Base Model (V1) of the recovery boiler, which would be further developed and edited by utilizing IPSEpro's strengths.

The scientific approach proposed by Tran & Grace (2018) offers the perfect starting point for the development and implementation of the first model (Base Model V1) (Tran & Grace, 2018). The calculations for mass and energy balances are shown in tabulated format, required inputs, including remarks, units, numerical values, as well as the calculated outputs, formulas to compute them, numerical values, and units. The whole calculation process is shown in the mentioned literature based on an example. Main advantages following that approach is establishing a valid and secure base model which can be tested altering the input values in the tabulated example from literature (in an excel worksheet; see appendix). These results can then be compared with the ones from Base Model V1 with the purpose of executing a detailed validation of the calculation outputs.

The comparison is carried out in chapter 7, which is dedicated to the validations of numerous simulations. Especially the validity of the base model is essential for further models and the outcome of this paper, hence it is handled with the required and necessary focus. Each parameter or variable used / calculated requires an entry implemented in MDK.

After ensuring a valid base model, the next step is to further deepen the model's complexity and make use of IPSEpro's functionalities / applications. For instance, one includes using stream enthalpies calculated in IPSEpro (PSE) with DLLs based on substance data from thermochemical tables, stream composition, and state variables, instead of using a simplified equations as shown below, in which the exact chemical composition of combustion air is not considered:

$$H_{Comb.Air} = (Dry\ Air\ x\ C_{p\ dry\ air} + Moisture\ x\ C_{p\ moisture})(T_{air} - T_{ref})$$

These mentioned enthalpies are, as shown in chapter 1 and are used for the calculations of heat inputs and heat losses. Therefore, in the second model – the Referenced Model V2 – links between IPSEpro's internally calculated enthalpies and the designed recovery boiler unit must be established. In this thesis that is meant by the term "referencing". Other applications of "referencing" are discussed in the following subsection 3.2.

3.2 "Referencing"

In this work the word "referencing" is used for establishing the link between the state-of-the-art calculation approaches described in chapter 1 and the applications of the software tool IPSEpro to design a well-functioning interface. The input values set, for example the black liquor chemical composition, influences various outputs such as the smelt's chemical composition. The results of the smelt's chemical composition are calculated inside the kraft recovery boiler unit. Each of the obtained values (in this case the mass fraction of each chemical compound present in the smelt) needs to further be set in the output stream of smelt illustrated in figure 26 below.

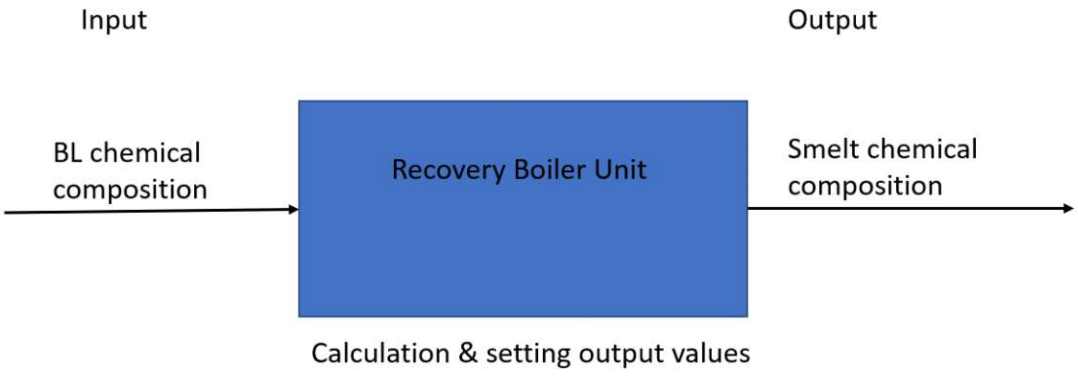
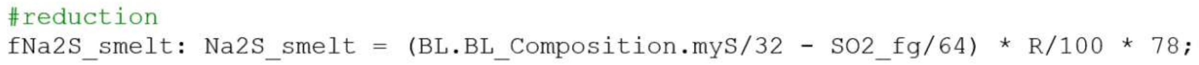


Fig. 26 Modeling KRB

For example, for the calculation of the mass fraction of Na2S in the smelt the following equations are used:



```
#reduction
fNa2S_smelt: Na2S_smelt = (BL.BL_Composition.myS/32 - SO2_fg/64) * R/100 * 78;
```

Fig. 27 Example of implementation of calculation and "referencing"

To obtain the mass fraction of Na2S in smelt, the previously calculated mass must be divided by the total mass of smelt applying:

$$w_{Na2S} = \frac{m_{Na2S}}{m_{smelt}}$$

Where w_{Na2S} is the mass fraction of Na2S in smelt, m_{Na2S} and m_{smelt} are the mass of Na2S and smelt, respectively.

To show the method of how the output is set the following equation is helpful:

$$\mathrm{smelt.KRB\_Composition.m\_Na2S} = w_{Na2S}$$

With “smelt.KRB_Composition.m_Na2S =” the calculated mass fraction w_Na2S is set as an output in the smelt stream.

“smelt.KRB_Composition.m_Na2S” consists of:

- “smelt” which references to the stream defined by the name “smelt”
- “.KRB_Composition” references to the global named “KRB_Composition”
- and “.m_Na2S” references to the mass fraction of Na2S in “KRB_Composition”.

“Referencing” is applied for calculating and setting heat inputs, heat outputs, mass flows and composition among other outputs, which will be further discussed in detail in chapter 5.

3.3 General Overview Model

This subchapter is dedicated to giving the reader a short overview of the different components needed in this work to simulate the kraft recovery boiler.

The newly implemented black liquor and smelt stream, as well as the kraft recovery boiler unit (Base Model V1) of the developed KRB Library are shown in figure 28. Furthermore, Advanced Power Plant Library (APP) & Refrigeration Process Library built in (default) streams are illustrated in figure 28, including air stream, flue gas stream, feedwater stream and steam stream.

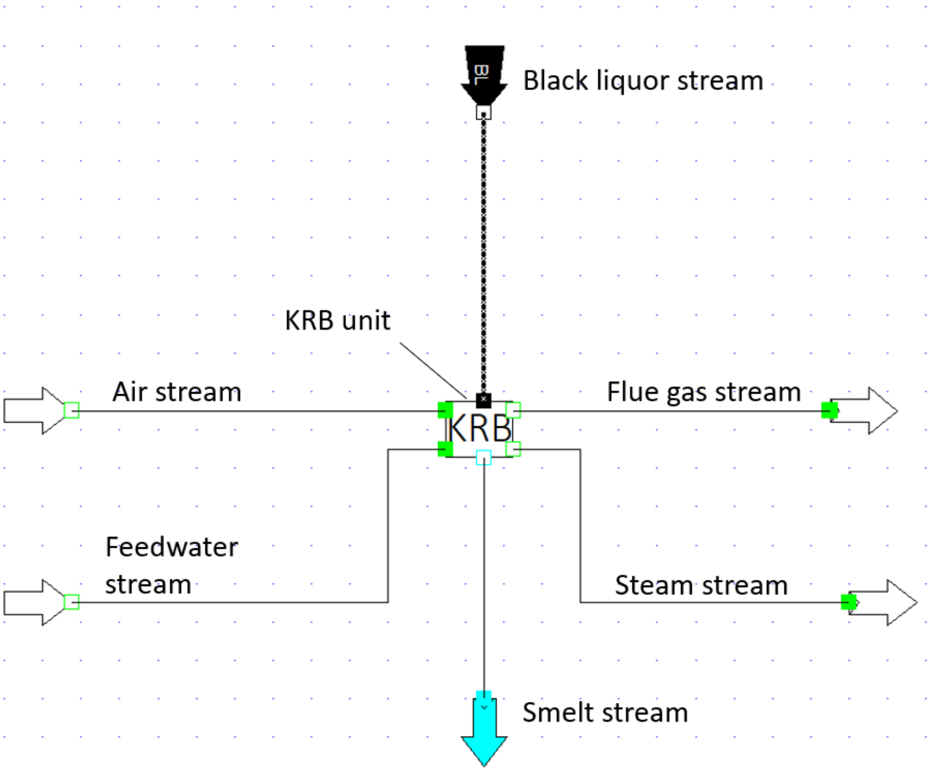


Fig. 28 KRB unit Base Model V1

The arrangement was chosen to best represent the “transformations” of in- and outflowing streams and facilitate the understanding of the underlying process as follows:

- Entering feedwater is converted to steam (on the waterside).
- The majority of (combustion) air reacts during combustion and exits the boiler as flue gas.
- Analogously entering black liquor is combusted and leaves the boiler as smelt.

By this opposite arrangement the logical link between the input and output streams in reference to its transformation inside the KRB unit through the chemical reactions taking place is emphasized.

The evolved KRB unit model (Referenced Model V2) gives the possibility to choose between an internal and external sootblowing option (see figure 29 and 30). Furthermore, additional streams such as blowdown and external sootblowing steam (in the external sootblowing option) are considered. Another difference between the models (V1 / V2) that can be seen in the figures is the usage of different colored terminals, which are dark blue instead of green. This is mainly because of two reasons: firstly, to better group all the waterside streams (feedwater, blowdown steam, and steam), and secondly to give the user the option to either display watersided enthalpies as total enthalpies or referenced to the triple point of water (default setting).

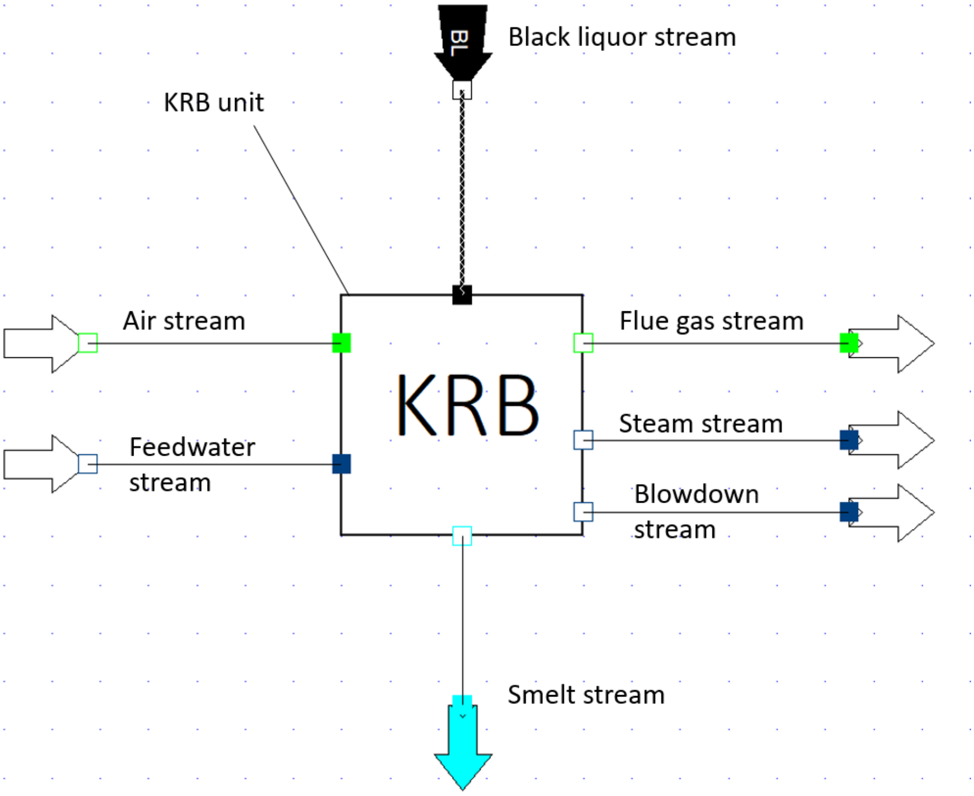


Fig. 29 KRB unit Referenced Model V2 (internal sootblowing)

Now, that the reader has obtained a broad overview and understanding of KRB Library, including its newly developed streams and its different unit models, Base Model V1 and

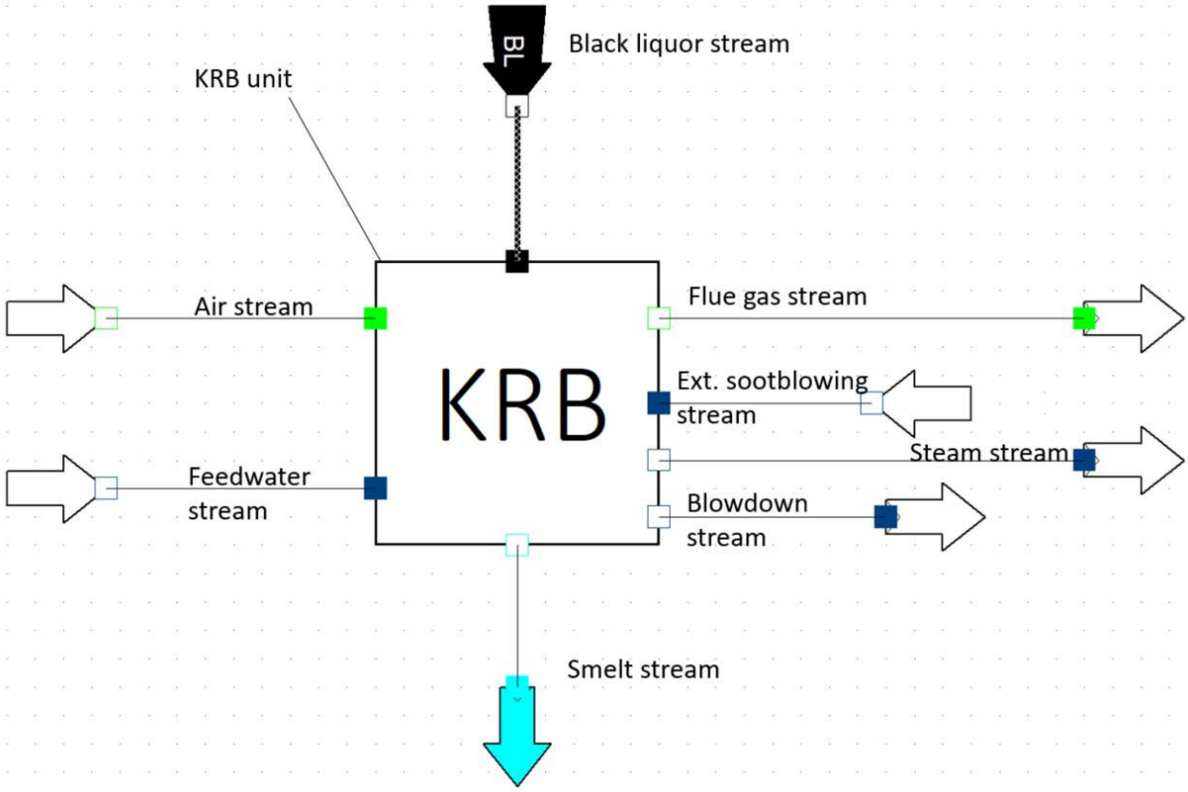


Fig. 30 KRB unit Referenced Model V2 (external sootblowing)

Referenced Model V2, as well as its option to select between internal / external sootblowing, each component will be discussed in a more detailed manner in the following chapters. Chapter 4 is dedicated to streams and its required globals. Chapter 5 gives a description of the different KRB unit models.

4. Model Development - Streams (Connection, Source, Sink)

The following chapter discusses the modification of the default / built-in streams of Advanced Power Plant Library and Refrigeration Process Library, and the development and implementation of streams that are required for the simulation of a kraft recovery boiler using KRB unit (V2). The first built-in stream modified is called "stream", which is used for modeling combustion air entering and flue gas leaving the recovery boiler (Chapter 4.1.1). The second modified stream is named "water" and is utilized for modeling feedwater, steam, external sootblowing steam and blowdown streams (Chapter 4.1.2). The newly developed streams for smelt (Chapter 4.2.1) and black liquor (Chapter 4.2.2.) also required the alteration of source and sink units for linking the connections and fully defining the problem in PSE. Figure 31 illustrates the four different streams "stream", "water", "smelt", and "black liquor" used in KRB Library.

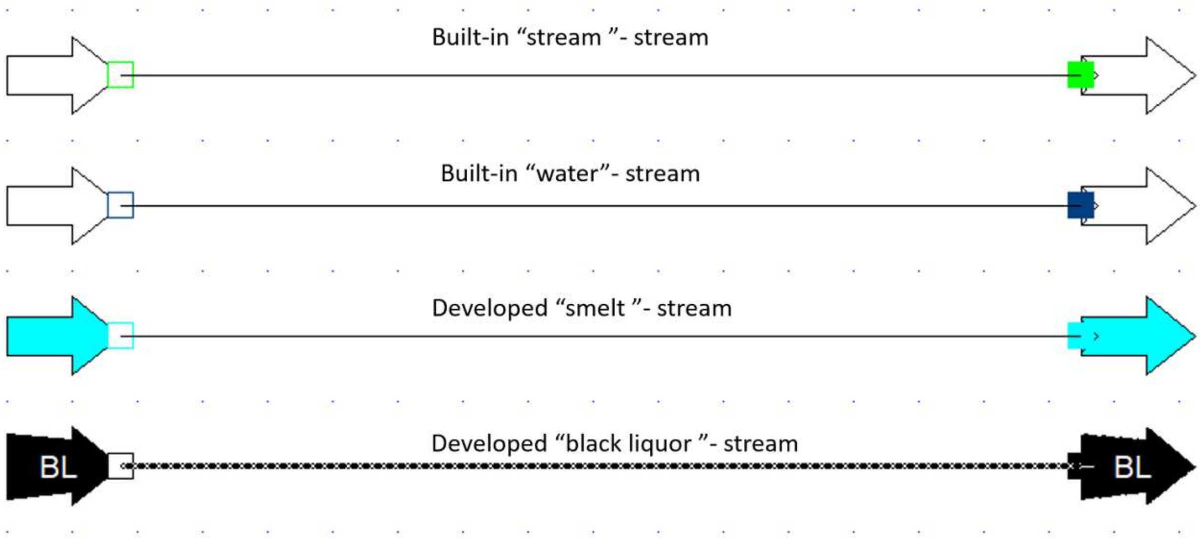


Fig. 31 Overview streams in KRB Lib.

4.1 Changes in built-in streams (connections)

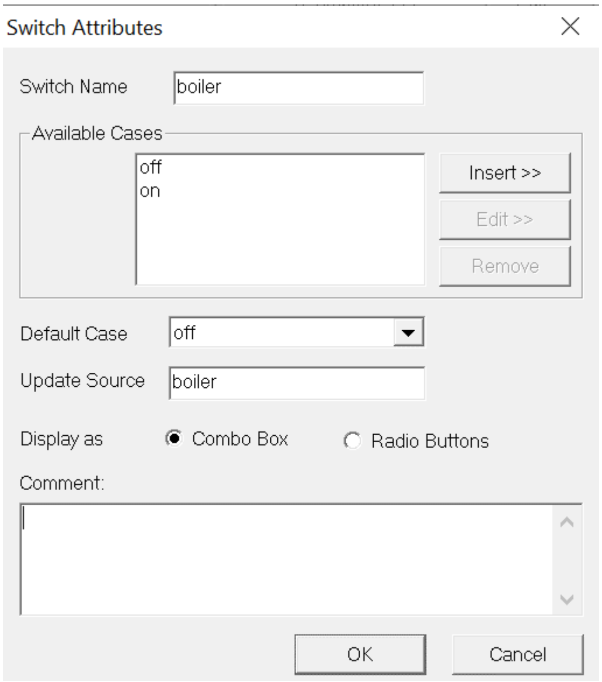
The changes carried out to adapt the built-in streams to the requirements needed for the simulation of the kraft recovery boiler as proposed in this thesis include:

- Shifting enthalpy from the referenced triple point of water to total enthalpy.
- The implementation of a switch that clarifies whether the stream is ("on") or is not ("off") connected to the boiler, which then determines if
- the enthalpy of the defined stream at ambient temperature (h_ambient at t_amb) is calculated.

4.1.1 Air / Flue Gas

Fig. 32 Modified built-in "stream"-stream

As previously mentioned, the changes applied include the implementation of a switch (see figure 33). Streams, which are not connected to the boiler do not require an input for ambient temperature.



Switch Attributes

Switch Name: boiler

Available Cases:
off
on

Default Case: off

Update Source: boiler

Display as: ● Combo Box ○ Radio Buttons

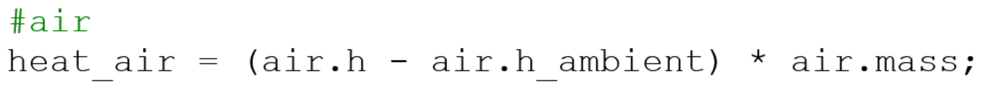
Comment:

Fig. 33 Boiler switch

The idea behind this implementation lies in the calculation approach of the energy balance, which is discussed in chapter 1: reference conditions (or ambient conditions) have a major impact on the calculation of heat inputs and output as the following equation emphasizes:

$$H_{Comb.Air} = (Dry\ Air\ x\ C_{p\ dry\ air} + Moisture\ x\ C_{p\ moisture})(T_{air} - T_{ref})$$

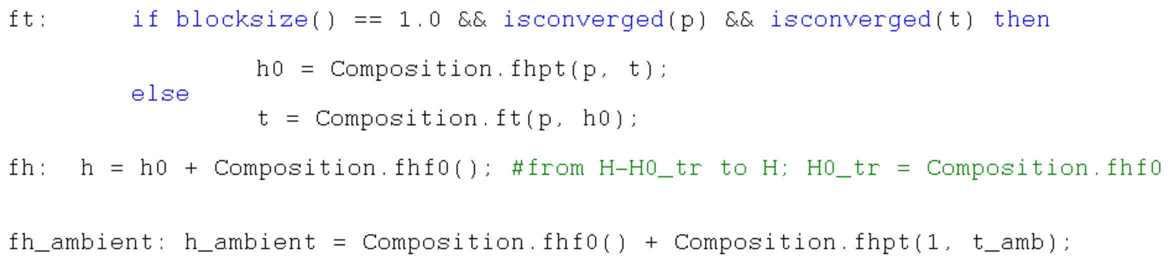
The Base Model V1 follows these equations. For the Referenced Model V2 the calculation of enthalpies is carried out through IPSE’s built-in functions. The function “fhpt(p, t)“ computes the enthalpy of a stream considering its chemical composition and state variables (pressure, temperature). This means that ambient enthalpy can be calculated in the exact same way, taking advantage of the possibility to consider the stream’s chemical composition, adding complexity to the model, and therefore reducing negligence errors. The approach used in the Referenced Model V2 follows exactly this approach when calculating the heat input originating from entering combustion air:



```
#air
heat_air = (air.h - air.h_ambient) * air.mass;
```

Fig. 34 Example implementation “referencing” heat input

Where air.h stands for the enthalpy of the combustion air entering the boiler, and air.h_ambient the enthalpy of combustion air at ambient temperature and (ambient) pressure at 1 bar (see figure 35).



```
ft:     if blocksize() == 1.0 && isconverged(p) && isconverged(t) then
                h0 = Composition.fhpt(p, t);
        else
                t = Composition.ft(p, h0);

fh:  h = h0 + Composition.fhf0(); #from H-H0_tr to H; H0_tr = Composition.fhf0

fh_ambient: h_ambient = Composition.fhf0() + Composition.fhpt(1, t_amb);
```

Fig. 35 Implementation enthalpy shift and ambient / reference enthalpy

The explanation of this code is the following:

The if command asks for convergence of pressure and temperature.

If convergent: the enthalpy is calculated using the given input chemical composition, temperature and pressure when applying the function fhpt(p,t).

If not convergent: the temperature is calculated using the given input chemical composition, enthalpy and pressure when applying the function ft(p,h0).

By adding the heat of formation at 0°C, utilizing the function fhf0(), enthalpy level is shifted to desired total enthalpy.

The same shift is executed for the stream at ambient level (1 bar and ambient / reference temperature).

4.1.2 Feedwater / Steam / External Sootblowing/ Blowdown

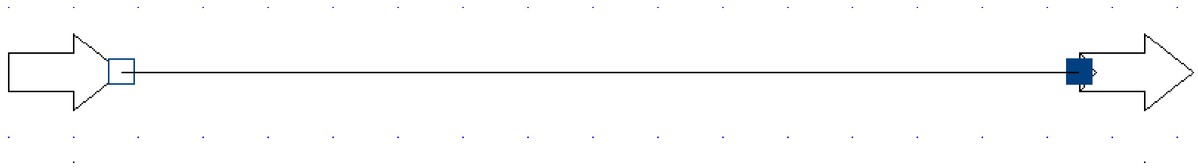


Fig. 36 Modified built-in "water"-stream

Analogously to the changes applied to the built-in stream “stream” in IPSEpro, the built-in stream “water” is modified. Due to the exact similarity in the implemented switch, the optional enthalpy shift, as well as the calculation of ambient enthalpy / reference enthalpy, only the differences are mentioned:

Additionally “water” stream carries the built-in function fx(), which calculates the steam quality (only being valid for pure steam). This gives further possibilities to test if a pure water stream is liquid or vaporous.

The default setting for enthalpies of feedwater, steam, external sootblowing and blowdown are referenced to the triple point of water because it is the most common approach. Furthermore, steam tables are formulated referencing to the triple point of water.

4.2 Newly Developed Streams (Connection, Source, Sink, Composition)

To emphasize the difference between modified built-in streams and the newly developed streams different colors for the source (unit), the sink (unit) and for the terminals are chosen: turquoise for the smelt stream (see chapter 4.2.1) and black for black liquor stream (see chapter 4.2.2).

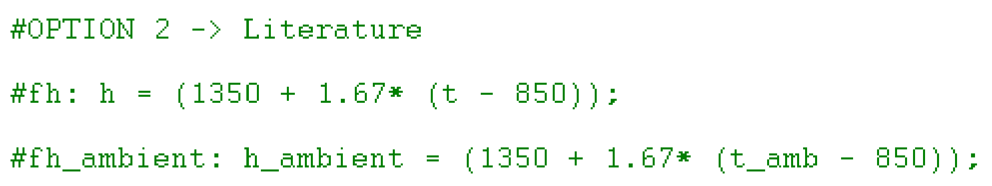
4.2.1 Smelt stream

Fig. 37 Developed "smelt"-stream

Calculations for smelt enthalpy can be executed in two ways:

1. The first is assuming smelt to be an ideal mixture and therefore neglecting enthalpies of mixing, which means neglecting the interactions between the components.

2. The second option is based the proposition that "*the effect of the smelt composition on heat content can be neglected*" (Tran & Grace, 2018, p. 340) and therefore, modelling smelt enthalpy as follows:



```
#OPTION 2 -> Literature
#fh: h = (1350 + 1.67* (t - 850));
#fh_ambient: h_ambient = (1350 + 1.67* (t_amb - 850));
```

Fig. 38 Implementation smelt enthalpy option 2

Where t_ref is the reference temperature (t_ref =850)

and h_smelt_ref is the smelt enthalpy referenced to 850°C (h_smelt_ref = 1350 kJ/kg)

and cp_smelt is the specific heat capacity of smelt (1.67 kJ/kg°C)

Option two already considers that the heat output is the difference between enthalpy of the smelt stream and the enthalpy at reference temperature as shown in figure 38, whereas option one needs to follow analogous principles applied as in chapter 4.1.1. In other words, this means that it is necessary to calculate the smelt enthalpy for the given composition also at reference state.

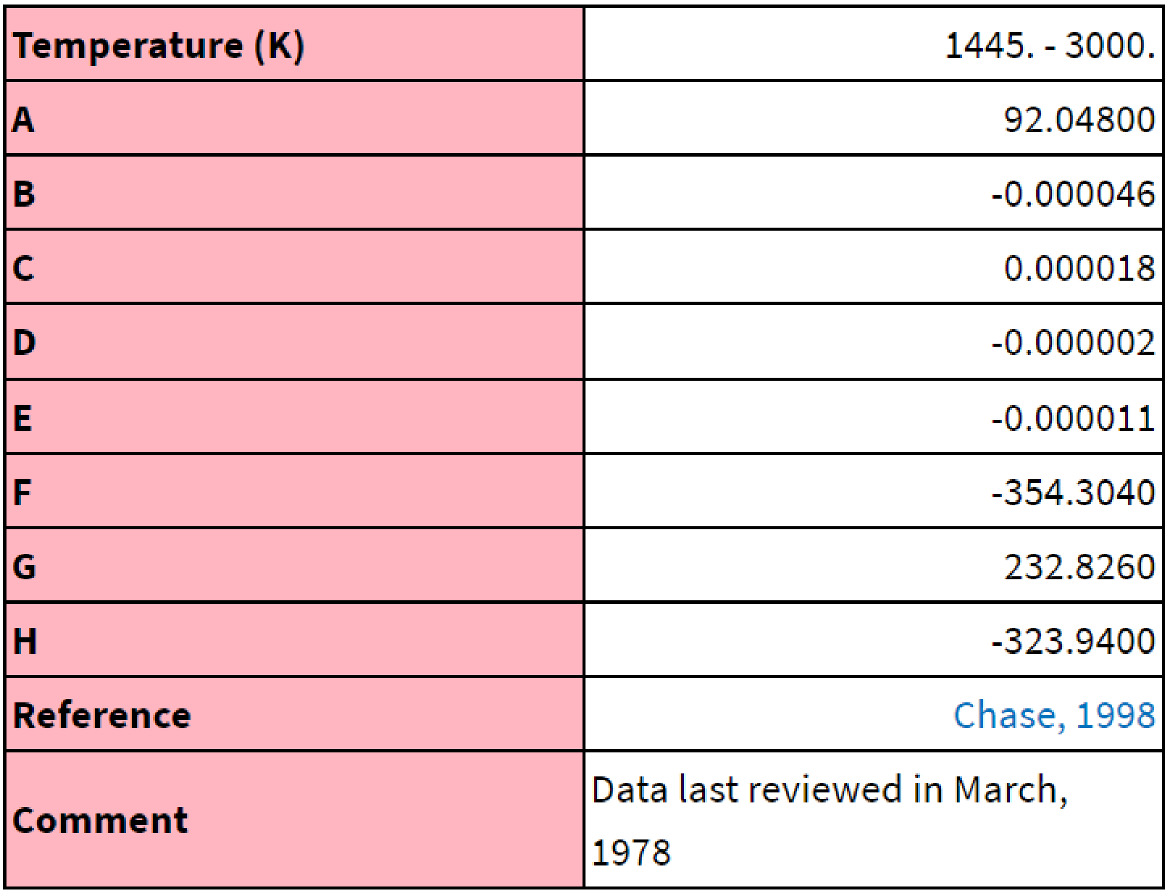
$$h_{smelt} = \sum w_i \, h_i(t_{smelt})$$

$$h_{smelt\ ref.} = \sum w_i \, h_i(t_{ref})$$

The smelt enthalpy is modelled as an ideal mixture. The calculation is executed through the sum of each chemical compound's mass fraction times the compound's enthalpy – at smelt temperature for smelt enthalpy, and at reference temperature for smelt reference enthalpy, respectively.

The different chemical compound's enthalpies are calculated based on polynomials collected on the webpage of the National Institute of Standards and Technology (NIST Chemistry WebBook). An example of one set of coefficients describing such polynomials is shown in tabulated format in figure 39. It is noted that each polynomial is only valid for a specific temperature interval, as in the shown example of Na2S (fig. 39) being [1445 -3000] Kelvin.

$$H^0 - H^0_{298.15} = A\,t + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} - \frac{E}{t} + F - H$$



Temperature (K)	1445. - 3000.
A	92.04800
B	-0.000046
C	0.000018
D	-0.000002
E	-0.000011
F	-354.3040
G	232.8260
H	-323.9400
Reference	Chase, 1998
Comment	Data last reviewed in March, 1978

Fig. 39 Thermochemical data N2S (Chase, 1998)

The implementation of these partially steady functions was carried out for all the following chemical compounds:

- S (Chase, 1998)
- SO3 (Chase, 1998)
- Na2SO4 (Chase, 1998)
- K2CO3 (Chase, 1998)
- Na2S (Chase, 1998)
- KCl (Chase, 1998)
- C (Chase, 1998)
- NaCl (Chase, 1998)
- Na2CO3 (Chase, 1998)
- NaOH (Chase, 1998)
- Na (Chase, 1998)
- K2SO4 (Chase, 1998)
- KOH (Chase, 1998)
- K (Chase, 1998)
- Cl (Chase, 1998)

The implementation of the partially steady function of enthalpies in IPSEpro can be seen in appendix KRB_stream / smelt (connection).

4.2.2 Black Liquor Stream

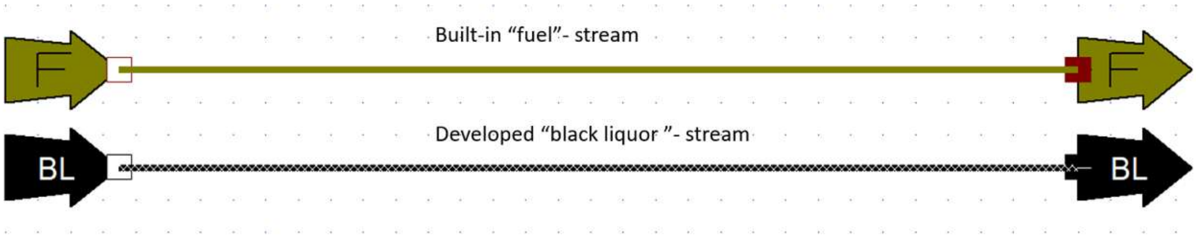
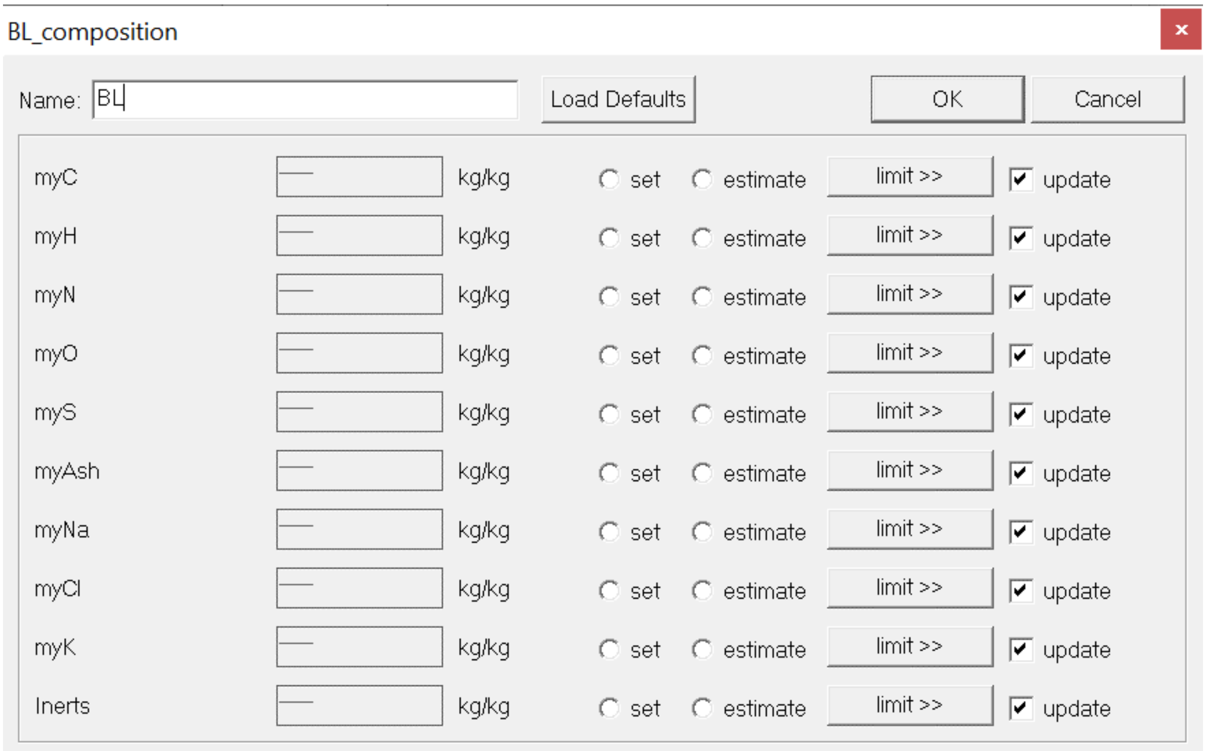


Fig. 40 Built-in "fuel"-stream as a basis for development of "black liquor"-stream

As shown in figure 40, “fuel”-stream’s sink and source units and the ones of “black liquor”-stream are very similar in design. This was carried out for the purpose of -on the one hand illustrating the basis– and on the other hand to emphasize the attributes fuel and black liquor share, making the modifications and implementations easier.

Black liquor stream gives the possibility to set the chemical component data including the following elements: carbon, hydrogen, nitrogen, oxygen, sulfur, sodium, chlorine, and potassium. Furthermore, ash content as well as inerts can be defined. A screenshot from the simulation environment of the implemented black liquor stream's composition in PSE is shown in figure 41. The inputs must be specified as mass fractions, hence the unit kg/kg.



BL_composition

Name: BL

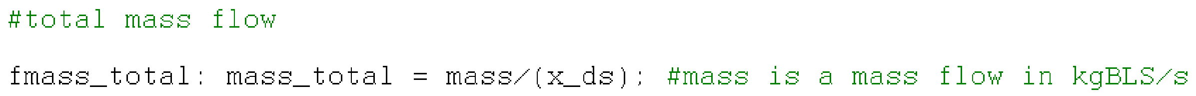
myC	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myH	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myN	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myO	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myS	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myAsh	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myNa	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myCl	—	kg/kg	○ set	○ estimate	limit >>	☑ update
myK	—	kg/kg	○ set	○ estimate	limit >>	☑ update
Inerts	—	kg/kg	○ set	○ estimate	limit >>	☑ update

Fig. 41 Black liquor composition

The requirements proposed by the state-of-the-art calculation models in Tran & Grace (2018), Vakkilainen (2005) and the built-in (default) "fuel"-stream already give a good starting point and framework for the development of the "black liquor"-stream. As pointed out in chapter 1, the most important entry for the calculations of the heat input is the higher heating value of black liquor, which accounts for more than 90% of the heat input to the KRB (Tran & Grace, 2018, p. 337). To reach common ground, later being of the essence in the validation process described in chapter 7, the decision was taken to follow the approach proposed by Vakkilainen (2005) in which the higher heating value is corrected with hydrogen and water as a fuel loss (see chapter 1). This approach per se has no influence on the outcome of the energy balance in comparison to the one stated in Tran & Grace (2018), it only changes how the loss is accounted for. In Vakkilainen (2005) the heat input is corrected by the heat loss caused by hydrogen and water in fuel already before entering the balance box, whereas in Tran & Grace (2018) the loss is accounted for inside the boiler.

Analogously to the calculations shown in figure 19, the implemented equations in the model of black liquor stream follow the exact same approach (see code below, fig 43).

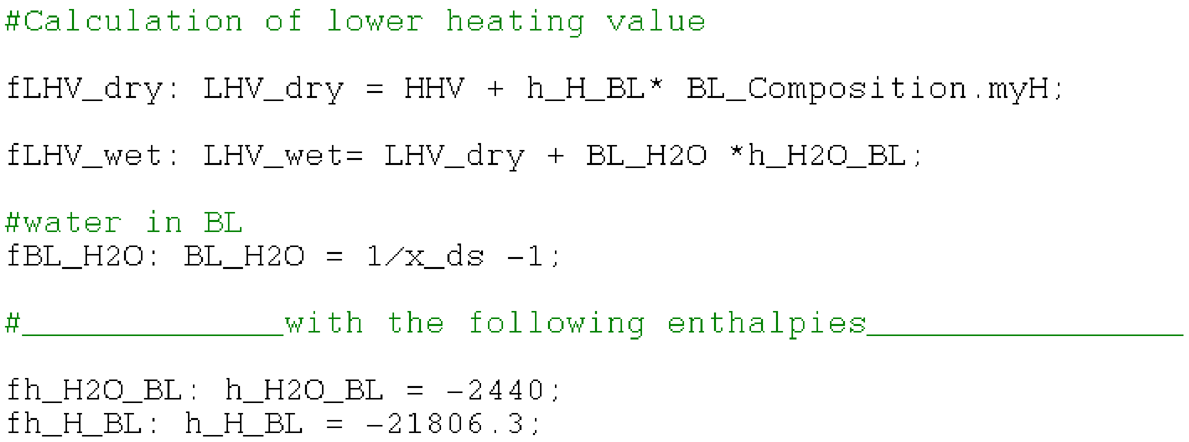
The mentioned higher heating value (HHV), the reduction efficiency (eta_red), and the reference temperature (t_ambient) are mandatory input parameters in black liquor stream as illustrated in figure 44. Furthermore, black liquor's mass flow is defined based on the dry solids mass flow (in kgBLS/s) mainly because calculations are based exactly on this mass flow, later making it easier and more consistent with literature to scale further output streams. Total black liquor mass flow is considered as "mass_total" in kg/s. The calculation follows the equation below scaling black liquor dry solids flow rate with 1/x_ds (dry solid content as mass fraction) as follows:



```
#total mass flow

fmass_total: mass_total = mass/(x_ds); #mass is a mass flow in kgBLS/s
```

Fig. 42 Implementation total mass flow black liquor



```
#Calculation of lower heating value

fLHV_dry: LHV_dry = HHV + h_H_BL* BL_Composition.myH;

fLHV_wet: LHV_wet= LHV_dry + BL_H2O *h_H2O_BL;

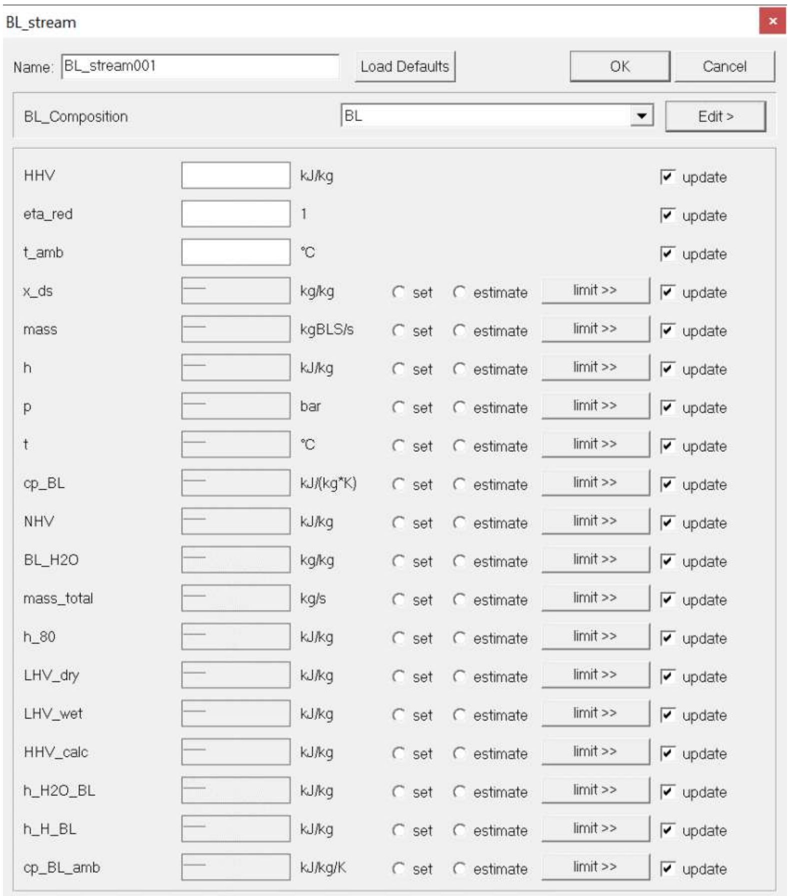
#water in BL
fBL_H2O: BL_H2O = 1/x_ds -1;

#_____________with the following enthalpies________________

fh_H2O_BL: h_H2O_BL = -2440;
fh_H_BL: h_H_BL = -21806.3;
```

Fig. 43 Implementation of lower heating value calculation

Remark: there is no possibility to change the fixed values h_H2O_BL= -2440 and h_H_BL = -21806.3 in PSE since they ought not be changed.



Name: BL_stream001

BL_Composition: BL

HHV	kJ/kg				☑ update
eta_red	1				☑ update
t_amb	°C				☑ update
x_ds	kg/kg	○ set	○ estimate	limit >>	☑ update
mass	kgBLS/s	○ set	○ estimate	limit >>	☑ update
h	kJ/kg	○ set	○ estimate	limit >>	☑ update
p	bar	○ set	○ estimate	limit >>	☑ update
t	°C	○ set	○ estimate	limit >>	☑ update
cp_BL	kJ/(kg*K)	○ set	○ estimate	limit >>	☑ update
NHV	kJ/kg	○ set	○ estimate	limit >>	☑ update
BL_H2O	kg/kg	○ set	○ estimate	limit >>	☑ update
mass_total	kg/s	○ set	○ estimate	limit >>	☑ update
h_80	kJ/kg	○ set	○ estimate	limit >>	☑ update
LHV_dry	kJ/kg	○ set	○ estimate	limit >>	☑ update
LHV_wet	kJ/kg	○ set	○ estimate	limit >>	☑ update
HHV_calc	kJ/kg	○ set	○ estimate	limit >>	☑ update
h_H2O_BL	kJ/kg	○ set	○ estimate	limit >>	☑ update
h_H_BL	kJ/kg	○ set	○ estimate	limit >>	☑ update
cp_BL_amb	kJ/kg/K	○ set	○ estimate	limit >>	☑ update

Fig. 44 Black liquor stream properties

Additionally, to the calculations of the corrected heating value, the specific heat capacity of black liquor and its enthalpy are defined / computed in BL_stream (connection).

The specific heat capacity of black liquor (cp_BL) can be set by choosing between two options.

In option 1 Cp = f(t,x_ds):

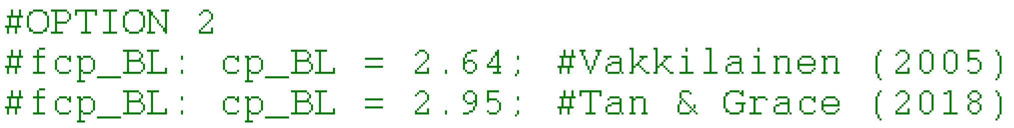
Cp it is modelled as a function of black liquor temperature (t in °C) and dry solid content (x_ds as a fraction) following the formula in (Tikka, 2008):

```
#HEAT CAPACITY of BL
#OPTION 1
fcp_BL: cp_BL = 4.216*(1 - x_ds) + (1.675 - 0.00331*t )* x_ds + (4.87 - 0.02*t)*(1 - x_ds)* x_ds^3;
```

Fig. 45 Implementation of specific heat capacity (option 1)

<u>In option 2 Cp = fixed value:</u>

As shown in chapter 1, Vakkilainen (2005) and Tran & Grace (2018) assume fixed black liquor's specific heat capacities, which is implemented as follows:



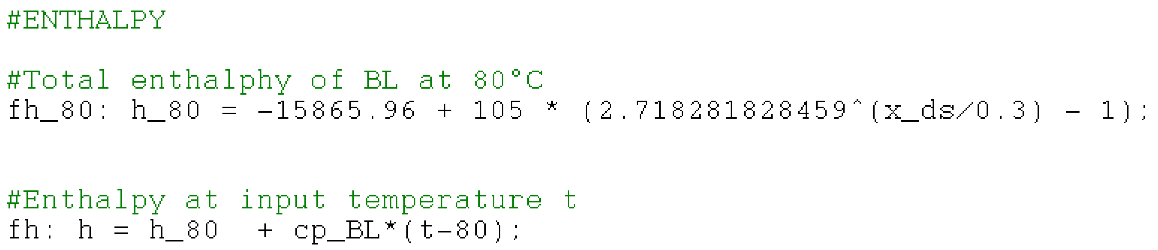
```
#OPTION 2
#fcp_BL: cp_BL = 2.64; #Vakkilainen (2005)
#fcp_BL: cp_BL = 2.95; #Tan & Grace (2018)
```

Fig. 46 Implementation of specific heat capacity (option 2)

Now, that the required specific heat capacities are defined, black liquor's enthalpy can be computed by applying the following equation described by Zaman, et al., (1994):

$$H_{80} = H_{w,80} + b\,[-1 + e^{\frac{x_{ds}}{c}}]$$

Where Hw_80 describes the water enthalpy at 80°C, x_ds is the black liquor dissolved solids fraction, and the constants b and c depend on the type of black liquor used. In the implementation in this work it is assumed that b = 105.0 kJ/kg.K and c = 0.300 (Neto, 2021, p. 60). After obtaining the enthalpy of black liquor at reference temperature 80°C it can be interpolated to black liquor's input temperature as shown below ("Enthalpy at input temperature t"):



```
#ENTHALPY

#Total enthalphy of BL at 80°C
fh_80: h_80 = -15865.96 + 105 * (2.718281828459^(x_ds/0.3) - 1);

#Enthalpy at input temperature t
fh: h = h_80  + cp_BL*(t-80);
```

Fig. 47 Implementation black liquor enthalpy

Remark: Because of the decision to define enthalpies on the fire-side of the boiler as total enthalpies, a shift of (-15865.96 kJ/kg) has to be applied.

5 Model Development - KRB unit

This chapter is dedicated to a detailed description of required input parameters for the KRB unit, the calculation methods, in other words how the outputs are calculated and further set as for example in the chemical composition of the mass flows. A broad overview of the main differences and procedure of development was given in chapter 3. Moreover, at this point it is noted that this chapter's main objective is to provide the reader with an explication of how the model was implemented and developed to help the user understand how to utilize the developed unit correctly and efficiently. A big difficulty in the development process was figuring out where which parameter should be defined (in the stream or in the KRB unit) to create the best functioning, most efficient and intuitive model.

5.1. Base Model V1

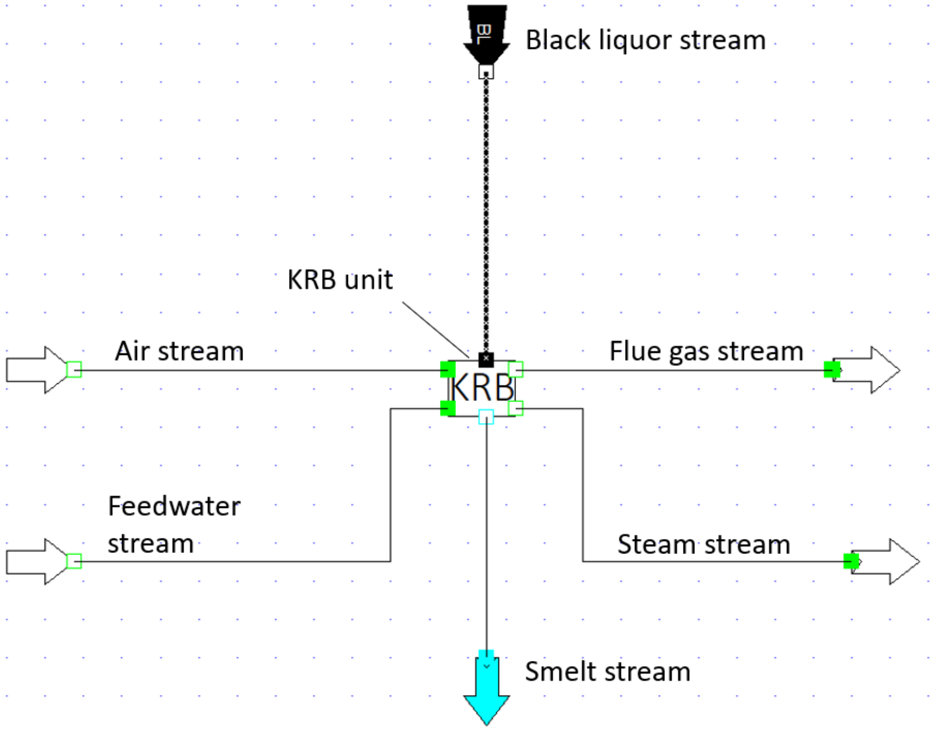


Fig. 48 KRB unit Base Model V1

The Base Model V1 (see figure 48) follows the exact approach applied in the state-of-the-art calculation method proposed in Tran & Grace (2018). As the basis for the development and implementation of the first model of the KRB unit the attached excel sheet (Excel worksheet Validation Base Model V1) was followed which is based on literature (Tran & Grace, 2018, pp. 348-353). The only main difference is the neglection of the inputs from the dust precipitator as shown in table 8, where “recycled ash/ dust”, “makeup saltcake” and precipitator dust removal efficiency” are set to zero. This simplification was proposed to isolate obtained results from additional units such as a dust precipitator and therefore facilitating the validation process and putting the focus of research on the KRB unit. An already developed excel sheet with the described calculation approach had been provided by the Institut für Thermodynamik und Energietechnik as a guideline and starting point for the Base Model V1 (see appendix Excel worksheet Validation Base Model V1).

Required Inputs:

The required inputs for the model are listed in the following tables divided into five different categories including boiler operating data (see table 8), heat capacity data (see table 9), enthalpy data (see table 10), heavy (virgin) black liquor analysis (see table 11), and precipitator dust analysis (is neglected as mentioned and because of this not illustrated) literature (Tran & Grace, 2018, pp. 348-353). For further and more detailed information and an explanation of the required inputs see chapter 1.2.1. Since no additional added value would be gained through an extensive description of where which parameter is defined in model V1, it is skipped. However, the calculation approaches are discussed due to their high significance for understanding how the model was developed as well as its importance for the comprehension of the modifications applied to develop the Referenced Model V2.

Remark: KRB Library does not include Base Model V1

INPUTS	**Value**	**Unit**
Boiler Operating Data		
Heavy (virgin) black liquor mass	1.00	kg BLS
Heavy BL gross heating value (HHV)	14000.00	kJ/kg BLS
Heavy BL solids content	70.00	% ds
Smelt reduction efficiency	92.00	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	2.00	vol. %
CO concentration in wet flue gas	100.00	ppmv
SO2 concentration in wet flue gas	10.00	ppmv
Humidity (H2O) in combustion air	0.013	kg/kg air
Sootblowing steam consumption	0.110	kg/kg BLS
Recycled ash/dust	0.00	% BLS
Makeup salt cake (as Na2SO4)	0.000	kg/kg BLS
Precipitator dust removal efficiency	0.00	%
BL temperature before indirect	125.00	C
BL temperature after indirect heater	130.00	C
Ambient air temperature	25.00	C
FD fan preheat air temperature	150.00	C
Economizer gas exit temperature	210.00	C
Smelt temperature	850.00	C
Feed water to econo. temperature	120.00	C
Sootblowing steam source	Internal	
Sootblowing steam temperature	315.00	C
Superheater outlet steam	482.00	C
Sootblowing steam pressure	17.30	bar
Steam drum pressure	65.50	bar
Superheater outlet steam pressure	62.00	bar
Feedwater blowdown steam (as % feedwater)	2.00	%
Radiation heat loss (as % of heat input)	0.24	%
Unaccounted heat loss (as % of heat input)	1.00	%

Table 8 Inputs KRB unit Base model V1 (Tran & Grace, 2018, p. 348)

INPUTS	**Value**	**Unit**
Heat Capacity Data		
Water	4.18	kJ/kg.C
Dry air	1.01	kJ/kg.C
Dry flue gas	1.02	kJ/kg.C
Water vapor	1.88	kJ/kg.C
Black liquor	2.95	kJ/kg.C
Smelt	1.72	kJ/kg.C

Table 9 Heat capacity data V1 (Tran & Grace, 2018, p. 348)

INPUTS	**Value**	**Unit**
Enthalpy data		
Smelt	1350	kJ/kg
Sulfide formation	12900	kJ/kg
Water evaporation	2442	kJ/kg
Sootblowing steam	3068	kJ/kg
Economizer feed water	508	kJ/kg
Steam drum blowdown water	1244	kJ/kg
Superheater outlet steam	3377	kJ/kg

Table 10 Enthalpy data V1 (Tran & Grace, 2018, p. 348)

An example of heavy black liquor chemical analysis as percentage of black liquor solids is shown in table 11. Oxygen content is computed as the difference between 100% and the sum of the other chemicals in heavy black liquor.

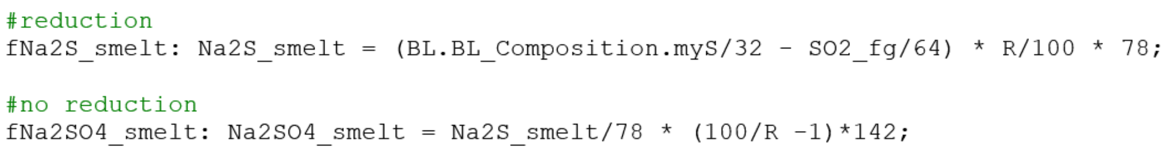
INPUTS	**Value**	**Unit**
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	34.70	% BLS
Hydrogen (H)	3.50	% BLS
Sulfur (S)	4.20	% BLS
Sodium (Na)	19.50	% BLS
Potassium (K)	1.80	% BLS
Chlorine (Cl)	0.50	% BLS
Inerts (N, Si, Mg, Ca, Mn, etc.)	0.20	% BLS
Oxygen (O)	35.60	% BLS

Table 11 Example input black liquor analysis (Tran & Grace, 2018, p. 349)

Calculation method for the smelt composition:

The most important inputs for the calculation of smelt composition and mass fractions are the reduction efficiency (R), and the inputs from heavy black liquor analysis (as shown in table 11). For balancing the smelt the sulfur reduction efficiency R is essential, because it defines the relative amount of sulfide to sulfate, measured or assumed, and therefore has a major impact on the calculation of the smelt composition.

An example for the calculation of the smelt mass flow of Na2S and Na2SO4, the calculation of its mass fraction in smelt and how the output value is set in the smelt stream is shown in figure 49 below.

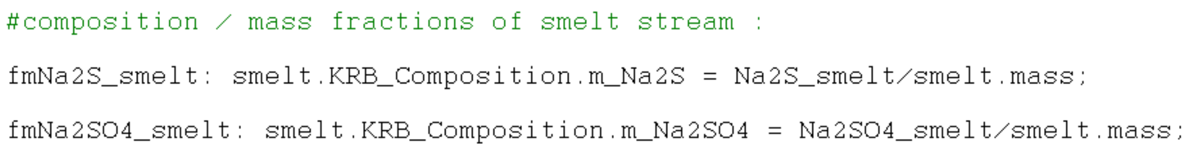


```
#reduction
fNa2S_smelt: Na2S_smelt = (BL.BL_Composition.myS/32 - SO2_fg/64) * R/100 * 78;

#no reduction
fNa2SO4_smelt: Na2SO4_smelt = Na2S_smelt/78 * (100/R -1)*142;
```

Fig. 49 Implementation smelt composition calculation principle (reduction)

Na2S mass flow is calculated by balancing sulfur contents (the one originating form black liquor minus the one leaving with flue gas as SO2), scaling it with the molar weight of Na2S and with the reduction efficiency, which defines the relative amount of Na2S and Na2SO4 in the smelt. The calculation of the mass flow of Na2SO4 is executed with the idea that the remaining sulfur in the smelt reacts to Na2SO4.



```
#composition / mass fractions of smelt stream :

fmNa2S_smelt: smelt.KRB_Composition.m_Na2S = Na2S_smelt/smelt.mass;

fmNa2SO4_smelt: smelt.KRB_Composition.m_Na2SO4 = Na2SO4_smelt/smelt.mass;
```

Fig. 50 Implementation smelt composition calculation principle (mass fractions)

The mass fractions of Na2S and Na2SO4 are calculated and set as shown in the screenshot above (figure 50). The calculation of the mass fraction is done by dividing the mass flow (whose mass fraction is calculated) by the total mass flow:

$$w_i = \frac{\dot{m}_i}{\dot{m}_{total}} = \frac{\dot{m}_i}{\sum \dot{m}_i}$$

For setting the composition of the previously calculated mass fraction of e.g. Na2S the command

$$\mathrm{smelt.KRB\_Composition.m\_Na2S}$$

is used, where

- “smelt” references to the smelt stream
- “.KRB_Composition” references to the smelt stream’s composition which is called “KRB_Composition” where
- “m_Na2S” is a defined variable (Na2S mass fraction) that is set.

The calculation of other components follows the same approach and is implemented based on formulas stated in Tran & Grace (2018).

<u>Calculation method for the flue gas mass flow and composition:</u>

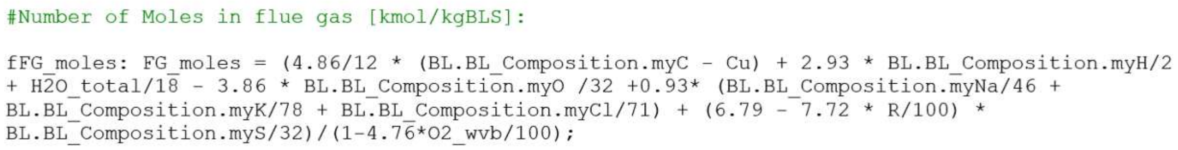
Due to the fact that certain components of the flue gas are only known in terms of volume contents, the flue gas’ amount of moles has to be calculated first with the following formula giving FGmoles per kg BLS:

$$FG_{moles} = \frac{4.86\frac{C-Cu}{12} + 2.93\frac{H}{2} + \frac{H2O}{18} - 3.86\frac{O}{32} + 0.93(\frac{Na}{46} + \frac{K}{78} + \frac{Cl}{71}) + (6.79 - 7.72\frac{R}{100})\frac{S}{32}}{1 - 4.76\frac{\%O2wvb}{100}}$$

Where

- C, H, Na, K, Cl, S are inputs determined from the black liquor analysis as a mass fractions (kg/kg)
- Cu (kg/kg BLS) is the unburnt carbon content in the smelt
- H2O is the amount of water entering the boiler with black liquor and sootblowing steam (kg/kg BLS)
- R represents the smelt reduction efficiency (in %) and
- %O2wvb stands for the percent excess oxygen on a wet volume basis.

In the development of the model in MDK the same formula is implemented as shown in figure 51.

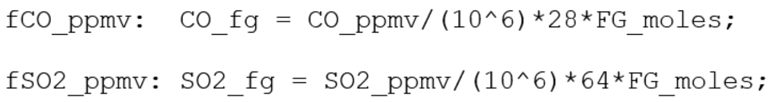


```
#Number of Moles in flue gas [kmol/kgBLS]:

fFG_moles: FG_moles = (4.86/12 * (BL.BL_Composition.myC - Cu) + 2.93 * BL.BL_Composition.myH/2
+ H2O_total/18 - 3.86 * BL.BL_Composition.myO /32 +0.93* (BL.BL_Composition.myNa/46 +
BL.BL_Composition.myK/78 + BL.BL_Composition.myCl/71) + (6.79 - 7.72 * R/100) *
BL.BL_Composition.myS/32)/(1-4.76*O2_wvb/100);
```

Fig. 51 Implementation calculation principles flue gas (FGmoles)

Now that the number of moles in flue gas in kmol/kgBLS is obtained, the calculation of the mass fractions of the different compounds in flue gas is computed applying the approach shown below (figure 52).



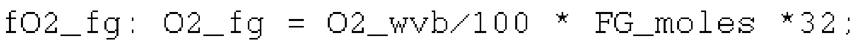
```
fCO_ppmv:  CO_fg = CO_ppmv/(10^6)*28*FG_moles;

fSO2_ppmv: SO2_fg = SO2_ppmv/(10^6)*64*FG_moles;
```

Fig. 52 Implementation calculation principles flue gas (CO, SO2)

In figure 52 mass flows of CO and SO2 in flue gas are determined. “ppmv” stands for parts per million volume. Therefore CO_ppmv and SO2_ppmv need to be divided by one million, multiplied by its molar weight and the number of moles in flue gas.

A similar approach is used for determining O2 mass flow in flue gas. Through the definition of the percentage of excess oxygen on a wet volume basis in flue gas (O2_wvb) as an input parameter (operating data) the calculation of the O2 mass flow is carried out applying the formula shown in figure 53.



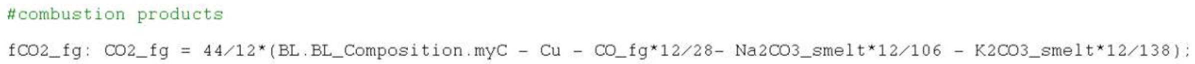
```
fO2_fg: O2_fg = O2_wvb/100 * FG_moles *32;
```

Fig. 53 Implementation calculation principles flue gas (O2)

Through the previously obtained results from the smelt composition and the inputs of the black liquor analysis, the carbon balance computes the amount of CO2 in the flue gas as follows:

$$CO_2 = \frac{44}{12} C_{BL} - Equiv. CO_2 \; in \; smelt$$

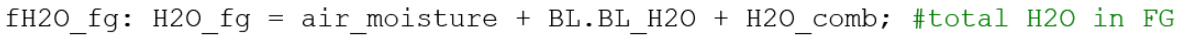
Additionally, to the shown equation above, where C_{BL} is the carbon content in dry black liquor solids, the CO mass flow leaving the boiler must be considered giving the following implementation of the mentioned equation in MDK for the model development:



```
#combustion products
fCO2_fg: CO2_fg = 44/12*(BL.BL_Composition.myC - Cu - CO_fg*12/28- Na2CO3_smelt*12/106 - K2CO3_smelt*12/138);
```

Fig. 54 Implementation calculation principles flue gas (CO2)

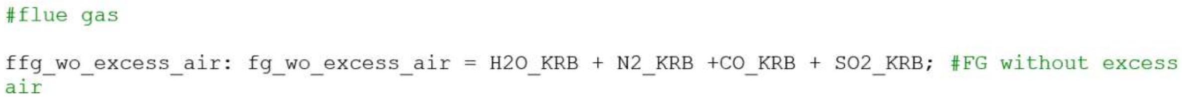
The H2O content in flue gas is calculated through the sum of the different water mass flows on the fire-side of the recovery boiler (fig. 55), which includes the moisture in (combustion) air (= air_moisture), the water in black liquor (= BL.BL_H2O), and the water from combustion products (of H in black liquor).



```
fH2O_fg: H2O_fg = air_moisture + BL.BL_H2O + H2O_comb; #total H2O in FG
```

Fig. 55 Implementation calculation principles flue gas (H2O)

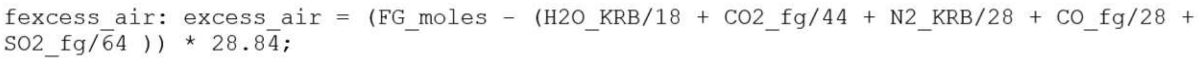
After each chemical compound’s mass flow in flue gas is calculated, the flue gas’ total mass flow without (yet) considering the excess air can be computed as the sum of each mass flow, with the one of H2O (= H2O_KRB), of N2 (= N2_KRB), of CO (= CO_KRB), and the one of SO2 (= SO2_KRB) (see fig. 56).



```
#flue gas
ffg_wo_excess_air: fg_wo_excess_air = H2O_KRB + N2_KRB +CO_KRB + SO2_KRB; #FG without excess
air
```

Fig. 56 Implementation calculation principles flue gas (fg w/o excess air)

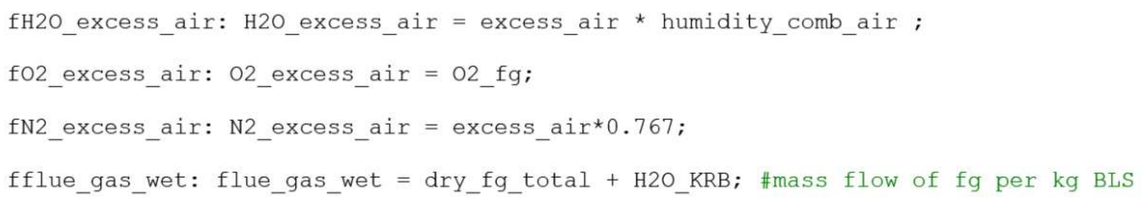
Remark: H2O_KRB = H2O_fg + H2O from sootblowing;
N2_fg = N2_KRB;
CO_fg = CO_KRB;
SO2_fg = SO2_KRB;
Setting of these variables was executed to follow the state-of-the-art calculation procedure (Tran & Grace, 2018).
Excess air is the amount of air entering the boiler beyond the theoretical air, which is required to achieve complete combustion. It increases the total gas mass flow: the one of combustion air entering the boiler, and the mass flow of flue gas leaving the boiler. Its mass flow is calculated by firstly substacting the moles of H2O, CO2, N2, CO, and SO2 (already having being accounted for) of the total amount of moles in flue gas and then secondly multiplying it (the difference) with the molar weight of air (= 28.84 kmol/kg) (see fig. 57) (Tran & Grace, 2018, p. 350).



```
fexcess_air: excess_air = (FG_moles - (H2O_KRB/18 + CO2_fg/44 + N2_KRB/28 + CO_fg/28 +
SO2_fg/64 )) * 28.84;
```

Fig. 57 Implementation calculation principles flue gas (excess air)

Now the different components of excess air (H2O, O2, N2), and the wet flue gas mass flow can be calculated as figure 58 shows:



```
fH2O_excess_air: H2O_excess_air = excess_air * humidity_comb_air ;

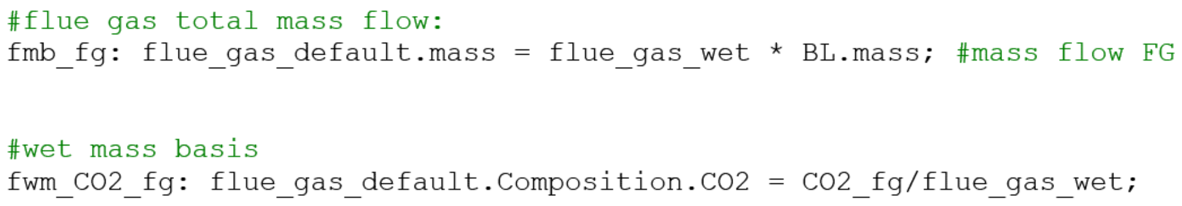
fO2_excess_air: O2_excess_air = O2_fg;

fN2_excess_air: N2_excess_air = excess_air*0.767;

fflue_gas_wet: flue_gas_wet = dry_fg_total + H2O_KRB; #mass flow of fg per kg BLS
```

Fig. 58 Implementation calculation principles flue gas (wet flue gas)

The last steps include scaling the mass flow (per kgBLS) with the kgBLS of black combusted and the computation and setting of the mass fractions of flue gas composition as shown in figure 59 analogously to the setting procedure in the smelt (fig. 50).



```
#flue gas total mass flow:
fmb_fg: flue_gas_default.mass = flue_gas_wet * BL.mass; #mass flow FG

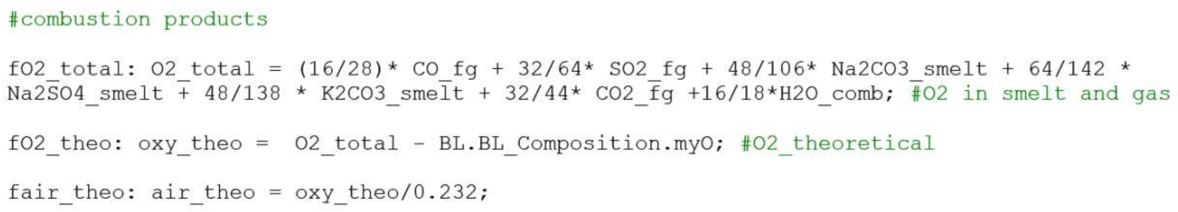

#wet mass basis
fwm_CO2_fg: flue_gas_default.Composition.CO2 = CO2_fg/flue_gas_wet;
```

Fig. 59 Implementation calculation principles flue gas (mass fractions)

Remark: Additionally, to the wet mass basis, the implementation of the formulas to calculate the dry mass basis, the wet volume basis, and the dry volume basis was carried out even though not being of further importance in setting output parameters essential for further calculations.

Calculation method for the (combustion) air mass flow:

The first step for calculating the air mass flow is determining the oxygen of all the combustion products by summing up the O content of carbonate and sulfate in the smelt as and in H2O, CO2, SO2 and CO in the flue gas. Afterwards the theoretical oxygen (oxy_theo) is computed by subtracting the oxygen entering with the black liquor mass flow (BL.BL_Composition.myO). Since the oxygen content of air is known (23.2%), the theoretical air required can be calculated easily. The following formulas are applied:



```
#combustion products

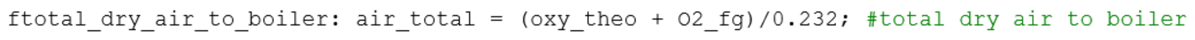
fO2_total: O2_total = (16/28)* CO_fg + 32/64* SO2_fg + 48/106* Na2CO3_smelt + 64/142 *
Na2SO4_smelt + 48/138 * K2CO3_smelt + 32/44* CO2_fg +16/18*H2O_comb; #O2 in smelt and gas

fO2_theo: oxy_theo =  O2_total - BL.BL_Composition.myO; #O2_theoretical

fair_theo: air_theo = oxy_theo/0.232;
```

Fig. 60 Implementation calculation principles combustion air (O2)

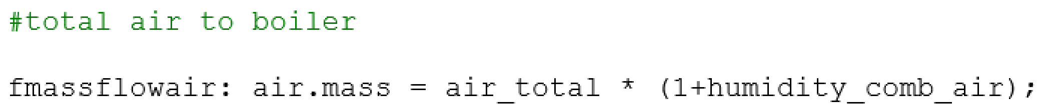
Now the total dry air entering the boiler is calculated as the sum of the theoretical air and excess air as shown in figure 61 below.



```
ftotal_dry_air_to_boiler: air_total = (oxy_theo + O2_fg)/0.232; #total dry air to boiler
```

Fig. 61 Implementation calculation principles combustion air (dry air)

In the total air mass flow, the humidity (H2O vapor) in air needs to be considered. Hence the total dry air to boiler mass flow is multiplied by 1 plus the fraction of humidity in combustion air (humidity_comb_air) as follows:

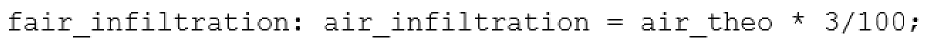


```
#total air to boiler

fmassflowair: air.mass = air_total * (1+humidity_comb_air);
```

Fig. 62 Implementation calculation principles combustion air (total air mass flow)

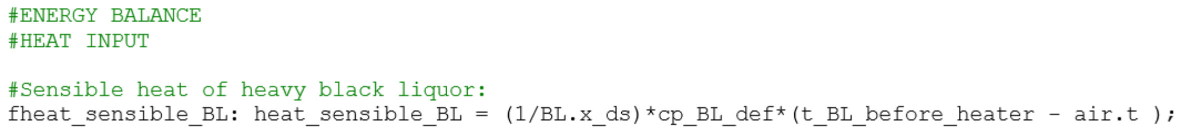
Furthermore, the infiltration air - the air entering the furnace by other means than through forced draft fans and the furnace air ports - needs to be accounted for. Infiltartion air is calculated as a percentage of the theoretical air input as 3%, which is illustrated in the implemented calculations of the KRB unit below (fig. 62).



```
fair_infiltration: air_infiltration = air_theo * 3/100;
```

Fig. 63 Implementation calculation principles combustion air (air infiltration)

For illustration purposes one example each of a heat input and a heat output is shortly described.



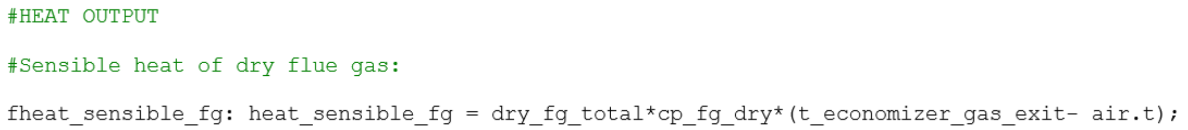
```
#ENERGY BALANCE
#HEAT INPUT

#Sensible heat of heavy black liquor:
fheat_sensible_BL: heat_sensible_BL = (1/BL.x_ds)*cp_BL_def*(t_BL_before_heater - air.t );
```

Fig. 64 Implementation calculation principles V1 heat input (sensible heat BL)

The sensible heat of black liquor above ambient temperature (figure 64) is calculated by considering the heat difference equal to heating one kgBLS from ambient temperature level (=air.t) to black liquor temperature before the black liquor preheater (t_BL_before_heater), which is computed as follows:

$$\dot{Q} = \dot{m}\, C_p \Delta \mathrm{T}$$



```
#HEAT OUTPUT

#Sensible heat of dry flue gas:

fheat_sensible_fg: heat_sensible_fg = dry_fg_total*cp_fg_dry*(t_economizer_gas_exit- air.t);
```

Fig. 65 Implementation calculation principles V1 heat output (sensible heat dry flue gas)

The sensible heat output with the dry flue gas mass stream is calculated (fig. 65) analogously to the one of sensible heat of black liquor, using the temperature difference between the temperature of the gas exiting the economizer (t_economizer_gas_exit) and ambient temperature level (=air.t).

Calculation of steam to mill and feedwater stream:

After all heat inputs and outputs are computed, the difference of the values is calculated, giving the net heat used to generate steam. Now, through an energy balance on the water-side the feedwater mass flow (=water.mass) is calculated. The steam to mill mass flow (=steam.mass) then is determined by a mass balance considering internal sootblowing (=sootblowing_steam) and a blowdown steam (= steam_blowdown) which both need to be subtracted from the steam produced. The described calculation procedure is executed by the following lines in the code of the KRB unit model V1 (fig. 66):

```
#STEAM GENERATION
#Heat to steam
fheat_to_steam: heat_to_steam = sum_heat_input - sum_heat_output;


#Feedwater to boiler flow
ffeedwater_to_boiler: water.mass = heat_to_steam/((1-
stream_blowdown_pct/100)*h_steam_superheated + stream_blowdown_pct/100* h_steam_drum_blowdown
- h_feedwater_economizer);


#Steam production
fsteam_production: steam_production = (1- stream_blowdown_pct/100) * water.mass;


#steam to mill
fsteamtomill: steam.mass = steam_production - sootblowing_steam - steam_blowdown;
```

Fig. 66 Implementation calculation principles V1 steam generation

Input and output distributions:

Remark: The heat input and output distributions (percentages of heat input and output respectively) are calculated. These values are not used further in model V2 due to a big number of additional variables making the model less clear.

5.2 Referenced Model V2

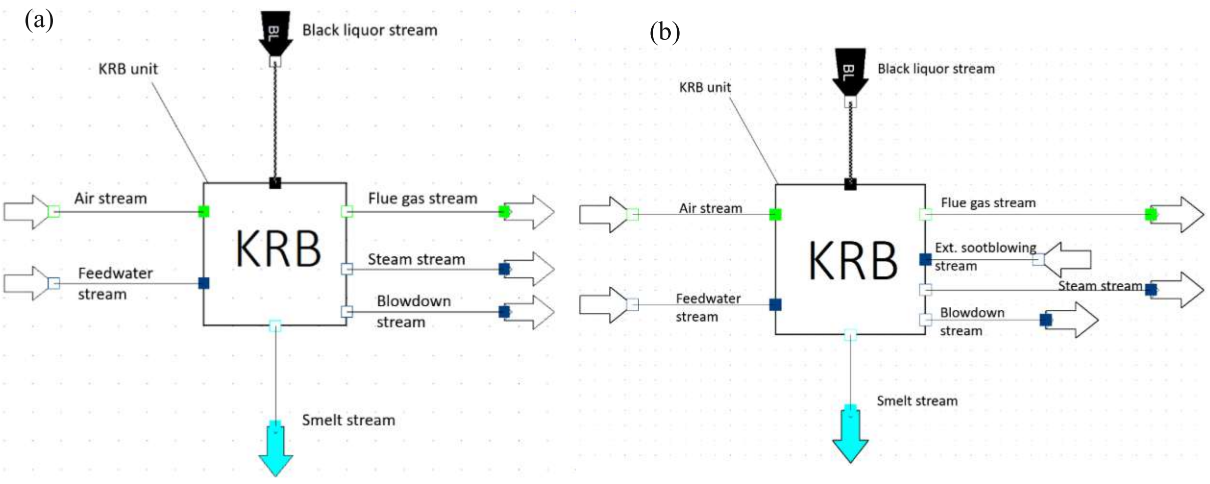


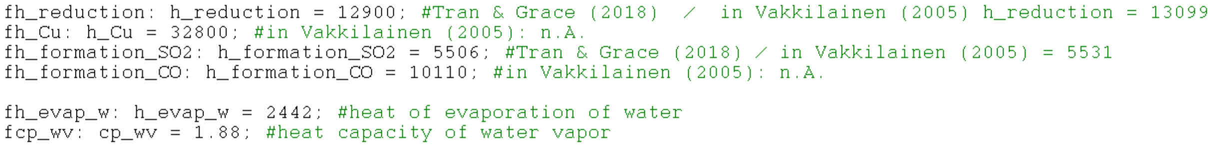
Fig. 67 KRB unit Referenced Model V2 (a) internal sootblowing (b) external sootblowing

The evolved model or Referenced Model V2 is based on the previously described Base Model V1. The calculation approach of computing smelt composition, smelt mass flow, flue gas composition, flue gas mass flow, and (combustion) air mass flow is adopted from model V1 representing the state-of-the-art approach proposed in Tran & Grace (2018). For the description of these calculations the reference is made to chapter 5.1. Further similarities can be found in the set-up of the KRB unit's terminals for the different stream connections. The layout / design of the KRB unit stayed the same as can be seen in figure 67. One major difference is that a new stream class "water" (dark blue ports) is used for feedwater stream, steam stream, and the newly added blowdown stream. Moreover, two different KRB unit options were developed: internal sootblowing (fig. 67 a) and external sootblowing (fig. 67 b). As the name suggests, the internal sootblowing steam is internally realized. The sootblowing stream does not cross the balancing box, hence cannot be seen, whereas the external sootblowing steam is realized as a new stream entering the recovery boiler, which originates from an external steam source.

The main modifications conducted, include the reduction of unit parameters and variables to the necessary minimum to guarantee a clear model with intuitive locations to define parameters (in stream or unit) and to avoid redundancy, hence boosting the performance of the model. For example, "t_BL_after_heater" is now integrated in the model through black liquor stream temperature and additionally implementing a reference temperature (defining the state before adding heat). This issue will be closely described in the next chapter (chapter

6 user manual) with the main purpose to explain which parameter / variable is defined where, and to show the user how to best apply the developed KRB Library.

In model V1 the enthalpies and specific heat capacities are implemented as required parameters, mandatory to be set. However, the conclusion was reached to implement enthalpy -inputs such as for example the specific heat of evaporation of water (h_evap_w = 2442 kJ/kg), or the specific heat capacity of water vapor (cp_wv = 1.88 kJ/kg/K) as fixed values, which can only be edited in MDK. This decision was taken to avoid careless mistakes when using the KRB Library. The fixed values are shown in figure 68. Since values between the two state-of-the-art models vary, the ones proposed in Tran & Grace (2018) were chosen to keep consistent.



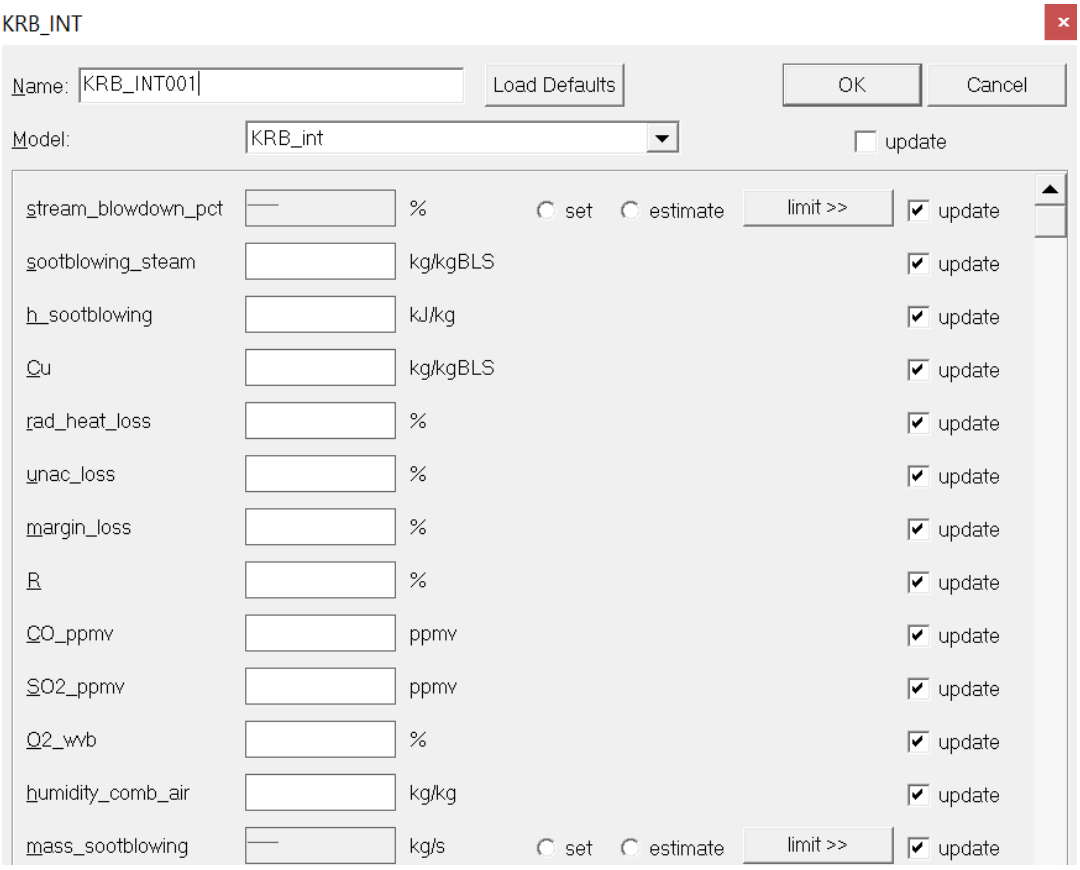
```
fh_reduction: h_reduction = 12900; #Tran & Grace (2018)  /  in Vakkilainen (2005) h_reduction = 13099
fh_Cu: h_Cu = 32800; #in Vakkilainen (2005): n.A.
fh_formation_SO2: h_formation_SO2 = 5506; #Tran & Grace (2018) / in Vakkilainen (2005) = 5531
fh_formation_CO: h_formation_CO = 10110; #in Vakkilainen (2005): n.A.

fh_evap_w: h_evap_w = 2442; #heat of evaporation of water
fcp_wv: cp_wv = 1.88; #heat capacity of water vapor
```

Fig. 68 Implementation fixed enthalpies and heat capacities

Required inputs:

The required / mandatory inputs in the KRB unit of model V2 are realized as parameters shown in figure 69 for the internal sootblowing option and in figure 70 for the external one. When comparing the list of needed inputs of model V1 and V2 one concludes that the efforts to make the KRB unit more user-friendly, more intuitive, and clearer were successful due to the usage of “referencing” and the definition of parameters the stream undergoes inside the streams.



KRB_INT

Name: KRB_INT001
Model: KRB_int
☐ update

stream_blowdown_pct	%	○ set ○ estimate	limit >>	☑ update
sootblowing_steam	kg/kgBLS			☑ update
h_sootblowing	kJ/kg			☑ update
Cu	kg/kgBLS			☑ update
rad_heat_loss	%			☑ update
unac_loss	%			☑ update
margin_loss	%			☑ update
R	%			☑ update
CO_ppmv	ppmv			☑ update
SO2_ppmv	ppmv			☑ update
O2_wvb	%			☑ update
humidity_comb_air	kg/kg			☑ update
mass_sootblowing	kg/s	○ set ○ estimate	limit >>	☑ update

Fig. 69 KRB unit V2 (internal sootblowing) required inputs

The internal sootblowing option of the KRB unit of the Referenced Model V2 requires eleven inputs:

- Sootblowing steam mass flow in kg/kgBLS = “sootblowing_steam”
- Enthalpy of internal sootblowing steam used in kJ/kg = ”h_sootblowing”
- Unburnt carbon present in smelt in kg/kg = “Cu”
- Radiation heat loss as % of heat input = “rad_heat_loss”
- Unaccounted heat loss as % of heat input = “unac_heat_loss”
- Margin heat loss as % of heat input = ”margin_loss”
- Reduction efficiency in % = ”R”
- CO concentration in wet flue gas in ppmv = “CO_ppmv”
- SO2 concentration in wet flue gas in ppmv = “SO2_ppmv”
- Excess O2 of flue gas (wet volume basis) in vol.% = “O2_wvb”
- Humidity (H2O) in combustion air in kg/kg = “humidity_comb_air”

The external sootblowing option on the contrary only requires nine inputs (defined inside the KRB unit). It includes the same ones minus the definition of sootblowing mass flow as well as sootblowing enthalpy, because these parameters are defined inside the stream called "sootblowing".

Name: KRB_EXT001

Model: KRB_ext ☐ update

stream_blowdown_pct	—	%	○ set ○ estimate	☑ update
sootblowing_steam	—	kg/kgBLS	○ set ○ estimate	☑ update
Cu		kg/kgBLS		☑ update
rad_heat_loss		%		☑ update
unac_loss		%		☑ update
margin_loss		%		☑ update
R		%		☑ update
CO_ppmv		ppmv		☑ update
SO2_ppmv		ppmv		☑ update
O2_wvb		%		☑ update
humidity_comb_air		kg/kg		☑ update

Fig. 70 KRB unit V2 (external sootblowing) required inputs

```
#total air to boiler -> multiplying with BL.mass (from (kg/kg_BLS)/s to kg/s)

fmassflowair: air.mass = air_total * (1+humidity_comb_air)*BL.mass;
```

Fig. 71 Implementation principles scaling with BL.mass

A further modification is the scaling of all different mass flows with the actual black liquor dry solids mass flow (BL.mass). This is of the essence because the calculations are based on firing 1 kgBLS. If one is to input a value different from 1 kgBLS for the black liquor stream the outputs must be scaled accordingly, which can easily be implemented with the approach shown in figure 71.

Energy Balance:

Heat Inputs:

The heat inputs considered for KRB unit model V2 (Referenced model) are:

1. Heating value of black liquor (=heat_LHV)
2. Sensible heat of black liquor (=heat_BL_sensible)
3. Sensible heat of air (=heat_air)
4. Sensible heat of sootblowing steam (=heat_sootblowing)
5. Heat in feedwater for blowdown steam (=heat_blowdown)

The mentioned heat inputs are also considered in the state-of-the-art model proposed in Tran & Grace (2018) as shown in table 4. The heating value of black liquor (=heat_LHV) used in the energy calculations is computed using the state-of-the-art approach applied in Vakkilainen (2005) by considering the correction of the higher heating value instead of accounting for it on the loss side of the energy balance. As already mentioned in chapter 4.2.2 this approach per se has no influence on the outcome of the energy balance, it only changes how the loss is accounted for. This approach was chosen to primarily have a clear model, in which data characterizing black liquor is calculated within the stream (see chapter 4.2.2) and handed on to the KRB unit via “referencing”.

The sensible heat of black liquor (=heat_BL_sensible) in the KRB unit is the same as the sum of “Sensible heat of black liquor” and “sensible heat from black liquor heating” in Tran & Grace (2018) (see table 4). Furthermore, the sensible heat of sootblowing steam (=heat_sootblowing) is not mentioned in table 4 because of the usage of an internal sootblowing steam. The sensible heat of air (=heat_air) and heat in feedwater for blowdown steam (=heat_blowdown) are accounted for analogously.

Remark: The heat input due to infiltration air as proposed in Vakkilainen (2005) is not considered to stay consistent with the model proposed in Tran & Grace (2018) (see chapter 1.2.3.).

```
#HEAT-INPUT:

#BL
fheat_LHV:heat_LHV = BL.mass*BL.LHV_wet;

fheat_BL_sensible: heat_BL_sensible =  BL.mass*(BL.cp_BL*BL.t-
BL.t_amb*BL.cp_BL_amb)*(1+BL.BL_H2O);
```

Fig. 72 Implementation calculation principles V2 heat input (black liquor)

As shown in figure 72 the two heat inputs originating from black liquor are calculated by multiplying BL.LHV_wet (black liquor's corrected lower heating value) with the dry solids mass flow of black liquor obtaining the heat input through the heating value / combustion of black liquor (=heat_LHV). The black liquor's sensible heat input follows the equation:

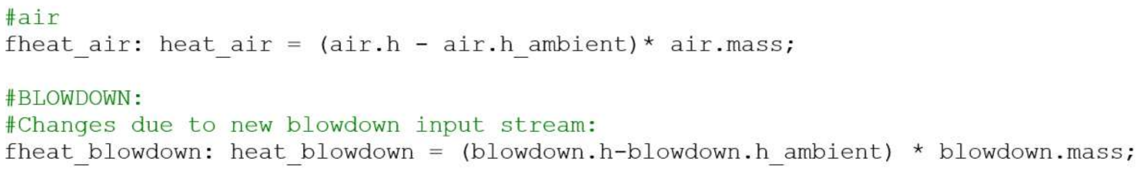
$$\dot{Q} = \dot{m}\ \Delta\mathrm{h}$$

where Δh is the enthalpy difference and $\dot{m}$ is the black liquor dry solids mass flow.
Δh is calculated as Δ(cp*T). Due to the two options for calculating cp_BL (see chapter 4.2.2) the implemented equation needs to work for both options. Because of option 1's dependency on temperature the following equation is applied:

$$\Delta(\mathrm{cp}(\mathrm{t},\mathrm{x\_ds}) * \mathrm{T}) \ = [\mathrm{cp}(\mathrm{t},\mathrm{x\_ds}) * \mathrm{BL.t}] - [\mathrm{cp}(\mathrm{t\_amb},\mathrm{x\_ds}) * \mathrm{BL.t\_amb}]$$

whereas when considering a fixed cp value (option 2), the following equation is used:

$$\Delta(\mathrm{cp} * \mathrm{T}) \ = \ \mathrm{cp} * [\mathrm{BL.t} \ - \ \mathrm{BL.t\_amb}]$$



```
#air
fheat_air: heat_air = (air.h - air.h_ambient)* air.mass;

#BLOWDOWN:
#Changes due to new blowdown input stream:
fheat_blowdown: heat_blowdown = (blowdown.h-blowdown.h_ambient) * blowdown.mass;
```

Fig. 73 Implementation calculation principles V2 heat input (sensible heat air, blowdown)

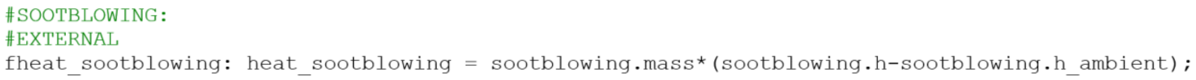
The sensible heat of air (=heat_air) and the heat in feedwater for blowdown steam (=heat_blowdown) are computed analogously to the equation Q°=m°*Δh, which states that the heat input is equal to the mass flow times the change in enthalpy (see figure 73).

Due to the two different options of sootblowing (internal/external), there is a need to differentiate on how to account for the heat inputs according to sootblowing. Internal sootblowing steam is generated inside the boiler (does not cross the balancing boundary) and is therefore equal to zero (Tran & Grace, 2018).

```
#SOOTBLOWING:
#INTERNAL
#internal sootblowing: input = 0* ...
fheat_sootblowing: heat_sootblowing = 0;
```

Fig. 74 Implementation calculation principles V2 heat input (heat internal sootblowing)

Sootblowing steam from an external source, on the other hand, does cross the balancing boundary and therefore needs to be accounted for as shown in figure 75 below.



```
#SOOTBLOWING:
#EXTERNAL
fheat_sootblowing: heat_sootblowing = sootblowing.mass*(sootblowing.h-sootblowing.h_ambient);
```

Fig. 75 Implementation calculation principles V2 heat input (heat external sootblowing)

Remark: “sootblowing.h_ambient” represents the reference state of sootblowing enthalpy defined in sootblowing stream through the input of reference state variables.

The total of all the mentioned heat inputs is formed and stored in the variable sum_heat_input.

Heat Outputs/ Losses

The heat outputs / losses considered for the KRB unit model V2 (Referenced model) are:

1. Flue gas loss (=loss_fg)
2. Smelt loss (=loss_smelt)
3. Sootblowing loss (=loss_sootblowing)
4. Loss due to formation of Na2S (=loss_Na2S)
5. Loss due to formation of SO2 (=loss_SO2)
6. Loss due to formation of CO (=loss_formation_CO)
7. Loss due to unburnt carbon in smelt
8. Radiation loss (=loss_radi)
9. Unaccounted loss (=loss_unaccounted)
10. Margin loss (=loss_margin)

The heat losses 1.- 3. flue gas loss (=loss_fg), smelt loss (=loss_smelt), and sootblowing loss (=loss_sootblowing) are calculated analogously to the sensible heat of air (=heat_air) and the heat in feedwater for blowdown steam (=heat_blowdown) by following the principle that the heat input / heat loss is equal to the mass flow times the change in enthalpy. To be more precise about the calculation of the sootblowing loss (=loss_sootblowing) equation Q°=m°*Δh becomes:

$$\dot{Q} = \dot{m}\,(\Delta \text{h\_evaporation\_water} + \text{cp\_water\_vapor} * \Delta \text{T})$$

which accounts for the enthalpy of evaporation (latent heat) in sootblowing steam as well its sensible component (cp_water_vapor*ΔT) (fig. 76).

```
#HEAT LOSSES:

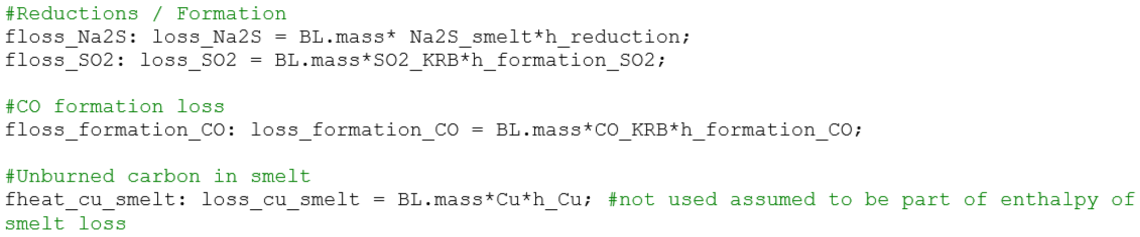
#Flue Gas
floss_fg: loss_fg = (flue_gas_default.mass* (flue_gas_default.h -
flue_gas_default.h_ambient));

#Smelt
floss_smelt: loss_smelt = smelt.mass*(smelt.h - smelt.h_ambient); #enthalpy of smelt at
ambient temp

#Sootblowing
floss_sootblowing: loss_sootblowing =
(BL.mass*sootblowing_steam)*(h_evap_w+cp_wv*(flue_gas_default.t - flue_gas_default.t_amb));
#2442 =h_evap, 1.88 =cp_wv
```

Fig. 76 Implementation calculation principles V2 heat output (loss fg,smelt , sootblowing)

Furthermore, the calculations of heat losses due to the reduction / formation is accounted for is calculated by multiplying the mass flow per kgBLS of each component (Na2S_smelt, SO2_KRB, CO_KRB, and Cu) with its according enthalpy and scaling it with the kgBLS fired (BL.mass) for computing the total heat loss of each (fig.77).



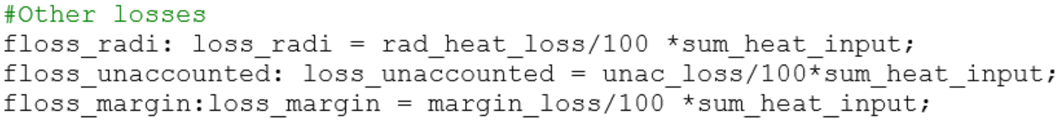
```
#Reductions / Formation
floss_Na2S: loss_Na2S = BL.mass* Na2S_smelt*h_reduction;
floss_SO2: loss_SO2 = BL.mass*SO2_KRB*h_formation_SO2;

#CO formation loss
floss_formation_CO: loss_formation_CO = BL.mass*CO_KRB*h_formation_CO;

#Unburned carbon in smelt
fheat_cu_smelt: loss_cu_smelt = BL.mass*Cu*h_Cu; #not used assumed to be part of enthalpy of
smelt loss
```

Fig. 77 Implementation calculation principles V2 heat output (loss reduction, formation, unburned carbon)

The losses 8.-10. radiation loss (=loss_radi), unaccounted loss (=loss_unaccounted), and margin loss (=loss_margin) are calculated as a percentage (rad_heat_loss, unac_loss, margin_loss in %) of the total heat input (=sum_heat_input) as shown below (fig. 78). The margin loss, which is not part of the calculation approach proposed in Tran & Grace (2018), is added in the model because it can easily be turned off by setting the input parameter percentage of margin loss to zero.



```
#Other losses
floss_radi: loss_radi = rad_heat_loss/100 *sum_heat_input;
floss_unaccounted: loss_unaccounted = unac_loss/100*sum_heat_input;
floss_margin:loss_margin = margin_loss/100 *sum_heat_input;
```

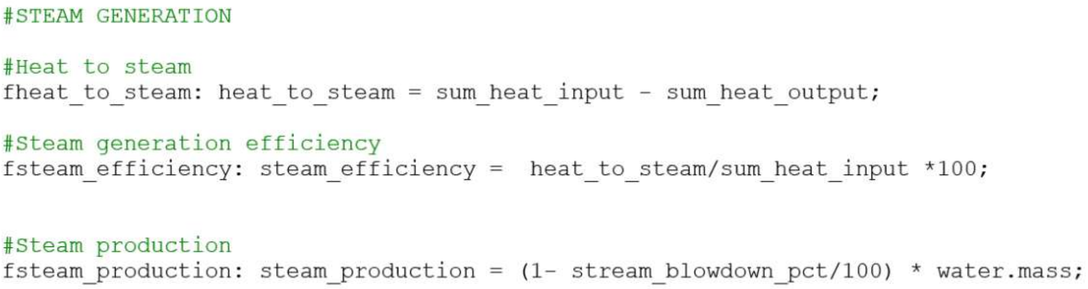
Fig. 78 Implementation calculation principles V2 heat output (loss radiation, unaccounted, margin)

Finally, the total of all the mentioned heat outputs is formed and stored in the variable sum_heat_output.

Remark: loss_K2S is implemented as a variable and set to zero since potassium exist in the smelt only K2CO3 and is not considered in Tran & Grace (2018). A heat loss goes along with the blowdown stream (loss_blowdown) but is not considered in either state-of-the-art model and therefore it is also neglected in this model.

Calculation of steam and feedwater:

The heat available for steam generation (=heat_to_steam) is the difference of total heat input (=sum_heat_input) and total heat output (=sum_heat_output). Steam efficiency is calculated by the ratio of heat to steam (=heat_to_steam) and total heat input (=sum_heat_input) and multiplying it with 100 to obtain the result in percentage. The total steam produced must be reduced by the one lost due to blowdown as shown in figure 79.



```
#STEAM GENERATION

#Heat to steam
fheat_to_steam: heat_to_steam = sum_heat_input - sum_heat_output;

#Steam generation efficiency
fsteam_efficiency: steam_efficiency =  heat_to_steam/sum_heat_input *100;


#Steam production
fsteam_production: steam_production = (1- stream_blowdown_pct/100) * water.mass;
```

Fig. 79 Implementation calculation principles V2 steam generation

For the two different sootblowing options (internal/external) a distinction between the equation for calculating the feedwater mass flow (water.mass) and the steam to mill mass flow (steam.mass) must be made as follows.

Internal sootblowing:

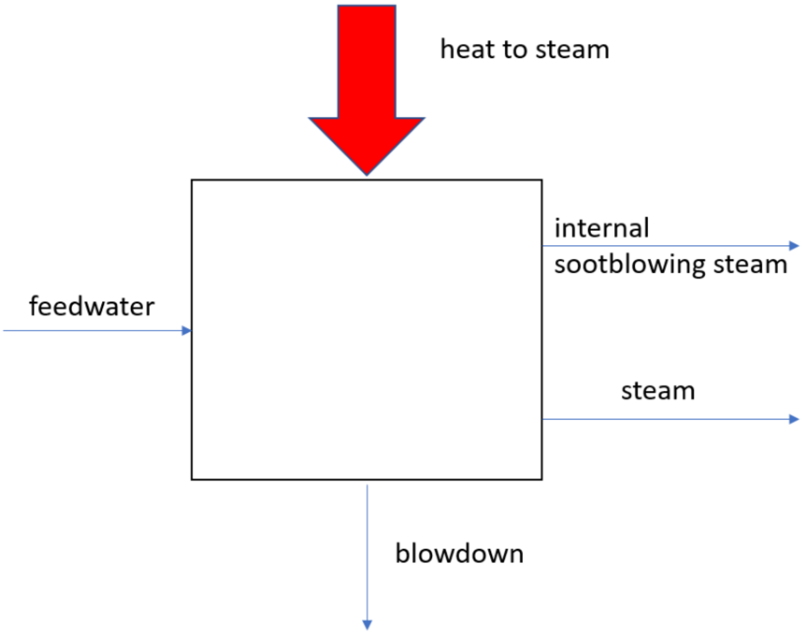


Fig. 80 KRB unit V2 balance box waterside (internal sootblowing)

In figure 80 the illustration of a balance box (internal sootblowing) is shown from which the energy balance and mass balance can be determined. The feedwater mass flow (water.mass) and the steam to mill mass flow (steam.mass) can be computed through the balance as shown in figure 81.

```
#feedwater:

ffeedwater_to_boiler: water.mass = (steam.mass*steam.h +(BL.mass*sootblowing_steam)*
h_sootblowing +blowdown.h * blowdown.mass - heat_to_steam)/(water.h);


#steam to mill
fsteamtomill: steam.mass = water.mass - blowdown.mass - BL.mass*sootblowing_steam;
```

Fig. 81 Implementation calculation principles V2 (internal sootblowing: feedwater, steam to mill)

<u>External sootblowing:</u>

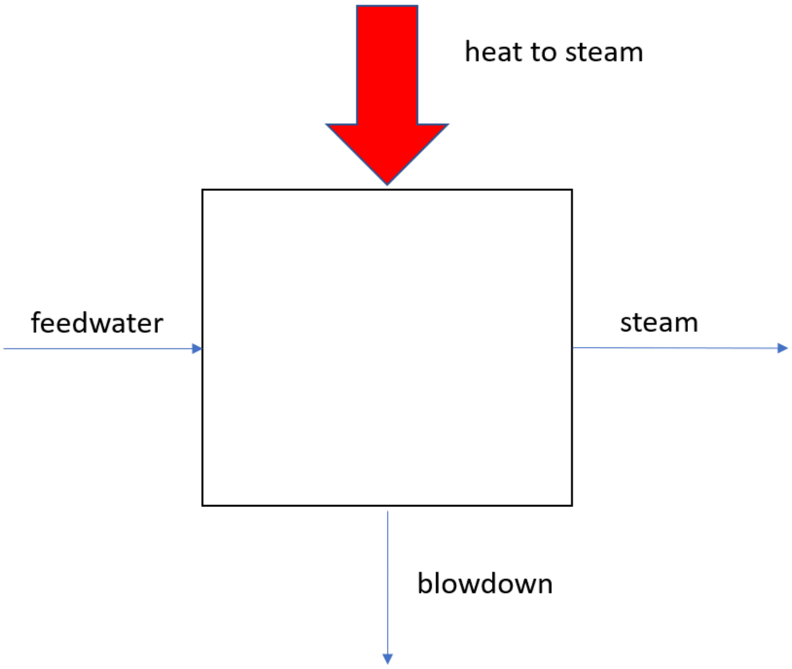
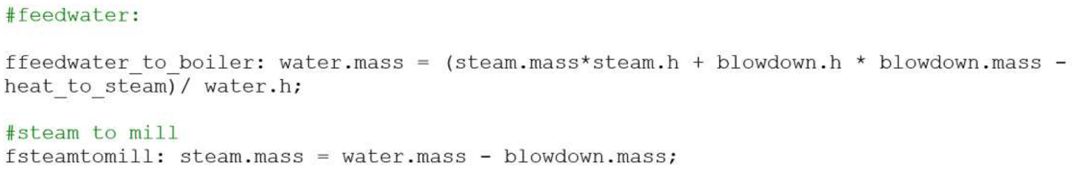


Fig. 82 KRB unit V2 balance box waterside (external sootblowing)

In figure 82 the illustration of a balance box (internal sootblowing) is shown from which the energy balance and mass balance can be derived. The feedwater mass flow (water.mass) and the steam to mill mass flow (steam.mass) can be computed through the balances as shown in figure 83.



```
#feedwater:

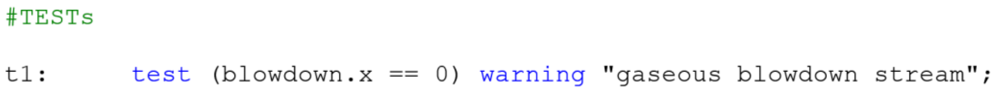
ffeedwater_to_boiler: water.mass = (steam.mass*steam.h + blowdown.h * blowdown.mass -
heat_to_steam)/ water.h;

#steam to mill
fsteamtomill: steam.mass = water.mass - blowdown.mass;
```

Fig. 83 Implementation calculation principles V2 (external sootblowing: feedwater, steam to mill)

Remark:

To check for the steam quality of blowdown mass flow a test is implemented (fig. 84) to guarantee that the input properties for blowdown stream are valid.



```
#TESTs

t1:      test  (blowdown.x == 0) warning "gaseous blowdown stream";
```

Fig. 84 Implementation test steam quality (blowdown)

6 User Manual

This chapter is dedicated to giving the user a step-by-step description of how to utilize the KRB Library for simulating kraft recovery boilers. The results of this simulation case are validated and discussed in chapter 7.2.

6.1 Flowsheet set up

The first step in the application of the KRB Library for simulating kraft recovery boilers is selecting one of the two developed options for the KRB unit, either using external or internal sootblowing. In this case the latter is chosen. Secondly, the units for the sources and the sinks for each corresponding connection are added to the flowsheet (black liquor source for black liquor connection, and so on). The outcome then looks like shown in figure 85 below.

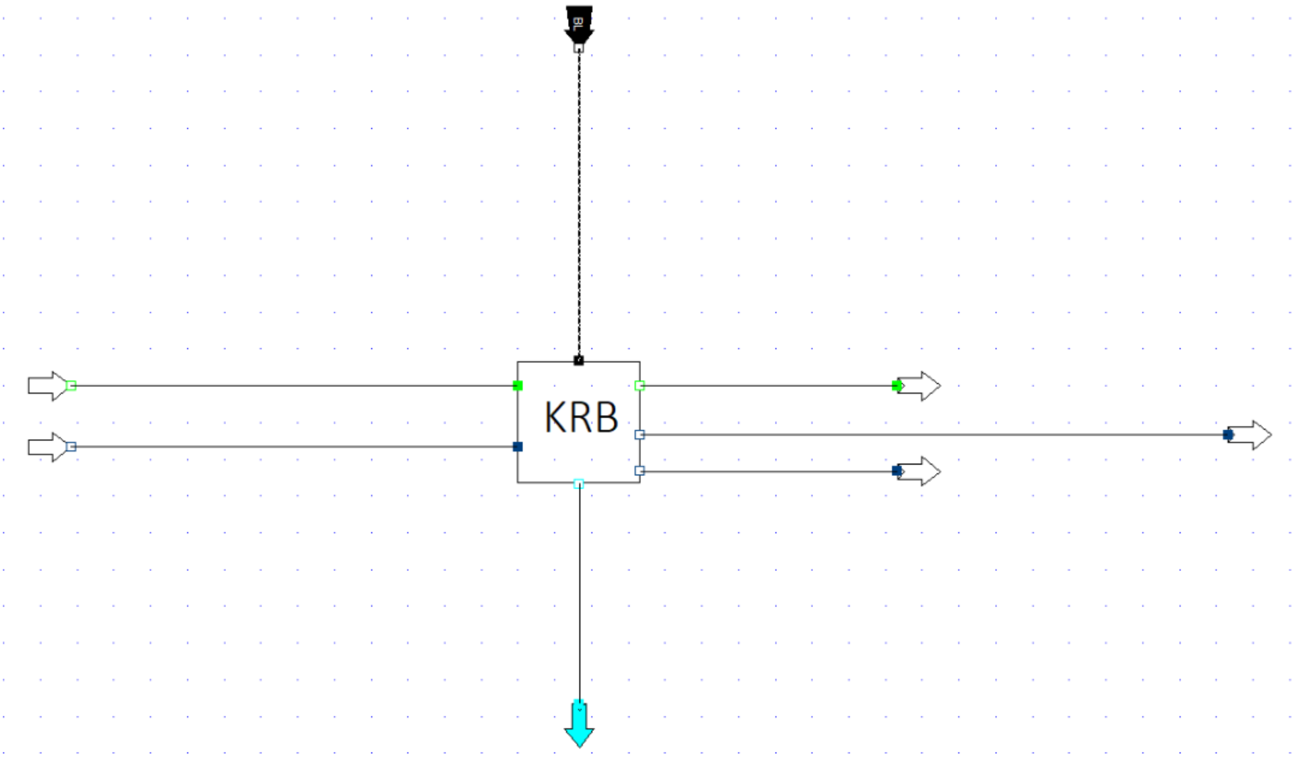


Fig. 85 Flowsheet setup KRB unit V2 (internal sootblowing)

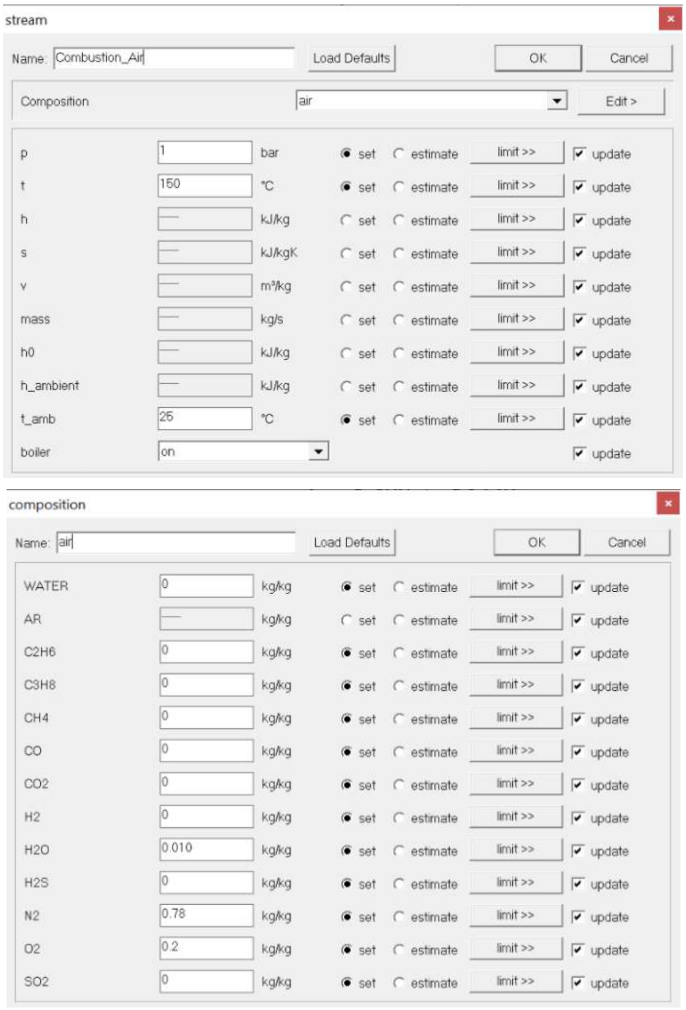
6.2 Streams and Compositions

It is noted that the user is advised to name the streams and their components with a clear nomenclature to prevent mistakes. Since all the following streams mentioned are connected to the boiler, the switch option “on” is selected for each of them.

6.2.1 Combustion Air

(a)

(b)



Name: Combustion_Air

Composition: air

p	1	bar	● set	○ estimate	limit >>	☑ update
t	150	°C	● set	○ estimate	limit >>	☑ update
h	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
s	—	kJ/kgK	○ set	○ estimate	limit >>	☑ update
v	—	m³/kg	○ set	○ estimate	limit >>	☑ update
mass	—	kg/s	○ set	○ estimate	limit >>	☑ update
h0	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
h_ambient	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
t_amb	25	°C	● set	○ estimate	limit >>	☑ update
boiler	on					☑ update

Name: air

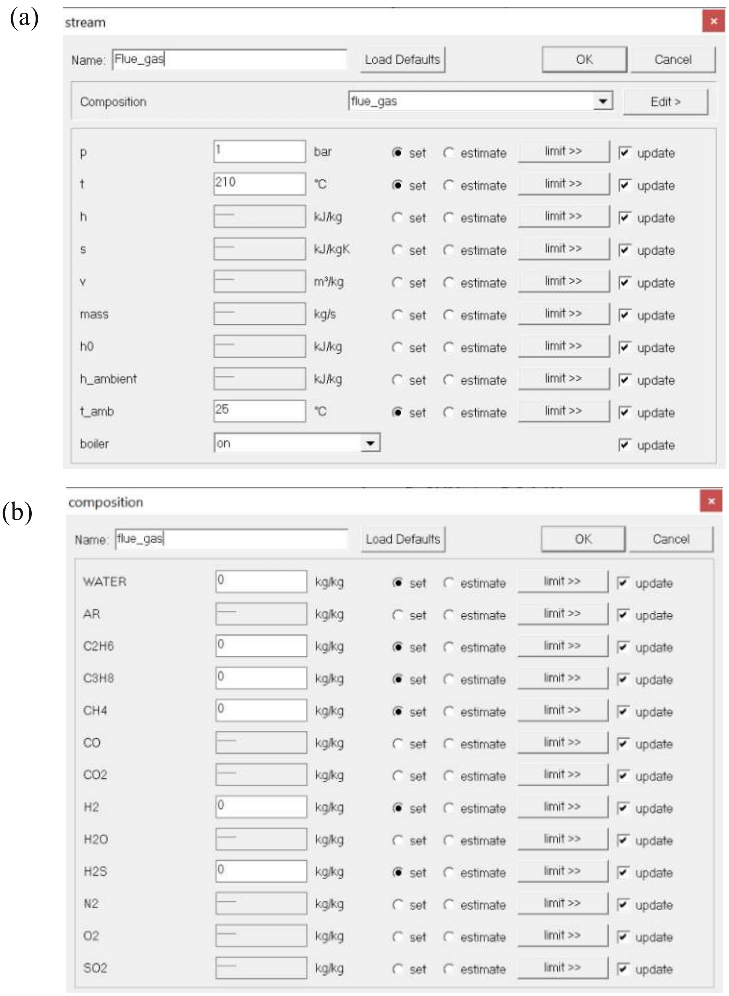
WATER	0	kg/kg	● set	○ estimate	limit >>	☑ update
AR	—	kg/kg	○ set	○ estimate	limit >>	☑ update
C2H6	0	kg/kg	● set	○ estimate	limit >>	☑ update
C3H8	0	kg/kg	● set	○ estimate	limit >>	☑ update
CH4	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2O	0.010	kg/kg	● set	○ estimate	limit >>	☑ update
H2S	0	kg/kg	● set	○ estimate	limit >>	☑ update
N2	0.78	kg/kg	● set	○ estimate	limit >>	☑ update
O2	0.2	kg/kg	● set	○ estimate	limit >>	☑ update
SO2	0	kg/kg	● set	○ estimate	limit >>	☑ update

Fig. 86 Inputs combustion air (a) thermodynamic properties (b) chemical composition

The input properties temperature and pressure of the entering combustion air after preheating are set to 150°C and 1 bar, respectively. Furthermore, the ambient temperature (t_amb) is set to 25°C.

As defined in the state-of-the-art model in Tran & Grace (2018) H_2O-, N_2-, and O_2-content are set to 0.01, 0.78 and 0.2 kg/kg, respectively. The remaining fraction are noble gases in air assumed to be Argon, which is calculated. Other chemical components need to be set to zero.

6.2.2 Flue Gas



(a) Name: Flue_gas

Composition: flue_gas

p	1	bar	● set	○ estimate	limit >>	☑ update
t	210	°C	● set	○ estimate	limit >>	☑ update
h		kJ/kg	○ set	○ estimate	limit >>	☑ update
s		kJ/kgK	○ set	○ estimate	limit >>	☑ update
v		m³/kg	○ set	○ estimate	limit >>	☑ update
mass		kg/s	○ set	○ estimate	limit >>	☑ update
h0		kJ/kg	○ set	○ estimate	limit >>	☑ update
h_ambient		kJ/kg	○ set	○ estimate	limit >>	☑ update
t_amb	25	°C	● set	○ estimate	limit >>	☑ update
boiler	on					☑ update

(b) Name: flue_gas

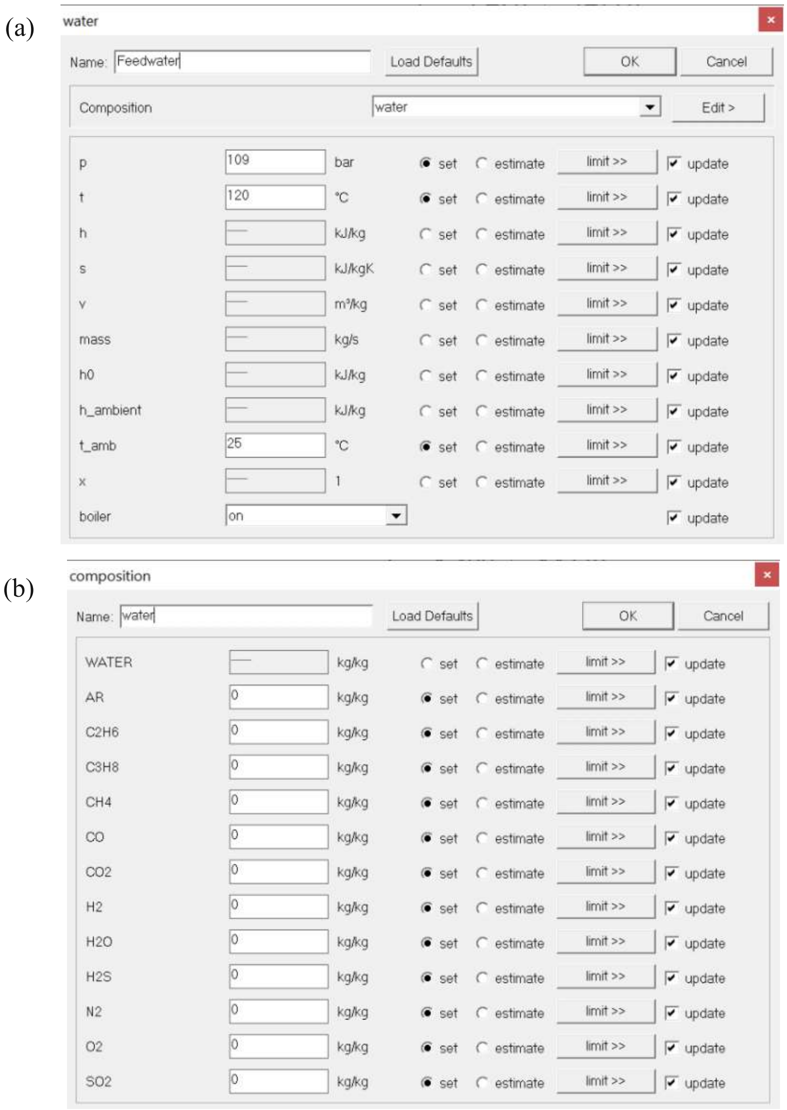
WATER	0	kg/kg	● set	○ estimate	limit >>	☑ update
AR		kg/kg	○ set	○ estimate	limit >>	☑ update
C2H6	0	kg/kg	● set	○ estimate	limit >>	☑ update
C3H8	0	kg/kg	● set	○ estimate	limit >>	☑ update
CH4	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO		kg/kg	○ set	○ estimate	limit >>	☑ update
CO2		kg/kg	○ set	○ estimate	limit >>	☑ update
H2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2O		kg/kg	○ set	○ estimate	limit >>	☑ update
H2S	0	kg/kg	● set	○ estimate	limit >>	☑ update
N2		kg/kg	○ set	○ estimate	limit >>	☑ update
O2		kg/kg	○ set	○ estimate	limit >>	☑ update
SO2		kg/kg	○ set	○ estimate	limit >>	☑ update

Fig. 87 Inputs flue gas (a) thermodynamic properties (b) chemical composition

The input properties temperature and pressure of the exiting flue gas are set to 210°C and 1 bar, respectively. The ambient temperature (t_amb) is set to 25°C.

The chemical components which are not present in the flue gas need to be set to zero, including WATER, C2H6, C3H8, CH4, H2 and H2S. The remaining chemical mass fractions are calculated in the KRB unit.

6.2.3 Feedwater



(a)

water

Name: Feedwater

Composition: water

p	109	bar	● set	○ estimate	limit >>	☑ update
t	120	°C	● set	○ estimate	limit >>	☑ update
h		kJ/kg	○ set	○ estimate	limit >>	☑ update
s		kJ/kgK	○ set	○ estimate	limit >>	☑ update
v		m³/kg	○ set	○ estimate	limit >>	☑ update
mass		kg/s	○ set	○ estimate	limit >>	☑ update
h0		kJ/kg	○ set	○ estimate	limit >>	☑ update
h_ambient		kJ/kg	○ set	○ estimate	limit >>	☑ update
t_amb	25	°C	● set	○ estimate	limit >>	☑ update
x		1	○ set	○ estimate	limit >>	☑ update
boiler	on					☑ update

(b)

composition

Name: water

WATER		kg/kg	○ set	○ estimate	limit >>	☑ update
AR	0	kg/kg	● set	○ estimate	limit >>	☑ update
C2H6	0	kg/kg	● set	○ estimate	limit >>	☑ update
C3H8	0	kg/kg	● set	○ estimate	limit >>	☑ update
CH4	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2O	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2S	0	kg/kg	● set	○ estimate	limit >>	☑ update
N2	0	kg/kg	● set	○ estimate	limit >>	☑ update
O2	0	kg/kg	● set	○ estimate	limit >>	☑ update
SO2	0	kg/kg	● set	○ estimate	limit >>	☑ update

Fig. 88 Inputs feedwater (a) thermodynamic properties (b) chemical composition

The input properties temperature and pressure of feedwater are set to 120°C and 109 bar, respectively. The ambient temperature (t_amb) is set to 25°C.

The only composition in feedwater is WATER, which is calculated by IPSEpro by setting all the remaining components to zero.

6.2.4 Steam

(a)

Name: Steam_to_Mill

Composition: superheated_steam

p	62	bar	● set	○ estimate	limit >>	☑ update
t	482	°C	● set	○ estimate	limit >>	☑ update
h	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
s	—	kJ/kgK	○ set	○ estimate	limit >>	☑ update
v	—	m³/kg	○ set	○ estimate	limit >>	☑ update
mass	—	kg/s	○ set	○ estimate	limit >>	☑ update
h0	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
h_ambient	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
t_amb	25	°C	● set	○ estimate	limit >>	☑ update
x	—	1	○ set	○ estimate	limit >>	☑ update
boiler	on					☑ update

(b)

Name: superheated_steam

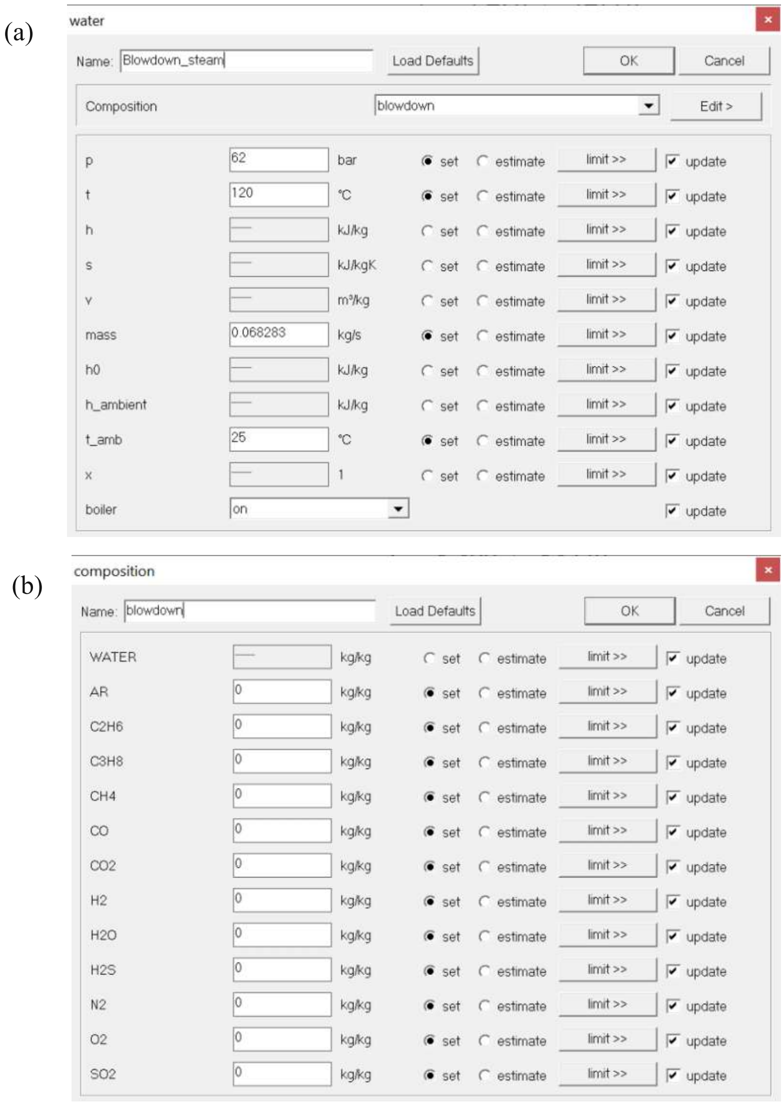
WATER	—	kg/kg	○ set	○ estimate	limit >>	☑ update
AR	0	kg/kg	● set	○ estimate	limit >>	☑ update
C2H6	0	kg/kg	● set	○ estimate	limit >>	☑ update
C3H8	0	kg/kg	● set	○ estimate	limit >>	☑ update
CH4	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2O	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2S	0	kg/kg	● set	○ estimate	limit >>	☑ update
N2	0	kg/kg	● set	○ estimate	limit >>	☑ update
O2	0	kg/kg	● set	○ estimate	limit >>	☑ update
SO2	0	kg/kg	● set	○ estimate	limit >>	☑ update

Fig. 89 Inputs steam (a) thermodynamical properties (b) chemical composition

The input properties temperature and pressure of steam to mill are set to 120°C and 109 bar, respectively. The ambient temperature (t_amb) is set to 25°C.

The only composition in feedwater is WATER, which is calculated by IPSEpro by setting all the remaining components to zero.

6.2.5 Blowdown


(a)

water

Name: Blowdown_steam

Composition: blowdown

p	62	bar	● set	○ estimate	limit >>	☑ update
t	120	°C	● set	○ estimate	limit >>	☑ update
h		kJ/kg	○ set	○ estimate	limit >>	☑ update
s		kJ/kgK	○ set	○ estimate	limit >>	☑ update
v		m³/kg	○ set	○ estimate	limit >>	☑ update
mass	0.068283	kg/s	● set	○ estimate	limit >>	☑ update
h0		kJ/kg	○ set	○ estimate	limit >>	☑ update
h_ambient		kJ/kg	○ set	○ estimate	limit >>	☑ update
t_amb	25	°C	● set	○ estimate	limit >>	☑ update
x		1	○ set	○ estimate	limit >>	☑ update
boiler	on					☑ update

(b)

composition

Name: blowdown

WATER		kg/kg	○ set	○ estimate	limit >>	☑ update
AR	0	kg/kg	● set	○ estimate	limit >>	☑ update
C2H6	0	kg/kg	● set	○ estimate	limit >>	☑ update
C3H8	0	kg/kg	● set	○ estimate	limit >>	☑ update
CH4	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO	0	kg/kg	● set	○ estimate	limit >>	☑ update
CO2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2O	0	kg/kg	● set	○ estimate	limit >>	☑ update
H2S	0	kg/kg	● set	○ estimate	limit >>	☑ update
N2	0	kg/kg	● set	○ estimate	limit >>	☑ update
O2	0	kg/kg	● set	○ estimate	limit >>	☑ update
SO2	0	kg/kg	● set	○ estimate	limit >>	☑ update

Fig. 90 Inputs blowdown (a) thermodynamical properties (b) chemical composition

The input properties temperature and pressure of blowdown steam are set to 120°C and 62 bar, respectively. The ambient temperature (t_amb) is set to 25°C. Additionally the mass flow can either be directly defined in blowdown stream as a mass flow (which is recommended as in this case) or in KRB unit as a percentage of feedwater mass flow.

The only composition in blowdown steam is WATER, which is calculated by IPSEpro by setting all the remaining components to zero.

6.2.6 Black Liquor


(a)

BL_stream

Name: Black_Liquor

BL_Composition: BL_TRAN

HHV	14000	kJ/kg		☑ update
eta_red	0.92	1		☑ update
t_amb	25	°C		☑ update
x_ds	0.7	kg/kg	● set ○ estimate	☑ update
mass	1	kgBLS/s	● set ○ estimate	☑ update
h	—	kJ/kg	○ set ○ estimate	☑ update
p	1	bar	● set ○ estimate	☑ update
t	130	°C	● set ○ estimate	☑ update

(b)

BL_composition

Name: BL_TRAN

myC	0.347	kg/kg	● set ○ estimate	☑ update
myH	0.035	kg/kg	● set ○ estimate	☑ update
myN	0	kg/kg	● set ○ estimate	☑ update
myO	—	kg/kg	○ set ○ estimate	☑ update
myS	0.042	kg/kg	● set ○ estimate	☑ update
myAsh	0	kg/kg	● set ○ estimate	☑ update
myNa	0.195	kg/kg	● set ○ estimate	☑ update
myCl	0.005	kg/kg	● set ○ estimate	☑ update
myK	0.018	kg/kg	● set ○ estimate	☑ update
Inerts	0.002	kg/kg	● set ○ estimate	☑ update

Fig. 91 Inputs black liquor (a) thermodynamical properties (b) chemical composition

The required input properties for the black liquor include the higher heating value (14000kJ/kg), the reduction efficiency ratio (0.92), the ambient temperature (25°C), the dry solids ratio of black liquor (0.7), the dry solids mass flow (1kgBLS/s), the pressure (1bar) and the temperature after heating (130°C).

The black liquor's chemical composition is defined through the input of the chemical analysis, in this case the values from table 11. All the variables are set, except for oxygen (myO), which is calculated by IPSEpro.

6.2.7 Smelt


(a)

KRB_stream

Name: Smelt

KRB_Composition: smelt_KRB

p	1	bar	● set	○ estimate	limit >>	☑ update
t	850	°C	● set	○ estimate	limit >>	☑ update
t_amb	25	°C				☑ update
h	—	kJ/kg	○ set	○ estimate	limit >>	☑ update
mass	—	kg/s	○ set	○ estimate	limit >>	☑ update

(b)

KRB_composition

Name: smelt_KRB

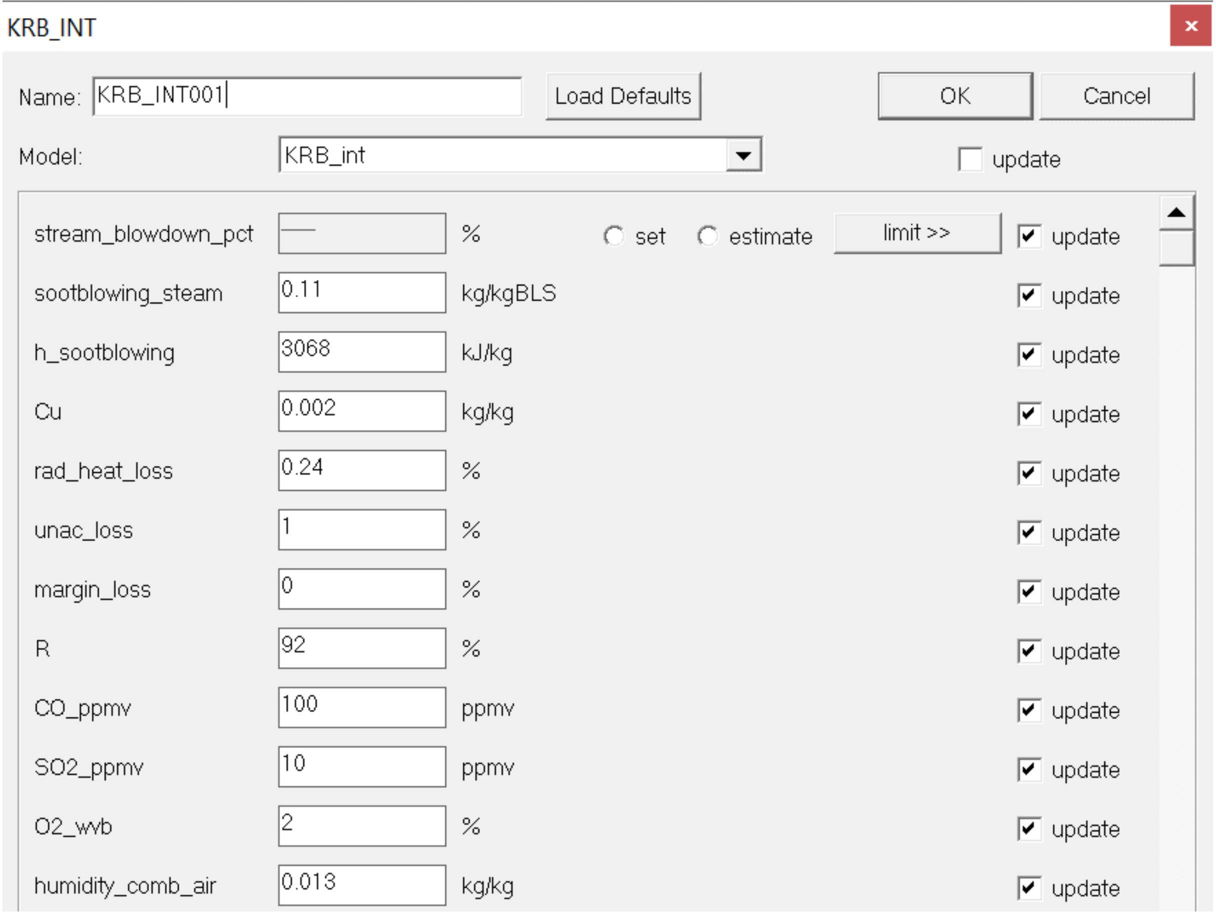
m_S	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_SO3	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_Na2SO4	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_K2CO3	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_Na2S	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_KCl	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_C	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_NaCl	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_Na2CO3	—	kg/kg	○ set	○ estimate	limit >>	☑ update
m_NaOH	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_Na	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_K2SO4	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_KOH	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_K	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_Cl	0	kg/kg	● set	○ estimate	limit >>	☑ update
m_Inerts	—	kg/kg	○ set	○ estimate	limit >>	☑ update

Fig. 92 Inputs smelt (a) thermodynamical properties (b) chemical composition

The input properties temperature and pressure of the smelt are set to 850°C and 1 bar, respectively. The ambient temperature (t_amb) is set to 25°C.

The mass fractions of the chemical compounds / elements which are assumed to not be present in smelt need to be set to zero, including S, SO3, KCl, NaOH, Na, K2SO4, KOH, K, Cl. The remaining chemical's mass fractions are calculated in the KRB unit.

6.3 KRB Unit



Name: KRB_INT001

Model: KRB_int

☐ update

stream_blowdown_pct	—	%	○ set ○ estimate	☑ update
sootblowing_steam	0.11	kg/kgBLS		☑ update
h_sootblowing	3068	kJ/kg		☑ update
Cu	0.002	kg/kg		☑ update
rad_heat_loss	0.24	%		☑ update
unac_loss	1	%		☑ update
margin_loss	0	%		☑ update
R	92	%		☑ update
CO_ppmv	100	ppmv		☑ update
SO2_ppmv	10	ppmv		☑ update
O2_wvb	2	%		☑ update
humidity_comb_air	0.013	kg/kg		☑ update

Fig. 93 Inputs KRB unit V2 (internal sootblowing)

The KRB unit requires the input parameters shown in figure 93 above, where:

- Sootblowing steam mass flow in kg/kgBLS = “sootblowing_steam”
- Enthalpy of internal sootblowing steam used in kJ/kg = ”h_sootblowing”
- Unburnt carbon present in smelt in kg/kg = “Cu”
- Radiation heat loss as % of heat input = “rad_heat_loss”
- Unaccounted heat loss as % of heat input = “unac_heat_loss”
- Margin heat loss as % of heat input = ”margin_loss”
- Reduction efficiency in % = ”R”
- CO concentration in wet flue gas in ppmv = “CO_ppmv”
- SO2 concentration in wet flue gas in ppmv = “SO2_ppmv”
- Excess O2 of flue gas (wet volume basis) in vol.% = “O2_wvb”
- Humidity (H2O) in combustion air in kg/kg = “humidity_comb_air”

6.4 Run Simulation

After specifying all the required inputs for this case, the simulation can be run, and the results look as shown in figure 94 below.

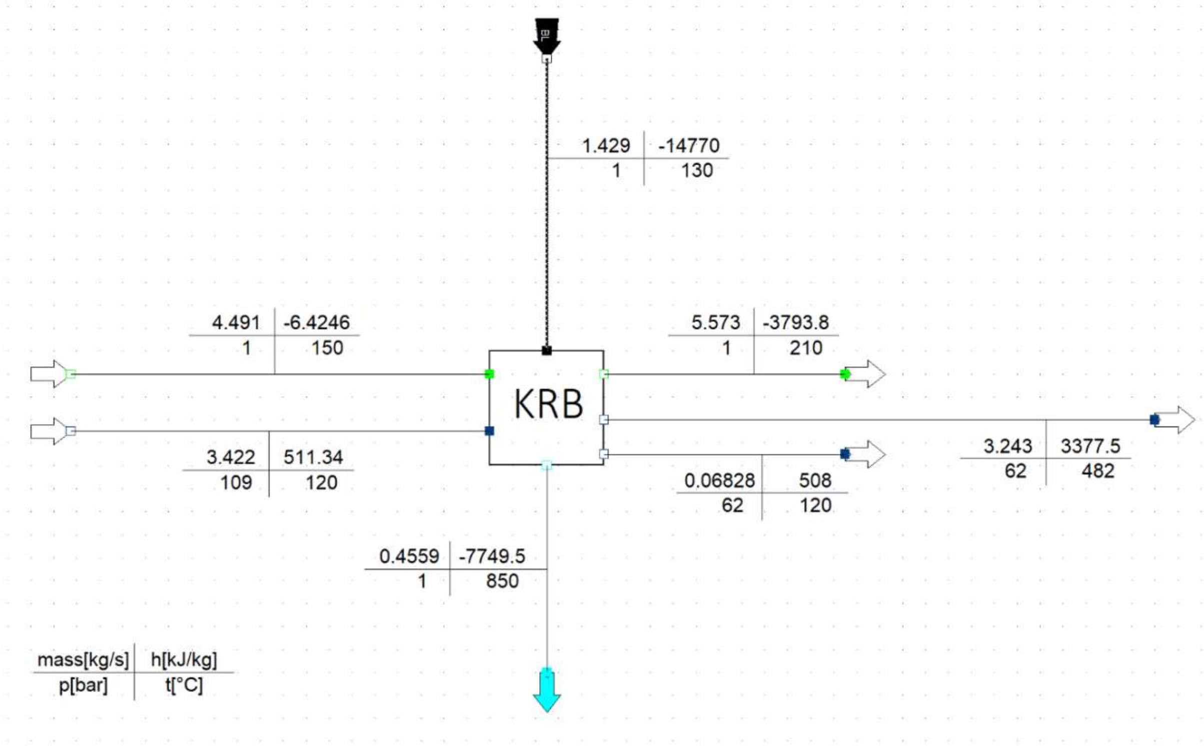


Fig. 94 Results simultation

7 Simulation and Validation

Chapter 7 is dedicated to the validation of the developed KRB Library with the focus on the KRB units. Firstly, the validity of the Base Model V1, and secondly of the Referenced Model V2 is proven.

7.1 Base Model V1 vs Tran & Grace (2018)

In the following subchapter a validation of the first model's results is carried out, in which it is compared with the obtained data from the proposed literature when considering the mentioned assumptions such as no dust precipitator and no saltcake makeup (see appendix Excel worksheet Validation Base Model V1).

7.1.1 Inputs

The following parameters (neglection of dust precipitator, saltcake makeup and recycled ash / dust) were used as inputs for the model:

INPUTS	**Value**	**Unit**
Boiler Operating Data		
Heavy (virgin) black liquor mass	1.00	kg BLS
Heavy BL gross heating value (HHV)	14000.00	kJ/kg BLS
Heavy BL solids content	70.00	% ds
Smelt reduction efficiency	92.00	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	2.00	vol. %
CO concentration in wet flue gas	100.00	ppmv
SO2 concentration in wet flue gas	10.00	ppmv
Humidity (H2O) in combustion air	0.013	kg/kg air
Sootblowing steam consumption	0.110	kg/kg BLS
Recycled ash/dust	0.00	% BLS
Makeup salt cake (as Na2SO4)	0.000	kg/kg BLS
Precipitator dust removal efficiency	0.00	%
BL temperature before indirect	125.00	C
BL temperature after indirect heater	130.00	C
Ambient air temperature	25.00	C
FD fan preheat air temperature	150.00	C
Economizer gas exit temperature	210.00	C
Smelt temperature	850.00	C
Feed water to econo. Temperature	120.00	C
Sootblowing steam source	Internal	
Sootblowing steam temperature	315.00	C
Superheater outlet steam	482.00	C
Sootblowing steam pressure	17.30	bar
Steam drum pressure	65.50	bar
Superheater outlet steam pressure	62.00	bar
Feedwater blowdown steam (as % feedwater)	2.00	%
Radiation heat loss (as % of heat input)	0.24	%
Unaccounted heat loss (as % of heat input)	1.00	%

Table 12 Inputs KRB unit V1 (Tran & Grace, 2018, p. 348)

The heat capacity and the enthalpy data are shown in tables 13 and 14.

INPUTS	**Value**	**Unit**
Heat Capacity Data		
Water	4.18	kJ/kg.C
Dry air	1.01	kJ/kg.C
Dry flue gas	1.02	kJ/kg.C
Water vapor	1.88	kJ/kg.C
Black liquor	2.95	kJ/kg.C
Smelt	1.72	kJ/kg.C

Table 13 Inputs heat capacity V1 (Tran & Grace, 2018, p. 348)

INPUTS	**Value**	**Unit**
Enthalpy data		
Smelt	1350	kJ/kg
Sulfide formation	12900	kJ/kg
Water evaporation	2442	kJ/kg
Sootblowing steam	3068	kJ/kg
Economizer feed water	508	kJ/kg
Steam drum blowdown water	1244	kJ/kg
Superheater outlet steam	3377	kJ/kg

Table 14 Inputs enthalpy V1 (Tran & Grace, 2018, p. 348)

The heavy black liquor analysis gives the input values for its chemical composition as shown in table 15.

INPUTS	**Value**	**Unit**
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	34.70	% BLS
Hydrogen (H)	3.50	% BLS
Sulfur (S)	4.20	% BLS
Sodium (Na)	19.50	% BLS
Potassium (K)	1.80	% BLS
Chlorine (Cl)	0.50	% BLS
Inerts (N, Si, Mg, Ca, Mn, etc.)	0.20	% BLS
Oxygen (O)	35.60	% BLS

Table 15 Inputs black liquor analysis (Tran & Grace, 2018, p. 349)

The required stream input properties include temperature, pressure, and chemical composition as table 16 below shows.

Stream / property	**Value**	**Unit**
Black liquor		
Temperature	25	°C
Pressure	1	bar
Smelt		
Temperature	850	°C
Pressure	1	bar
Air		
Temperature	25	°C
Pressure	1	bar
Composition set ≠ 0	$H_2O = 0.013$; $N_2 = 0.78$; $O_2 = 0.2$	kg/kg
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, CO, CO_2, H_2, H_2S, SO_2	kg/kg
Composition calculated / not set	Ar	kg/kg
Flue Gas		
Temperature	400	°C
Pressure	1	bar
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, H_2, H_2S	kg/kg
Composition calculated / not set	Ar, CO, CO_2, H_2O, N_2, O_2, SO_2	kg/kg
Feedwater		
Temperature	25	°C
Pressure	1	bar
Composition	only WATER not set = 0	kg/kg
Steam		
Temperature	482	°C
Pressure	62	bar
Composition	only WATER not set = 0	kg/kg

Table 16 Inputs stream properties V1 (Tran & Grace, 2018, p. 348)

7.1.2 Results

Energy Balance:

The following tables show heat inputs (table 17), and heat outputs (table 18).

Heat Input	**Literature**	**Simulation**	**Unit**
Heat from liquor combustion	14000.000	14000.000	kJ/kg BLS
Sensible heat of heavy black liquor	421.429	421.430	kJ/kg BLS
Sensible heat from liquor heating	20.000	20.207	kJ/kg BLS
Sensible heat in combustion air	552.253	552.250	kJ/kg BLS
Sensible heat in sootblowing steam	0.000	0.000	kJ/kg BLS
Heat in feedwater for blowdown steam	26.234	26.234	kJ/kg BLS
Total Heat Input	**15019.91542**	**15020.121**	**kJ/kg BLS**

Table 17 Results heat input V1

Heat Output	**Literature**	**Simulation**	**Unit**
Sensible heat of dry flue gas	879.728	879.730	kJ/kg BLS
Sensible heat of water vapor	281.037	281.040	kJ/kg BLS
Evaporation of combustion water	769.230	769.230	kJ/kg BLS
Evaporation of water in liquor	1046.571	1046.600	kJ/kg BLS
Sootblowing steam in flue gas	306.878	306.880	kJ/kg BLS
Sensible heat of smelt	615.531	615.530	kJ/kg BLS
Smelt reduction (Na2S formation)	1213.127	1213.100	kJ/kg BLS
Unburned carbon in smelt	65.600	65.600	kJ/kg BLS
CO formation	5.688	5.688	kJ/kg BLS
SO2 formation	0.708	0.708	kJ/kg BLS
Radiaton loss	36.048	36.048	kJ/kg BLS
Unaccounted losses	150.199	150.200	kJ/kg BLS
Total Heat Loss	**5370.344714**	**5370.3536**	**kJ/kg BLS**

Table 18 Results heat output V1

The computed results by the model are almost identical as shown in the previous tables (17 & 18). Especially the table 19 highlights the minimal errors committed by the model. Per kilogram black liquor solids fired the difference in heat to steam is 0.0024%, which is a neglectable error.

	Literature	**Simulation**	**Unit**	**Abs. error**	**Rel. error in %**
Total Heat Input	**15019.92**	**15020.12**	**kJ/kg BLS**	**0.2056**	**0.0014**
Total Heat Loss	**5370.34**	**5370.35**	**kJ/kg BLS**	**0.0089**	**0.0002**
Heat to steam	**9649.57**	**9649.80**	**kJ/kg BLS**	**0.2293**	**0.0024**

Table 19 Summary results V1

Mass Balance:

STREAMS	**Literature**	**Simulation**	**Abs. error (kg/s)**	**Rel. error in %**
Black Liquor	1.43	1.428571	4.28571E-07	0.00
Feedwater	3.41	3.4142	4.22179E-05	0.00
Air	4.49	4.4906	4.53102E-05	0.00
Blowdown	0.07	0.068285	1.84436E-06	0.00
Smelt	0.46	0.45595	8.14299E-07	0.00
Steam Production	3.35	3.3459	2.53736E-05	0.00
Flue Gas	5.57	5.57325	2.46251E-06	0.00

Table 20 Results mass balance V1

The results of the computed mass flows and the absolute and relative errors, as displayed in table 20 prove the model’s precision to the proposed model from literature (Tran & Grace, 2018). The absolute errors are assumed to be roundoff errors.

Smelt composition:

Smelt Composition	**Literature**	**Simulation**	**Unit**
Na2S	20.625	20.625	wt%
Na2SO4	3.265	3.265	wt%
NaCl	1.807	1.807	wt%
Na2CO3	66.448	66.448	wt%
K2CO3	6.977	6.977	wt%
Inerts	0.439	0.439	wt%
Unburned carbon (char)	0.439	0.439	wt%

Table 21 Results smelt composition V1

The smelt's chemical composition computed by the model gives identical results as shown in table 21.

Flue gas composition (wet mass basis):

Flue Gas Composition	**Literature**	**Simulation**	**Unit**
H2O	16.350	16.350	wt%
CO2	20.243	20.243	wt%
N2	60.691	60.691	wt%
O2	2.307	2.307	wt%
CO	100.941	100.940	ppm
SO2	23.072	23.072	ppm

Table 22 Results flue gas V1

The flue gas' chemical composition (on a wet mass basis) computed by the model gives almost identical results as illustrated in table 22. The small discrepancies are assumed due to a roundoff error as in the case of CO.

7.1.3 Summary

As shown in the previous section, the KRB unit model 1 (Base model V1) was proven to be valid in terms of estimating the energy balances' inputs and outputs, mass flows, as well as chemical compositions. The results are almost identical with the proposed state-of-the-art calculation model, considering the assumptions made to neglect the saltcake makeup, and the dust precipitator (Tran & Grace, 2018).

7.2 Referenced Model (internal) V2 vs Tran & Grace (2018)

The same case as in the previous chapter is simulated using the evolved model or Referenced Model V2, which is based on the Base Model V1, and its previously discussed and validated results.

The options set are:

- Cp = f(x_ds,t)
- H_smelt = h ideal mixture (NIST polynomials)
- Internal Sootblowing

7.2.1 Inputs

Even though the simulated case is the same, input parameters are specified in different parts in the model (unit, stream). Instead of defining most inputs in the KRB unit, in the Referenced Model V2 different properties are defined in the streams as the following tables (23-25) will illustrate.

INPUTS KRB Unit (internal sootblowing)	**Value**	**Unit**
Smelt reduction efficiency	92.00	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	2.00	vol. %
CO concentration in wet flue gas	100.00	ppmv
SO2 concentration in wet flue gas	10.00	ppmv
Humidity (H2O) in combustion air	0.013	kg/kg air
Sootblowing steam consumption	0.110	kg/kg BLS
Sootblowing steam enthalpy	3068.00	kJ/kg
Radiation heat loss (as % of heat input)	0.24	%
Unaccounted heat loss (as % of heat input)	1.00	%
Margin heat loss (as % of heat input)	0.00	%

Table 23 Inputs KRB unit V2 (Case 1) (Tran & Grace, 2018, p. 348)

The heavy black liquor composition is shown in table 24.

INPUTS	**Value**	**Unit**
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	34.70	% BLS
Hydrogen (H)	3.50	% BLS
Sulfur (S)	4.20	% BLS
Sodium (Na)	19.50	% BLS
Potassium (K)	1.80	% BLS
Chlorine (Cl)	0.50	% BLS
Inerts (N, Si, Mg, Ca, Mn, etc.)	0.20	% BLS
Oxygen (O)	35.60	% BLS

Table 24 Input black liquor analysis V2 (Case 1) (Tran & Grace, 2018, p. 349)

The stream properties and compositions of black liquor, smelt, air, flue gas, feedwater, steam, and blowdown steam are illustrated in table 25 below.

Stream / property	**Value**	**Unit**
Black liquor		
Temperature (BL temp after ind. heater)	130	°C
Ambient temperature	25	°C
Pressure	1	bar
Smelt reduction efficiency	0.92	1
Heavy black liquor solid content	0.7	kg/kg
Higher heating value (HHV)	14000	kJ/kg
Mass flow	1	kgBLS/s
Smelt		
Temperature	850	°C
Ambient temperature	25	°C
Pressure	1	bar
Air		
Temperature (temp after air preheat)	150	°C
Ambient temperature	25	°C
Pressure	1	bar
Composition set ≠ 0	$H_2O = 0.013$; $N_2 = 0.78$; $O_2 = 0.2$	kg/kg
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, CO, CO_2, H_2, H_2S, SO_2	kg/kg
Composition calculated / not set	Ar	kg/kg
Flue Gas		
Temperature	210	°C
Ambient temperature	25	°C
Pressure	1	bar
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, H_2, H_2S	kg/kg
Composition calculated / not set	Ar, CO, CO_2, H_2O, N_2, O_2, SO_2	kg/kg
Feedwater		
Temperature (feedwater to economizer temp)	120	°C
Ambient temperature	25	°C
Pressure	109	bar
Composition	only WATER not set = 0	kg/kg
Steam		
Temperature	482	°C
Ambient temperature	25	°C
Pressure	62	bar
Composition	only WATER not set = 0	kg/kg
Blowdown		
Enthalpy	508	kJ/kg
Ambient temperature	25	°C
Pressure	62	bar
Mass flow	0.068283	kg/s
Composition	only WATER not set = 0	kg/kg

Table 25 Input stream properties V2 (Case 1) (Tran & Grace, 2018, p. 348)

7.2.2 Results

Energy balance:

As can be seen in table 26, the heat from liquor combustion, as calculated in the Referenced Model V2, is reducing the higher heating value by the losses due to evaporation (already as a reduced heat input), instead of accounting for an additional loss. Hence, table 26 shows the lower heating value as a heat input.

Heat Input	**Literature**	**Simulation**	**Unit**
Heat from black liquor combustion (LHV_wet)	12184.2	12191.0	kJ/kg BLS
Total sensible heat of heavy black liquor	441.4	339.0	kJ/kg BLS
Sensible heat in combustion air	552.3	574.3	kJ/kg BLS
Sensible heat in sootblowing steam	0.0	0.0	kJ/kg BLS
Heat in feedwater for blowdown steam	26.2	27.5	kJ/kg BLS
Total Heat Input	**13204.1**	**13131.9**	**kJ/kg BLS**

Table 26 Results heat input V2 (Case 1)

The highest total error of the heat inputs calculated in the Referenced Model V2 is the heat input “total sensible heat of heavy black liquor”. This is because of the two different approaches of setting black liquor heat capacity. In Tran & Grace (2018) a constant value, 2.95 kJ/(kg*C) is used, whereas in this simulation cp and cp_amb are modelled as a function of the black liquor temperature (t in °C) as well as the dry solid content (x_ds as a fraction) following the formula from Tikka (2008). The fixed heat capacities and the calculated ones are shown in table 27.

	cp	**cp_amb**
Simulation	2.370	2.829
Literature	2.950	2.950
Ratio	**0.803**	**0.959**

Table 27 Results heat capacity V2 (Case 1)

The ratio of the specific heat capacity at 130°C and a dry solid content at 70% with the fixed cp from literature already gives a value of approximately 0.8. Furthermore, the computed value for the heat capacity at ambient conditions is slightly lower than the one proposed in Tran & Grace (2018), resulting in the high disparity in the results of the heat inputs of approximately 23.3%.

Further discrepancies that should be noted are the ones in the sensible heat in combustion air. The calculation of the required enthalpies in IPSEpro using DLLs with its exact chemical composition is assumed to be more precise than the approach applied in Tran & Grace (2018).

The differences of the literature and the simulation of the total sensible heat of flue gas can be explained analogously. In the simulation each chemical component has an impact on the sensible heat / the enthalpy of the flue gas, whereas in Tran & Grace (2018) the composition does not impact the enthalpy.

The calculated results of the smelt reduction, the unburned carbon in smelt, the CO formation, and the SO2 formation are identical because following the identical approach of computing them.

The disparity of the radiation loss and the unaccounted losses can be explained due to its calculation as a percentage of the total heat input.

Heat Output	**Literature**	**Simulation**	**Unit**
Total sensible heat flue gas	1160.8	1192.5	kJ/kg BLS
Sootblowing steam in flue gas	306.9	306.9	kJ/kg BLS
Total loss with flue gas	**1467.6**	**1499.4**	**kJ/kg BLS**
Sensible heat smelt	615.5	607.7	kJ/kg BLS
Smelt reduction (Na2S formation)	1213.1	1213.1	kJ/kg BLS
Unburned carbon in smelt	65.6	65.6	kJ/kg BLS
CO formation	5.7	5.7	kJ/kg BLS
SO2 formation	0.7	0.7	kJ/kg BLS
Radiation loss (0.24%)	29.2	31.6	kJ/kg BLS
Unaccounted losses (1%)	121.8	131.5	kJ/kg BLS
Margin Loss (0%)	0.0	0.0	kJ/kg BLS
Total Heat Loss	**3519.4**	**3555.2**	**kJ/kg BLS**

Table 28 Results heat output V2 (Case 1)

Overall, the estimated total heat inputs by the simulation vary only by about 0.55 %. The total heat losses deviate by -1.02% and the heat to steam by differs by 1.12%. The committed errors are around 1% can be stated to be valid.

	Literature	**Simulation**	**Unit**	**Abs. error**	**Rel. error in %**
Total Heat Input	**13204.1**	**13131.9**	**kJ/kg BLS**	**72.22**	**0.55**
Total Heat Loss	**3519.4**	**3555.2**	**kJ/kg BLS**	**-35.84**	**-1.02**
Heat to steam	**9684.7**	**9576.7**	**kJ/kg BLS**	**108.06**	**1.12**

Table 29 Summary results V2 (Case 1)

Mass balance:

STREAMS	**Literature**	**Simulation**	**Abs. error in (kg/s)**	**Rel. error in %**
Black Liquor	1.4286	1.4286	-2.857E-05	-0.002
Feedwater	3.4142	3.4216	-7.442E-03	-0.218
Air	4.4906	4.4906	0.000E+00	0.000
Blowdown	0.0683	0.0683	0.000E+00	0.000
Smelt	0.4559	0.4559	4.919E-05	0.011
Steam to Mill	3.2358	3.2433	-7.500E-03	-0.232
Flue Gas	5.5732	5.5732	4.754E-05	0.001

Table 30 Results mass balance V2 (Case 1)

The biggest errors committed in calculating the mass streams are the ones on the waterside, including the feedwater stream and the steam to mill mass flows, which are 0.218% and 0.232% higher than the ones from literature respectively. The differences of the calculated mass flows between the simulation model and the literature are within tolerable boundaries.

Chemical Compositions:

Since the Base Model (V1) and the Referenced Model (V2) calculate the composition of the flue gas and the smelt identically the same results as in chapter 7.1.2 are obtained (see table 21 and table 22).

7.2.3 Summary

The major differences in the calculations are the total sensible heat of heavy black liquor, the sensible heat in smelt, the sensible heat in combustion air and flue gas.

The total sensible heat of heavy black liquor is due to the option of computing the heat capacity as a function of black liquor temperature and the dry solid content (x_ds as a fraction) instead of a constant value.

The difference of the results of the sensible heat in combustion air and flue gas is also due to the neglection of the exact composition of air and flue gas (Tran & Grace, 2018).

The consequence of the differences in the mentioned heat inputs and heat losses results in a discrepancy in the heat to steam generated, which then further impacts the mass flows on the waterside.

The chemical compositions calculated are identical with the results from the state-of-the-art model when neglecting the dust precipitator and the saltcake makeup.

The overall results look promising, errors could be identified and explained.

7.3 Referenced Model V2 vs Vakkilainen (2005) (calculation example)

The Referenced Model V2 was proven to be valid in comparison with state-of-the-art calculation approach proposed in Tran & Grace (2018). A further validation is carried out comparing the developed model V2 with the calculation example from literature in Vakkilainen (2005). For validating the chemical compositions of smelt the results from the simulation are compared with the excel sheet's output data (see appendix Excel Worksheet Validation Vakkilainen (2005) calculation example) based on the calculation approach proposed in Vakkilainen (2005) with the mere difference of neglecting the dust precipitator, the saltcake makeup, and setting the Boron in black liquor to zero and in return increasing the input of inerts. The heat inputs, heat losses and mass flows are compared with the ones from Vakkilainen (2005).

The options set are:

- Cp = f(x_ds,t)
- H_smelt = h ideal mixture (NIST polynomials)
- External Sootblowing

7.3.1 Input

The inputs for the KRB unit and for the stream properties are shown in table 31 and table 32 below.

INPUTS KRB Unit (external sootblowing)	**Value**	**Unit**
Smelt reduction efficiency	96.000	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	3.000	vol. %
CO concentration in wet flue gas	100.000	ppmv
SO2 concentration in wet flue gas	52.000	ppmv
Humidity (H2O) in combustion air	0.0135	kg/kg air
Radiation heat loss (as % of heat input)	0.283	%
Unaccounted heat loss (as %of heat input)	0.300	%
Margin heat loss (as % of heat input)	0.500	%

Table 31 Inputs KRB unit V2 (Case 2) (Vakkilainen, 2005)

Stream / property	**Value**	**Unit**
Black liquor		
Temperature (BL temp after ind. heater)	140	°C
Ambient temperature	0	°C
Pressure	1	bar
Smelt reduction efficiency	0.96	1
Heavy black liquor solid content	0.85	kg/kg
Higher heating value (HHV)	13000	kJ/kg
Mass flow	1	kgBLS/s
Smelt		
Temperature	850	°C
Ambient temperature	25	°C
Pressure	1	bar
Air		
Temperature (temp after air preheat)	108.8	°C
Ambient temperature	0	°C
Pressure	1	bar
Composition set ≠ 0	$H_2O = 0.013$; $N_2 = 0.78$; $O_2 = 0.2$	kg/kg
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, CO, CO_2, H_2, H_2S, SO_2	kg/kg
Composition calculated / not set	Ar	kg/kg
Flue Gas		
Temperature (after economizer)	155	°C
Ambient temperature	0	°C
Pressure	1	bar
Composition set = 0	WATER, C_2H_6, C_3H_8, CH_4, H_2, H_2S	kg/kg
Composition calculated / not set	Ar, CO, CO_2, H_2O, N_2, O_2, SO_2	kg/kg
Feedwater		
Temperature (feedwater to economizer temp)	115	°C
Ambient temperature	0.1	°C
Pressure	110	bar
Composition	only WATER not set = 0	kg/kg
Steam		
Temperature	490	°C
Ambient temperature	0.1	°C
Pressure	91	bar
Composition	only WATER not set = 0	kg/kg
Blowdown		
Temperature	100	°C
Ambient temperature	0.1	°C
Pressure	100	bar
Mass flow	0.1	kg/s
Composition	only WATER not set = 0	kg/kg
Ext. sootblowing		
Temperature	344.5	°C
Ambient temperature	0.1	°C
Pressure	50	bar
Mass flow	0.15	kg/s
Composition	only WATER not set = 0	kg/kg

Table 32 Input stream properties V2 (Case 2) (Vakkilainen, 2005)

The ambient temperature of the feedwater stream, steam stream, blowdown stream and sootblowing stream was set to 0.1°C, which is the boundary limit of application for the water stream in IPSEpro, whereas an ambient temperature of 0° Celsius is proposed in Vakkilainen (2005).

For the smelt stream the limit of application for the implemented NIST polynomials is at 25°C, so the ambient temperature is set at that mentioned smallest possible value.

Remark: With the sootblowing steam's temperature and pressure set at 344.5°C and 50 bar an enthalpy of 3054.6 kJ/kg is calculated by IPSEpro instead of the defined 3054.8 kJ/kg as from literature.

The heavy black liquor analysis from Vakkilainen (2005) is adapted: Boron (B) is set to 0% and the remaining 0.5% is set as inerts instead (Vakkilainen, 2005, p. 2). All the other chemical components are kept identical as shown in table 33.

INPUTS	**Value**	**Unit**
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	32.50	% BLS
Hydrogen (H)	3.30	% BLS
Sulfur (S)	6.10	% BLS
Sodium (Na)	20.00	% BLS
Potassium (K)	3.00	% BLS
Chlorine (Cl)	0.25	% BLS
Nitrogen (N)	0.09	% BLS
Boron (B)	0.00	% BLS
Inerts	0.60	% BLS
Oxygen (O)	34.16	% BLS

Table 33 Inputs black liquor analysis V2 (Case 2) (Vakkilainen, 2005)

7.3.2 Results

Heat Input	**Literature**	**Simulation**	**Unit**
Heat from black liquor combustion (LHV_wet)	11849.8	11850.0	kJ/kg BLS
Total sensible heat of heavy black liquor	434.8	305.2	kJ/kg BLS
Sensible heat in combustion air	471.9	490.9	kJ/kg BLS
Sensible heat in sootblowing steam / corrected	83.1	458.11 / 48.13	kJ/kg BLS
Heat in feedwater for blowdown steam	0.0	42.6	kJ/kg BLS
Infiltration	6.8	0.0	kJ/kg BLS
Total Heat Input	**12846.4**	**12736.8**	**kJ/kg BLS**

Table 34 Results heat inputs V2 (Case 2) (Vakkilainen, 2005, p. 7)

The calculated heat inputs are displayed in table 34. The total sensible heat of heavy black liquor differs notably in value as it was the case in the previous validation due to the fact that in Vakkilainen (2005) a constant value of 2.94 kJ/(kg*C) is used, whereas in this simulation cp and cp_amb are modelled as a function of the black liquor temperature (t in °C) and the dry solid content (x_ds as a fraction) following the formula in (Tikka, 2008). The constant heat capacity and the one calculated in the model are shown in table 35.

	cp	**cp_amb**
Simulation	2.370	2.829
Literature	2.940	2.940
Ratio	**0.806**	**0.962**

Table 35 Results heat capacity V2 (Case 2) (Vakkilainen, 2005, p. 7)

The ratio of the heat capacities at 140°C and the dry solid content at 85% with the fixed cp from literature already gives a value of approximately 0.8. Furthermore, the computed value for the heat capacity at ambient conditions is slightly lower than the one proposed in Vakkilainen (2005) with a ratio of about 0.96. These differences of modeling black liquor heat capacity influence the calculated total sensible heat significantly.

Further discrepancies that should be mentioned are the ones in the sensible heat in combustion air. The calculation of the required enthalpies in IPSEpro using DLLs considering its exact chemical composition is assumed to be more precise than approach applied in Vakkilainen (2005), where a fixed/constant heat capacity is used.

The sensible heat in sootblowing in the simulation is 458.11 kJ/kgBLS. When correcting it with the loss due to sootblowing steam in flue gas of 410.01 kJ/kgBLS, which is not accounted for in Vakkilainen (2005), it gives a corrected value of 48.13 kJ/kgBLS. The big discrepancy is due to the different lower limits of enthalpy set. In Vakkilainen (2005) it is set at 2500.9 kJ/kg. In the developed model the lower state is defined at ambient conditions but therefore considering the heat loss of sootblowing steam in flue gas (Tran & Grace, 2018).

In Vakkilainen (2005) the heat in feedwater for the blowdown steam is not considered. Furthermore, the heat input due to infiltration air is accounted for individually but could be added to the sensible heat input of combustion air instead. Table 36 shows the heat outputs for this validation.

Heat Output	**Literature**	**Simulation**	**Unit**
Total sensible heat flue gas	903.8	910.6	kJ/kg BLS
Sootblowing steam in flue gas / corrected	0.0	410.01 / 0	kJ/kg BLS
Total loss with flue gas corrected	**903.8**	**910.6**	**kJ/kg BLS**
Sensible heat smelt	509.0	592.7	kJ/kg BLS
Smelt reduction (Na2S formation)	1607.3	1832.0	kJ/kg BLS
Unburned carbon in smelt	0.0	65.6	kJ/kg BLS
CO formation	0.0	5.3	kJ/kg BLS
SO2 formation	0.3	3.4	kJ/kg BLS
Reduction to K2S	134.0	0.0	kJ/kg BLS
Autocausticization	72.6	0.0	kJ/kg BLS
Radiation loss	36.4	37.2	kJ/kg BLS
Unaccounted losses	38.5	39.4	kJ/kg BLS
Margin Loss	64.2	65.7	kJ/kg BLS
Total Heat Loss	**3366.1**	**3551.9**	**kJ/kg BLS**

Table 36 Heat outputs V2 (Case 2) (Vakkilainen, 2005, p. 7)

The differences of the literature and the simulation of the total sensible heat of flue gas can be explained analogously. In the simulation each chemical component has an impact on the sensible heat / the enthalpy of the flue gas. In Vakkilainen (2005) the same heat is computed by using a fixed specific heat capacity (Q°=m°*cpΔT). The correction of the heat loss of sootblowing steam is due to the previously mentioned difference in the two proposed approaches. The corrections are chosen for the purpose of reaching a more consistent comparison of the models.

The sensible heat lost with the smelt is calculated to be higher as the estimation in Vakkilainen (2005). Possible reasons for this discrepancy are the simplified approach in literature to neglect the impact of the smelt's chemical composition on its enthalpy. The calculated smelt enthalpy in the Referenced Model V2 on the other hand does account for its chemical composition, even though modeling it as an ideal mixture (neglecting enthalpy of mixing of the individual components).

The heat loss due to the smelt reduction varies because of two main reasons: the first one is due to the different approach of calculating the smelt's chemical composition resulting in dissimilar mass fractions used for the computation of the heat losses, which leads to a and proportional influence of the errors committed. The second reason is due to the different enthalpies of formations considered in the two models. In Vakkilainen (2005) the energy of formation of Na2S is 13099 kJ/kg. In the developed KRB model the value of 12900 kJ/kg is based on the approach proposed in Tran & Grace (2018). When considering the following assumptions used in the developed model (neglecting Boron, and saltcake makeup from collected dust) and applying the same calculation approach proposed in Vakkilainen (2005), the heat loss computed would be notably higher value of 2016.2 kJ/kg (= 0.154 kgNa2S/kgBLS * 13099 kJ/kg) instead of 1607.3 kJ/kg (see Excel worksheet Validation Vakkilainen (2005) calculation example).

The heat losses due to unburned carbon in smelt, and the formation of CO are not considered in Vakkilainen (2005). The calculations of SO2 formation are different because of using unequal enthalpies of formation: 5531 kJ/kg in Vakkilainen (2005), and 5506 kJ/kg in Tran & Grace (2018) respectively.

The reduction loss from K2S is not considered in the developed model. This is because of following the calculation approach for the smelt composition proposed in Tran & Grace which assumes potassium exist in the smelt only as K2CO3. This greatly influences the complexitiy of the calculation especially when considering heat losses due to formations of K2S which are considered in Vakkilainen (2005).

Since the calculation approach in Tran & Grace (2018) does not include the chemical component Boron, no autocausticization of Na3BO3 is accounted for in the developed model. The differences in the radiation loss, the unaccounted losses and the margin loss are due to its calculation method as a percentage of the total heat input and therefore vary proportionally.

	Literature	**Simulation**	**Unit**	**Abs. error**	**Rel. error in %**
Total Heat Input	**12846.4**	**12736.8**	**kJ/kg BLS**	**109.56**	**0.85**
Total Heat Loss	**3366.1**	**3551.9**	**kJ/kg BLS**	**-185.82**	**-5.52**
Heat to steam	**9480.3**	**9184.9**	**kJ/kg BLS**	**295.38**	**3.12**

Table 37 Summary Results V2 (Case 2) (Vakkilainen, 2005, p. 7)

The relative errors committed by the developed model in reference to the calculations in Vakkilainen (2005) are 0.85% for the heat input, -5.52% for the heat loss and 3.12% for the heat to steam. The difference in the sensible heat inputs of black liquor is due to the dissimilar specific heat capacities influencing the result strongly. Furthermore, the calculations of heat input of sootblowing steam, even after making correcting for reaching common grounds vary noticeable due to the different approaches of computation.

The discrepancy of heat losses between the two models is mainly due to the assumptions made for the calculations of the chemical composition of smelt. This greatly influences the various heat losses accounted for.

Even though following different calculation approaches, the results calculated for the energy balance by the developed KRB model prove to be plausible and can therefore be seen as valid.

Mass balance:

STREAMS	Literature	Simulation	Abs. error in (kg/s)	Rel. error in %
Black Liquor	1.1755	1.1765	-1.000E-03	-0.085
Feedwater	3.3700	3.3021	6.790E-02	2.015
Air (+ Infiltration)	4.4170	4.4203	-3.300E-03	-0.075
Sootblowing steam (external)	0.1500	0.1500	0.000E+00	0.000
Blowdown	0.1000	0.1000	0.000E+00	0.000
Smelt (+ recycled ash)	0.4770	0.4740	2.970E-03	0.623
Dust loss	0.00038	0	3.800E-04	100.000
Steam to Mill	3.2700	3.2021	6.790E-02	2.076
Flue Gas	5.2650	5.2718	-6.800E-03	-0.129

Table 38 Results mass balance V2 (Case 2)

The computed mass flows from the simulation as well as its counterpart from Vakkilainen (2005) are shown in table 38. The largest errors in the estimation of the mass flows by the developed model are the ones on the waterside, including the feedwater stream and the steam to mill mass flow, which differ by 2.015% and 2.076% respectively. This result is a consequence of the errors made (relative to ones proposed by literature) in the calculations for the heat inputs and heat outputs, leading to a 3.12% difference in the heat to steam computed. The smelt mass flow in Vakkilainen (2005) is added up with the ash recycled from dust precipitator which results in a mass flow of 0.477 kg/s, whereas the estimated mass flow from the developed model is 0.474 kg/s. This gives a relative error of 0.623%. The dust loss is not considered in the KRB unit model. The air mass flow from Vakkilainen (2005) is added up with the infiltration air mass flow, which is already considered as such in the developed model based on the calculation approach proposed in Tran & Grace (2018). The computed air mass flow (corrected with infiltration air), and the flue gas mass flow differ only slightly from the results in literature overestimating them only by 0.075% and 0.129% respectively.

Smelt composition:

For the validation of the chemical compositions of smelt the results from the simulation are compared with the excel sheet's output data (see appendix Excel Worksheet Validation Vakkilainen (2005) calculation example) based on the calculation approach proposed in Vakkilainen (2005) with the mere difference of neglecting the dust precipitator, the saltcake makeup, and setting the Boron in black liquor to zero and in return increasing the input of inerts.

The assumption made in Tran & Grace (2018) that potassium exist in the smelt only as K2CO3 has a great impact on the chemical compounds and its mass fractions as can be see in table 39 below. Hence adding up various potassium compounds as calculated in Vakkilainen (2005) gives 10.45% of smelt compositon in comparison to 11.19% K2CO3 in the one predicted by the simulation. Two other compounds that differ noticable are Na2S and Na2CO3. The other parts of the smelt composition are relatively well estimated.

Smelt Composition	**Literature**	**Simulation**	**Unit**
K2CO3	5.95	11.19	wt%
K2S	4.14	0.00	wt%
K2SO4	0.27	0.00	wt%
KCI	0.09	0.00	wt%
Sum K-compounds	**10.45**	**11.19**	**wt%**
Na2S	33.20	29.96	wt%
Na2SO4	2.52	2.27	wt%
NaCl	0.82	0.87	wt%
Na2CO3	51.73	54.03	wt%
Na3BO3	0.00	0.00	wt%
NaBO2	0.00	0.00	wt%
Inerts	1.29	1.27	wt%
Unburned carbon (char)	0.00	0.42	wt%
Total	**100.00**	**100.00**	**wt%**

Table 39 Results smelt composition V2 (Case 2)

7.3.3 Summary

The assumptions made for the calculations of the smelt chemical composition have a big impact on the energy balance resulting in an overestimation of the heat losses by the developed model by 5.52% relative to the data from Vakkilainen (2005). Interestingly the calculated mass flows differ by only 2% on the waterside (feedwater, steam to mill) even though following different approaches and assumptions. Hence the results of the simulation prove to be plausible and can therefore be seen as valid.

7.4 Referenced Model V2 vs Vakkilainen (2005) (tables)

The following validation is based on the results presented in Vakkilainen (2005) in tabulated format which gives an overview of how each mass flow, heat input and heat output varies when increasing the black liquor dry solid content from 65% to 90% in 5-%-steps, whereas the dry solid mass flow is kept almost constant. The two mentioned restrictions result in a decrease of the total mass flow of black liquor from 53.4 to 38.5 kg/s as an input parameter.

The aim of this validation is to prove that the developed model follows similar gradients and changes caused by the alterations of the mentioned dry solid content.

The general options set are:

- Cp = f(x_ds,t)
- H_smelt = h ideal mixture (NIST polynomials)
- External Sootblowing

7.4.1 Input

The inputs specified in Vakkilainen (2005) for the simulation case are considered, the ones that are not mentioned but required by the model are taken from the previous case (chapter 7.3) due to its similarities.

INPUTS KRB Unit (external sootblowing)	**Value**	**Unit**
Smelt reduction efficiency	95.000	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	3.000	vol. %
CO concentration in wet flue gas	100.000	ppmv
SO2 concentration in wet flue gas	52.000	ppmv
Humidity (H2O) in combustion air	0.0135	kg/kg air
Radiation heat loss (as % of heat input)	0.283	%
Unaccounted heat loss (as % of heat input)	0.300	%
Margin heat loss (as % of heat input)	0.500	%

Table 40 Inputs KRB unit V2 (Case 3) (Vakkilainen, 2005, p. 9)

The ambient temperature of feedwater, steam, blowdown and sootblowing is set to 0.1°C, which is the lower boundary limit of application for water streams in IPSEpro. In Vakkilainen (2005) instead a value of 0°C is considered.

For the smelt stream the lower limit of application for the implemented NIST polynomials is at 25°C, so the ambient temperature is set at that mentioned smallest possible value.

The air temperature was calculated through accounting for primary, secondary, and tertiary air temperature with their respective percentage [= (50%+35%) *120°C + 15%*50°C] (Vakkilainen, 2005). The input values for the stream properties are shown in table 41.

Remark: With sootblowing steam's temperature and pressure set at 344.5°C and 50 bar an enthalpy of 3054.6 kJ/kg is calculated by IPSEpro instead of defined 3054.8 kJ/kg as from literature.

Stream / property	**Value**	**Unit**
Black liquor		
Temperature (BL temp after ind. heater)	140	°C
Ambient temperature	0	°C
Pressure	1	bar
Smelt reduction efficiency	0.95	1
Heavy black liquor solid content	0.65 ÷ 0.9	kg/kg
Higher heating value (HHV)	14000	kJ/kg
Total mass flow	53.4 ÷ 38.5	kg/s
Smelt		
Temperature	850	°C
Ambient temperature	25	°C
Pressure	1	bar
Air		
Temperature (temp after air preheat)	109.5 [=(50%+35%) *120°C+15%*50°C]	°C
Ambient temperature	0	°C
Pressure	1	bar
Composition set ≠ 0	H2O = 0.013; N2 = 0.78; O2 = 0.2	kg/kg
Composition set = 0	WATER, C2H6, C3H8, CH4, CO, CO2, H2, H2S, SO2	kg/kg
Composition calculated / not set	Ar	kg/kg
Flue Gas		
Temperature (after economizer)	150	°C
Ambient temperature	0	°C
Pressure	1	bar
Composition set = 0	WATER, C2H6, C3H8, CH4, H2, H2S	kg/kg
Composition calculated / not set	Ar, CO, CO2, H2O, N2, O2, SO2	kg/kg
Feedwater		
Temperature (feedwater to economizer temp)	115	°C
Ambient temperature	0.1	°C
Pressure	109	bar
Composition	only WATER not set = 0	kg/kg
Steam		
Temperature	490	°C
Ambient temperature	0.1	°C
Pressure	90	bar
Composition	only WATER not set = 0	kg/kg
Blowdown		
Temperature	100	°C
Ambient temperature	0.1	°C
Pressure	100	bar
Mass flow	0.5	kg/s
Composition	only WATER not set = 0	kg/kg
Ext. sootblowing		
Temperature	344.5	°C
Ambient temperature	0.1	°C
Pressure	50	bar
Mass flow	5	kg/s
Composition	only WATER not set = 0	kg/kg

Table 41 Inputs stream properties V2 (Case 3) (Vakkilainen, 2005, p. 9)

7.4.2 Results

For displaying the results, the format of the table in Vakkilainen (2005) was used. The exiting streams of mass and the heat losses were removed of its negative sign. Further entries that are accounted for in the developed model were added but kept blank in the dataset from literature since they are not considered. The values used for this validation are shown in table 42 and table 43.

Literature:

Liquor dry solids	**%**	**65**	**70**	**75**	**80**	**85**	**90**
Liquor flow	kg/s	53.4	49.6	46.3	43.4	40.8	38.5
Air flow	kg/s	161.9	161.9	161.9	161.9	161.9	161.9
Sootblowing	kg/s	5	5	5	5	5	5
Ash and dust	kg/s	3.5	3.5	3.5	3.5	3.5	3.5
Smelt flow	kg/s	12.8	12.8	12.8	12.8	12.8	12.8
Smelt + ash and dust	kg/s	16.3	16.3	16.3	16.3	16.3	16.3
Flue gas flow	kg/s	204	200.2	196.9	194	191.4	189.2
Steam flow	kg/s	124.6	127.5	130.1	132.3	134.3	136
Black liquor LHV,	kJ/kgds	11923	12191	12423	12627	12806	12966
Sensible heat in BL	kJ/kgds	569	528	493	462	435	411
Air preheating	kJ/kgds	509	509	509	509	509	509
Heat in feedwater for blowdown steam	kJ/kgds						
Sootblowing	kJ/kgds	80	80	80	80	80	80
Total heat available	kJ/kgds	13080	13307	13505	13677	13829	13965
Heat in smelt	kJ/kgds	545	545	545	545	545	545
Reduction	kJ/kgds	1024	1024	1024	1024	1024	1024
Heat in wet FG	kJ/kgds	976	958	942	928	916	905
SO2 formation	kJ/kgds						
CO formation	kJ/kgds						
Unburned carbon in smelt	kJ/kgds						
Radiation Loss	kJ/kgds						
Unaccounted losses	kJ/kgds						
Margin Loss	kJ/kgds						
Sootblowing loss	kJ/kgds						
Unacc.etc. losses (sum)	kJ/kgds	142	144	146	148	150	151
Total losses	kJ/kgds	2687	2671	2657	2645	2635	2625
Heat for steam	kJ/kgds	10393	10636	10847	11032	11194	11339

Table 42 Results (Case 3) (Vakkilainen, 2005, p. 10)

Simulation:

Liquor dry solids	**%**	**65**	**70**	**75**	**80**	**85**	**90**
Liquor flow	kg/s	53.4	49.6	46.3	43.4	40.8	38.5
Air flow	kg/s	167.0	166.0	165.2	164.4	163.5	162.7
Sootblowing	kg/s	5.0	5.0	5.0	5.0	5.0	5.0
Ash and dust	kg/s	0.0	0.0	0.0	0.0	0.0	0.0
Smelt flow	kg/s	15.4	15.4	15.4	15.4	15.4	15.4
Smelt + ash and dust	kg/s	15.4	15.4	15.4	15.4	15.4	15.4
Flue gas flow	kg/s	210.0	205.2	201.1	197.4	193.9	190.8
Steam flow	kg/s	118.0	120.9	123.3	125.4	127.1	128.6
Black liquor LHV,	kJ/kgds	11923	12191	12423	12627	12806	12966
Sensible heat in BL	kJ/kgds	530	465	407	354	305	259
Air preheating	kJ/kgds	540	537	534	531	529	527
Heat in feedwater for blowdown steam	kJ/kgds	6	6	6	6	6	6
Sootblowing (corrected)	kJ/kgds	48	48	48	48	48	48
Total heat available	kJ/kgds	13439	13639	13810	13958	14087	14198
Heat in smelt	kJ/kgds	591	591	591	591	591	591
Reduction	kJ/kgds	1423	1423	1424	1424	1424	1424
Heat in wet FG (w/o sootblowing loss)	kJ/kgds	1048	1012	981	954	931	909
SO2 formation	kJ/kgds	4	4	4	4	4	4
CO formation	kJ/kgds	6	6	6	6	6	5
Unburned carbon in smelt	kJ/kgds	66	66	66	66	66	66
Radiation Loss	kJ/kgds	38	39	39	40	40	40
Unaccounted losses	kJ/kgds	40	41	41	42	42	43
Margin Loss	kJ/kgds	67	68	69	70	70	71
Sootblowing loss	kJ/kgds	392	392	392	392	393	393
Unacc.etc. losses (sum)	kJ/kgds	146	148	150	151	153	154
Total losses	kJ/kgds	3675	3641	3612	3587	3565	3546
Heat for steam	kJ/kgds	9764	9997	10198	10371	10522	10653

Table 43 Results simulation Referenced Model V2 (Case 3)

7.4.3 Summary

Similar overall insights as from the simulation in chapter 7.3 are gained:

The developed model tends to

- Overestimate the air and flue gas mass flows and the total heat losses.
- Underestimate the heat to steam and therefore the steam mass flow.

in relative comparison with Vakkilainen (2005). On the contrary the total heat available (total heat input) is larger for each output generated by the simulation. The heat input's discrepancies from sootblowing show equal characteristics because of their different approaches of computation. The overall behavior of the total heat available, the total heat loss and the heat to steam as a function of the dry solids content of black liquor fired are shown for the data from literature (Lit) and the simulations (Sim) in figures 95 a, b, c, respectively.

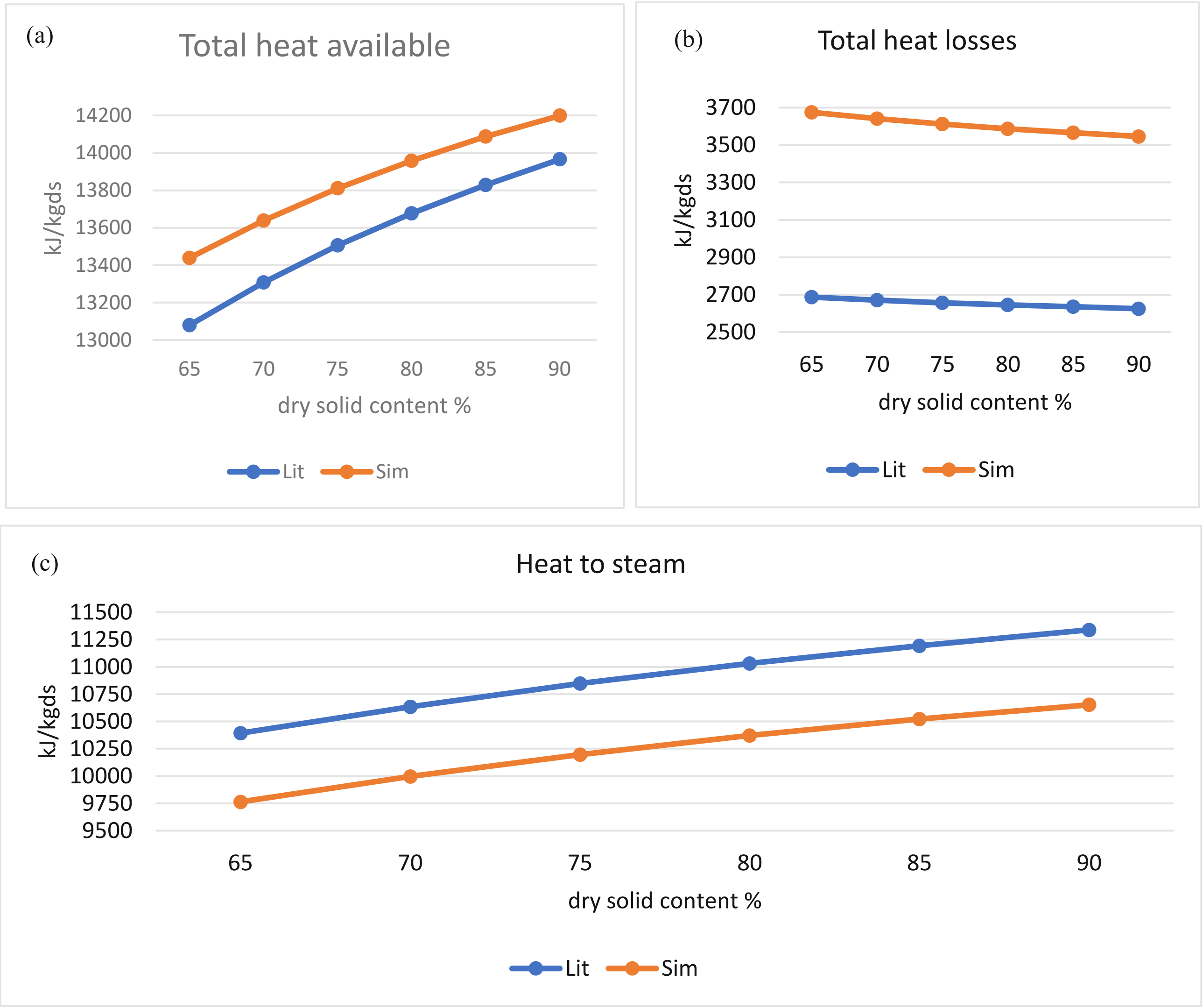


Fig. 95 Comparisons of literature and simulation results (a) total heat available (b) total heat losses (c) heat to steam as functions of dry solid content in %

The explanations for the discrepancies shown in figure 95 are the following:

The air mass flow decreases as the dry solid content increases in the calculation approach followed by the developed model, whereas the mass flow in Vakkilainen (2005) is kept constant.

An increased heat input from sensible heat in air and a decreased sensible heat loss with exiting flue gas referenced to kg dry solids is a logical consequence of the heightened dry solids content / the lowered total mass of black liquor combusted, when setting the input parameter of excess air in flue gas as constant. These facts underline the difference of the underlying calculation approaches proposed by Vakkilainen (2005) and Tran & Grace (2018), as used in the developed model.

Additionally, the deviation of the sensible heat in black liquor, which had previously already caused discrepancies, is noticeable. Again, the influence of a non-fixed heat capacity, depending on the black liquor temperature and the dry solid content impacts the results strongly, especially when firing black liquor with a higher dry solid content as shown in figure 96 (a).

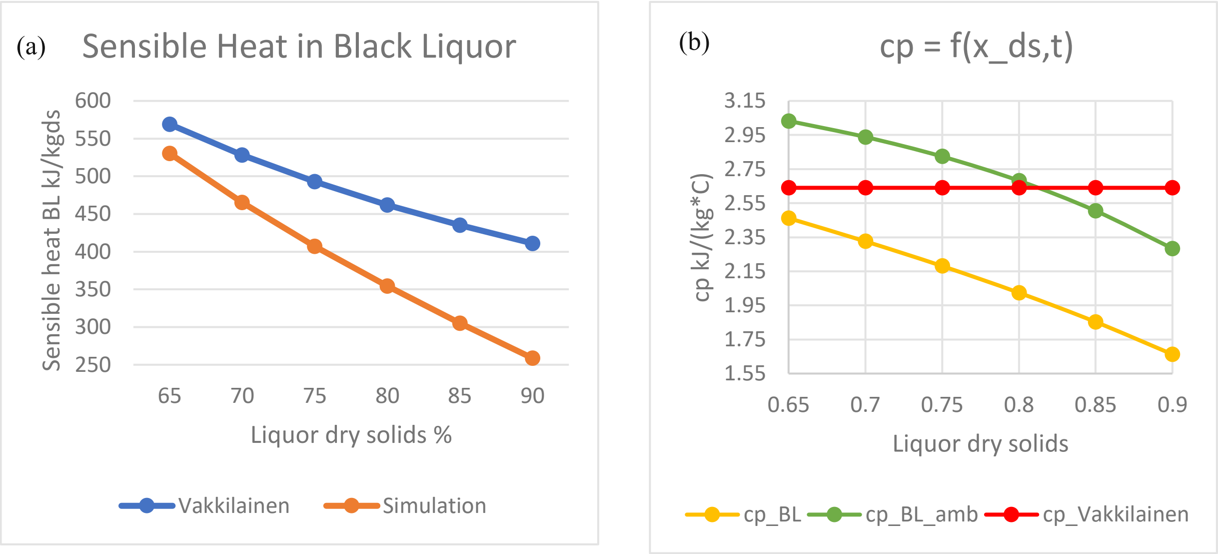


Fig. 96 Comparisons of literature and simulation results (a) sensible heat in black liquor (b) specific heat capacity as functions of dry solid content

Other heat losses such as the heat loss in smelt, the loss due to reduction to Na2S, the unaccounted etc. losses (unaccounted, radiation and margin losses) show similar tendencies in the two compared models.

The biggest differences originate from the non-constant specific heat capacity, which strongly influences the results of the sensible heat in black liquor, particularly for high dry solid contents. This leads to the conclusion that further research should be done on the integration of a more detailed model of black liquor heat capacity. Moreover, further measures should be executed to include a dust mass flow from a dust precipitator for additional enhancement of the simulation results of entire mill.

Discrepancies were illustrated and were explained, which were mainly due to the different calculation approaches followed by the two compared models. Therefore, the developed model was proven to show similar gradients and changes of the overall results caused by the alterations of the dry solid content.

7.5 Referenced Model V2 vs Saari et al. (2021)

The following chapter compares the results from the simulation with a recently published study Saari et al. (2021), in which the improvement of the energy efficiency in kraft recovery boilers through the back-end heat recovery was investigated. Due to the study's scope on the back-end heat recovery its exact calculation approach and assumptions etc. are not explained in detail. Nevertheless, the simulation was carried out with the goal of showing its validity and pin-point areas where further research needs to be carried out to enhance the model.

7.5.1 Inputs

The inputs for the simulation of the examined case in Saari et al (2021) are shown in table 44. The unburned carbon in smelt, the CO concentration, the SO concentration in the wet flue gas, and the humidity in combustion air values are not mentioned in the study, therefore similar representative values from the previous simulations are considered. The required inputs excess O2, the percentage of the unaccounted heat loss, and the percentage of the radiation loss were derived from the study through the mentioned parameters such as an excess air ratio λ of 1.18, the radiation and conduction loss of 2.9 MW and the other unaccounted losses amount to 3.9 MW (Saari, et al., 2021, p. 7).

INPUTS KRB Unit (external sootblowing)	**Value**	**Unit**
Smelt reduction efficiency	94.000	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	2.650	vol. %
CO concentration in wet flue gas	100.000	ppmv
SO2 concentration in wet flue gas	10.000	ppmv
Humidity (H2O) in combustion air	0.0135	kg/kg air
Radiation heat loss (as % of heat input)	0.245	%
Unaccounted heat loss (as %of heat input)	0.329	%
Margin heat loss (as % of heat input)	0.000	%

Table 44 Inputs KRB unit V2 (Case 4) (Saari, et al., 2021, pp. 5-7)

The input values for the streams and their chemical compositions are shown in table 45. The higher heating value was derived from the heat input from black liquor lower heating value stated to be 1053.7 MW. The ambient temperature for all streams is assumed to be equal to the ambient air temperature of 25°C. The blowdown stream's pressure of 25 bar is mentioned in Saari et al (2021). The temperature of the blowdown stream is assumed to be 500°C, which is only 10°C below the temperature of the steam generated in the boiler. This was done because of estimating the heat input assumed in the study of 233.7 MW to be extremely high. Dividing this heat input by the sootblowing steam mass flow of 13.2 kg/s a heat flow of 17704.5 kJ/kg is computed. This value is above the temperature limits that are implemented in IPSEpro's DLLs. Therefore, the calculations of the corresponding sootblowing steam temperature could not be carried out by the developed model. At a temperature level of 1726.85°C (=2000K) and 25 bar (=2.5 MPa) the steam enthalpy is only 6587 kJ/kg (referenced to the triple point of water), whereas the one in Saari et al (2021) is 17704.5 kJ/kg.

Stream / property	**Value**	**Unit**
Black liquor		
Temperature (BL temp after ind. heater)	140	°C
Ambient temperature	25	°C
Pressure	1	bar
Smelt reduction efficiency	0.94	1
Heavy black liquor solid content	0.83	kg/kg
Higher heating value (HHV)	13161	kJ/kg
Total mass flow	106.1	kg/s
Smelt		
Temperature	980	°C
Ambient temperature	25	°C
Pressure	1	bar
Air		
Temperature (temp after air preheat)	200	°C
Ambient temperature	25	°C
Pressure	1	bar
Composition set ≠ 0	H2O = 0.0135; N2 = 0.78; O2 = 0.2	kg/kg
Composition set = 0	WATER, C2H6, C3H8, CH4, CO, CO2, H2, H2S, SO2	kg/kg
Composition calculated / not set	Ar	kg/kg
Flue Gas		
Temperature (after economizer)	130	°C
Ambient temperature	25	°C
Pressure	1	bar
Composition set = 0	WATER, C2H6, C3H8, CH4, H2, H2S	kg/kg
Composition calculated / not set	Ar, CO, CO2, H2O, N2, O2, SO2	kg/kg
Feedwater		
Temperature (feedwater to economizer temp)	186	°C
Ambient temperature	25	°C
Pressure	116	bar
Composition	only WATER not set = 0	kg/kg
Steam		
Temperature	510	°C
Ambient temperature	25	°C
Pressure	100	bar
Composition	only WATER not set = 0	kg/kg
Blowdown		
Temperature	80	°C
Ambient temperature	25	°C
Pressure	8	bar
Mass flow	3.2	kg/s
Composition	only WATER not set = 0	kg/kg
Ext. sootblowing		
Temperature	500	°C
Ambient temperature	25	°C
Pressure	27	bar
Mass flow	13.2	kg/s
Composition	only WATER not set = 0	kg/kg

Table 45 Inputs stream properties V2 (Case 4) (Saari, et al., 2021, pp. 5-7)

The input values of the heavy black liquor analysis used in the simulation are shown in table 46. The value for inerts was set to reach the same sum as in the study of 99.9%. A roundoff error is assumed.

INPUTS	**Value**	**Unit**
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	31.52	% BLS
Hydrogen (H)	3.19	% BLS
Sulfur (S)	5.42	% BLS
Sodium (Na)	20.74	% BLS
Potassium (K)	2.59	% BLS
Chlorine (Cl)	0.33	% BLS
Nitrogen (N)	0.09	% BLS
Boron (B)	0.00	% BLS
Inerts	0.07	% BLS
Oxygen (O)	36.05	% BLS

Table 46 Inputs black liquor analysis V2 (Case 4) (Saari, et al., 2021, p. 5)

7.5.2 Results

Mass balance

STREAMS	**Literature**	**Simulation**	**Unit**	**Abs. error in kg/s**	**Rel. error in %**
Black Liquor	106.1	106.1	kg/s	0.0	0.0
Combustion air	262.8	359.6	kg/s	-96.8	-36.8
Sootblowing steam (external)	13.2	13.2	kg/s	0.0	0.0
Blowdown	3.2	3.2	kg/s	0.0	0.0
Smelt (corrected)	44.3	42.8	kg/s	1.5	3.4
Steam to Mill	333.5	337.8	kg/s	-4.3	-1.3
Flue Gas	358.5	436.1	kg/s	-77.6	-21.6

Table 47 Results mass balance V2 (Case 4) (Saari, et al., 2021, p. 7)

The results of the mass flows are shown in table 47. The set mass flows, including the black liquor, sootblowing, and blowdown mass flow logically show no discrepancy. The required combustion air mass flow estimated by the developed model deviates by 36.8% or 98.8 kg/s. This results in an increase of the flue gas mass flow, exceeding the results from the study by 77.6 kg/s or 21.6%. The corrected smelt mass flow is calculated by adding up the recycled dust being refired, to the smelt mass flow (uncorrected). This shows a discrepancy of only 1.5 kg/s or 3.4%. Interestingly, the steam to mill mass flow calculated by the simulation only exceeds the one in Saari et al (2021) by 4.3 kg/s or 1.3% respectively.

Energy Balance

Literature	**Flow rate (kg/s)**	**Heat rate (MW)**	**heat rate/mass flow (kJ/kg)**
Black liquor, LHV	106.1	1053.7	9931.2
Black liquor, sensible heat	106.1	32.1	302.5
Combustion air	262.8	53.7	204.3
Sootblowing steam	13.2	233.7	17704.5
Heat transfer to live steam	333.5	872.1	2615.0
Heat transfer to blowdown	3.2	2.1	656.3
Heat transfer to heat recovery water circuit	240.7	30.5	126.7
Stack loss	358.5	53.4	149.0
Radiation and conduction loss	n/a	2.9	n/a
Reaction heat of reduction reactions	n/a	133.4	n/a
Smelt sensible heat loss	35.6	48.2	1353.9
Ash sensible heat loss	8.7	1.1	126.4
Other unaccounted losses	n/a	3.9	n/a

Table 48 Results energy balance (Case 4) (Saari, et al., 2021, p. 7)

Simulation	**Flow rate (kg/s)**	**Heat rate (MW)**	**heat rate/mass flow (kJ/kg)**
Black liquor, LHV	106.1	1053.7	9931.2
Black liquor, sensible heat	106.1	22.0	207.7
Combustion air	359.6	64.9	180.4
Sootblowing steam	13.2	44.3	3355.5
Heat transfer to live steam	337.8	879.0	2602.0
Heat transfer to blowdown	3.2	0.7	230.6
Heat transfer to heat recovery water circuit	-	-	-
Stack loss	436.1	51.4	118.0
Radiation and conduction loss	n/a	2.9	n/a
Reaction heat of reduction reactions	n/a	140.9	n/a
Smelt sensible heat loss	42.8	66.5	1554.7
Ash sensible heat loss	0.0	0.0	0.0
Other unaccounted losses	n/a	3.9	n/a
Further losses	n/a	40.9	n/a

Table 49 Results energy balance V2 (Case 4)

The heat inputs from lower heating value (LHV) were set and are therefore equal to the ones from the study.

Black liquor's sensible heat varies, even though using the same formula for the specific heat capacity. The logical conclusion is that a different calculation approach for the sensible heat is used. The developed model underestimates the value of the sensible heat proposed in Saari et. al (2021) of 32.1 MW with a value of 22 MW.

The combustion air shows a higher mass flow and heat rate in simulation but a smaller specific heat flow (per kg mass) of 180.4 kJ/kg instead of 204.3 kJ/kg as calculated in Saari et. al (2021). This leads to the thought that a different air composition and humidity had been considered.

The previously mentioned problem is that using the same heat input of sootblowing steam as in the study (233.7 MW) or a specific heat flow of 17704.5 kJ/kg (1.78-fold of the one of LHV of black liquor), the calculation of the stream's temperature in the simulation is not working because of exceeding the function's limits.

The smelt sensible heat loss calculated by the simulation overestimates the one computed in Saari et. al (2021) noticeably. Absolute stack loss deviations between the developed model and the study are 2 MW or 3.7%, even though differing strongly in the mass flows (21.6%). The radiation and conduction losses, and other unaccounted losses were set as input values.

The discrepancies shown arise due to a different scope of the two compared models: one is focused on the back-end heat recovery (study), whereas the developed model in this work aims to account for a wide range of heat inputs and heat losses (thesis). This is illustrated in table 49 mentioning further losses of 40.9 MW. With the developed KRB model heat transfer to heat recovery water circuit cannot be estimated in the same manner as proposed in Saari et. al due to its different scopes of research.

The lack of insight into the study's exact calculation approach of the mass and energy balance and how each is accounted for, as well as the missing input values required by the developed model, which had to be assumed based on previous cases, additionally increase the dissimilarities and difficulties of comparison.

Smelt composition:

Smelt Composition	**Literature**	**Simulation**	**Unit**
K2CO3	5.31	9.42	wt%
K2S	2.53	0.00	wt%
K2SO4	0.25	0.00	wt%
KCI	0.06	0.00	wt%
Sum K-compounds	**8.16**	**9.42**	**wt%**
Na2S	26.77	25.53	wt%
Na2SO4	3.12	2.97	wt%
NaCl	0.79	1.12	wt%
Na2CO3	60.91	60.42	wt%
Other / Inerts	0.25	0.14	wt%
Unburned carbon (char)	0.00	0.41	wt%
Total	**100.00**	**100.00**	**wt%**

Table 50 Results smelt composition V2 (Case 4) (Saari, et al., 2021, p. 18)

The assumption in Tran & Grace (2018) used in the developed model that potassium exist in the smelt only as K2CO3 has great impact on the chemical compounds and its mass fractions, as can be see in table 50, where the chemical compositions of smelt are compared.

Hence, adding up various potassium compounds from literature (Saari, et al., 2021) gives 8.16% of smelt's compositon in comparison to 9.42 wt% K2CO3 in the one predicted by the simulation. Another compound that differs noticable by more than one percent is Na2S which varies by 1.24 wt%. The other parts of the smelt's composition are relatively well estimated even though following different assumptions and approaches.

7.5.3 Summary

For the estimation of the mass flows of combustion air and flue gas the results of the simulation differ significantly from the one from the study, which is assumed to be due to a different calculation method used and the lack of the exact input values required.

The corrected smelt mass flow's discrepancies are tolerated but call the attention to the necessity for the implementation of a dust precipitator and considering saltcake makeup, which could reduce that difference noticeably. The smelt's chemical compositions differ due to the assumptions that potassium exist in the smelt only as K2CO3 as proposed in Tran & Grace (2018).

The steam to mill mas flow calculated, which represents the overall energy balance, shows good results only varying by 1.3%.

The lack of insight into the study's exact calculation approach, the assumptions made, the missing input values required by the developed model, as well as the different scopes of research of the models, complicated the comparison of the results and validation process.

The big discrepancies in the results of the combustion air mass flow show the necessity to compare all the previous results to highlight the similarities of the previous results in the validations with Tran & Grace (2018), Vakkilainen (2005) and Saari et al (2021). Hence the following table 51 is used to highlight how the results differ significantly from the other state-of-the-art calculation methods. The table shows the dry combustion air mass flow divided by the higher heating value. The value calculated from the study Saari et al (2021) shows the only noticeable divergence from all the previous results from literature / simulation.

	Simulation	**Literature**	**Unit**
Validation	m°dry_comb_air/HHV	m°dry_comb_air/HHV	(kg/MJ)
Referenced Model V2 vs Tran & Grace (2018)	0.317	0.317	(kg/MJ)
Referenced Model V2 vs Vakkilainen (2005) calc ex.	0.335	0.335	(kg/MJ)
Referenced Model V2 vs Saari et al (2021)	0.306	0.188	(kg/MJ)

Table 51 Comparison of results of dry air mass flow divided by HHV

8 Conclusion

8.1 Conclusion

In the first chapter of this thesis an overview of the Pulp and Paper Industry is given including the Kraft Pulping Process and the general design of Kraft Recovery Boilers. Moreover, two different state-of-the-art calculation approaches proposed in Tran & Grace (2018) and Vakkilainen (2005) are introduced and compared for the purpose of giving a broad understanding of the underlying models preparing the reader for the model development.

Chapter two is dedicated to discussing the utilized software IPSEpro, its applications, how it is functioning, structured, and which built-in streams and units are used for facilitating the comprehension of the implementation and simulation processes.

Chapter three aims to explain the overall procedure of the implementation and development of the model, which gives the reader further insight on the underlying structure. Furthermore, the general model used in the simulation is demonstrated.

In chapter four the implementation and development of new streams (black liquor and smelt stream) and the modification of built-in streams (air, flue gas, and water streams) are discussed. This includes the calculations, possible options from which the user can choose, and the input parameters required by the model.

Chapter five is devoted to the implementation and development of the KRB unit version V1 (Base Model) and version V2 (Referenced Model). The Base Model's calculation approach for the mass flows (combustion air, flue gas, smelt) and the chemical compositions is described in a detailed manner since the same method is used in the Referenced Model. Furthermore, an explanation of the executed modifications in the advancement from the Base Model V1 to the Referenced Model V2 and its required inputs, is given. The heat inputs and the heat losses considered in the energy balance are listed and its calculation approach is discussed. Specific details on the waterside mass balance for the two different options (internal or external sootblowing) are illustrated and explained.

The aim of chapter 6 is to give the user a practice-oriented step-by-step user manual, including the general flowsheet set up, the required inputs for each stream, the KRB unit and the illustration of the results of the simulation.

Chapter seven deals with the validation following the development procedure, starting with validating the Base Model V1, upon whose results a basis for the Referenced Model V2 is verified through numerous simulation cases: firstly, comparing the results with the ones in Tran & Grace (2018) following a similar calculation approach. Secondly the developed model is tested through a detailed comparison with the solutions in the calculation example in Vakkilainen (2005). The shown discrepancies originating from the different approaches are explained and discussed. The third validation of the Referenced Model V2 aims to prove that a similar behavior and the changes in the mass and energy balances when varying the dry solid content. The fourth and last validation of the Referenced Model V2 was carried out with the goal of showing its validity in a comparison with a recent study Saari et al (2021), and pin-point areas where further research needs to be conducted to enhance the model.

Based on the validated results from the KRB unit model 1 (Base Model V1) with the consideration of the applied assumptions the Referenced Model V2 was developed and compared with different examples and cases from literature such as by Tran & Grace (2018), Vakkilainen (2005) and Saari et al (2021) to demonstrate its validity. In each validation carried out the developed model's discrepancies from literature's results could be explained through the consideration of the underlying calculation approach used.
Due to the model's similarity to the state-of-the-art model proposed in Tran & Grace (2018) the similar results prove the model's validity, conclusiveness, and strength.
From the comparison with the data in Vakkilainen (2005) the different approaches and assumptions impacted the solutions and therefore the discrepancies of about 2% of the generated steam to mill mass flow (in the calculation example) could be explained.
Based on this previously mentioned verification similar tendencies of behaviors were shown and illustrated when altering the dry solid content of black liquor in the validation with Vakkilainen (2005) (tables).
In the validation with Saari et al (2021) the lack of insight into the study's exact calculation approach, the assumptions made, the missing input values required for the simulation, and the different scopes of research of the models, complicated the comparison of the results and the

validation process. The steam to mill mas flow calculated, which is a good representation of the overall energy balance, showed good results only varying by 1.3%.

Finally, the main outcomes and findings of this thesis on the *Development, Implementation, and Validation of a Kraft Recovery Boiler IPSEpro Simulation Model based on State-of-the-Art Calculation Methods* are:

- The assumption that potassium exist in the smelt only as K2CO3 has a strong impact on the chemical composition, its mass fractions and on the energy balance.
- The approach of calculating black liquor's specific heat capacity as a function of the black liquor temperature and the dry solid content influences the results of sensible heat in black liquor noticeably, particularly for high dry solid contents.
- The different approaches for computing the combustion air mass flow requirement have a relevant effect on the sensible heat input from air mass flow as well as the sensible heat loss with the exiting flue gas.
- Considering an internal dust precipitator and dust combustion along with black liquor can lead to an improvement of the model's results, especially in terms of smelt mass flow and its chemical composition.
- Modeling smelt enthalpy as a real mixture considering enthalpies of mixing instead of an ideal mixture could enhance the model's quality.

8.2 Recommendation for further work

From the outcomes and findings of this thesis a proposition for further work on a more detailed model and research of smelt enthalpy as a real mixture is recommended. This could include the consideration of additional chemical compounds in the smelt and considering their influences on the mass and energy balances in the simulated Kraft Recovery Boiler.

Another suggestion would be a further advancement of the established KRB model by including an internalized dust precipitator and refiring the collected dust with black liquor (Model V3). This could also include the possibility to add or extract steam mass flows at specified enthalpies.

The possibility to choose from different calculation methods for the mass balances as proposed in Vakkilainen (2005) could be of interest for the user.

The integration of the developed KRB unit model in relevant topics of research such as for instance energy storage, or the simulation of an entire plant or mill are recommended. This would require additional units (e.g., to transform the modified built-in streams into the default streams).

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List of Abbreviations and Symbols

air_moisture	moisture in (combustion) air
air_theo	theoretical air input
amb	ambient
APP	Advanced Power Plant Library
BL	Black liquor
BLS	Black liquor dry solids
CFD	Computational Fluid Dynamics
CO_ppmv	CO concentration in wet flue gas
comb	combustion
Cp	Specific heat capacity at constant pressure
Cu	unburned carbon content in the smelt
DCE	Direct Contact Evaporator
def	defined
DLL	Dynamic Link Library
evap	evaporation
Fg / FG / fg	Flue gas
FGmoles	amount of moles in flue gas
H / h	Enthalpy
HHV	Higher heating value
humidity_comb_air	Humidity in combustion air
IPSE	Integrated Process and System Engineering
KRB	Kraft Recovery Boiler
LHV	Lower heating value
Lib	Library

$\dot{m}$ / m°	Mass flow
margin_loss	Margin heat loss
MDK	Model Development Kit
MDL	Model Description Language
n	material amount
NIST	National Institute of Standards and Technology
O2_wvb / %O2wvb	percent excess oxygen on a wet volume basis
ppmv	parts per million volume
PSE	Process Systems Engineering
Q°	Heat flux
R	Sulfur reduction efficiency
rad_heat_loss	Radiation heat loss
ref	reference
s	black liquor dry solids content
SimTech	Simulation Technology
SO2_ppmv	SO2 concentration in wet flue gas
sootblowing_steam	Sootblowing steam mass flow
T / t	Temperature
TAPPI	Technical Association of the Pulp and Paper Industry
unac_heat_loss	Unaccounted heat loss
V1 / V2	Version 1 / Version 2
w	mass fraction
w	water
w/o	without
wv	water vapor

x	steam quality
x_ds	dry solid content
Δ	Difference
λ	Excess air ratio

References

Adams, T. N. & Jones, A. K., 2018. Recovery Boiler Design. In: M. LeBel & L. Ericson, eds. *Kraft Recovery Boilers.* s.l.:TAPPI Press, pp. 299-312.

Benda, L. C., 2020. *Advanced Chemical and Thermodynamic Simulation of Kraft Recovery Boilers.* Vienna: TU Wien.

Chase, M. W., 1998. *NIST Chemistry WebBook.* [Online]
Available at: https://webbook.nist.gov/cgi/formula?ID=C1313822&Mask=2#ref-1
[Accessed October 2022].

Jiang, S., Li, B. & Shen, Y., 2021. The Influence of Pulp and Paper Industry on Environment. *EDP Sciences.*

Neto, M. R. V., 2021. Synthesis and optimization of Kraft process evaporator plants. In: E. K. Vakkilainen & É. D. Oliveira, eds. Minas Gerais : Universidade federal de Minas Gerais .

Saari, J. et al., 2021. Evaluation of the Energy Efficiency Improvement Potential through Back-End Heat Recovery in the Kraft Recovery Boiler. *Energies,* Issue 14.

SimTech Simulation Technology, 2014. *IPSEpro Process Simulator Advanced Power Plant Library Manual Version 9.0.001.* s.l.:s.n.

SimTech Simulation Technology, 2014. *IPSEpro Process Simulator Model Development Kit Manual Version 6.0.001.* s.l.:s.n.

SimTech Simulation Technology, n.d. *SimTech Simulation Technology.* [Online]
Available at: https://www.simtechnology.com/cms/ipsepro-menu/ipse-pro
[Accessed 17 March 2023].

SimTech Simulation Technology, n.d. *SimTech Simulation Technology.* [Online]
Available at: https://www.simtechnology.com/cms/ipsepro-menu/model-libraries
[Accessed 17 March 2023].

Tikka, P., 2008. *Chemical pulping part 2: recovery of chemicals and energy.* 2nd ed. Helsinki: Paper Engineers' Association.

Tomei, G. L., 2007. *Steam: Its Generation and Use.* 42 ed. s.l.:Babcock & Wilcox Company.

Tran, H. & Grace, T. M., 2018. APPENDICES Material & Energy Balance Calculations. In: *Kraft Recovery Boilers.* s.l.:s.n., pp. 348-353.

Tran, H. & Grace, T. M., 2018. Recover Boiler Material and Energy Balances. In: A. K. Jones & E. K. Vakkilainen, eds. *Kraft Recovery Boilers.* s.l.:s.n., pp. 327-346.

Tran, H. & Vakkilainen, E. K., 2007. *THE KRAFT CHEMCIAL RECOVERY PROCESS,* s.l.: TAPPI.

Tran, H. & Vakkilainnen, E. K., 2007. *THE KRAFT CHEMCIAL RECOVERY PROCESS,* s.l.: TAPPI.

Vakkilainen, E. K., 2005. Material and energy balance. In: *Kraft recovery boilers – Principles and practice.* s.l.:Valopaino Oy, pp. 3-1 - 3-10.

Vakkilainen, E. K. & Ahtila, P., 2011. Modern Method to Determine Recovery Boiler Efficiency. *O PAPEL,* 72(12), pp. 58-65.

Zaman, A., Fricke, A. L. & Wight, M. O., 1994. *Density and thermal expansion of black liquors.* s.l.:Tappi Journal.

Appendix

BL_stream (connection)

```
#total mass flow

fmass_total: mass_total = mass/(x_ds); #mass is a mass flow in kgBLS/s


fHHV_calc: HHV_calc =  1000*(25.04 * BL_Composition.myC + 0.1769 * BL_Composition.myS + 2.582* BL_Composition.myNa +
48.92 * BL_Composition.myH + 42.31); #if 40% > C% > 30 %; higher heating value BL in kJ/kg
#used for the Input in the Saari Model


#net heating value
fNHV: NHV = HHV_calc - 2442*(18/2 * BL_Composition.myH) - 12900 *(78/32 *BL_Composition.myS *eta_red);

#Calculation of lower heating value

fLHV_dry: LHV_dry = HHV + h_H_BL* BL_Composition.myH;

fLHV_wet: LHV_wet= LHV_dry + BL_H2O *h_H2O_BL;

#water in BL
fBL_H2O: BL_H2O = 1/x_ds -1;

#_____________with the following enthalpies________________________________

fh_H2O_BL: h_H2O_BL = -2440;
fh_H_BL: h_H_BL = -21806.3;



#HEAT CAPACITY of BL
#OPTION 1
fcp_BL: cp_BL = 4.216*(1 - x_ds) + (1.675 - 0.00331*t )* x_ds + (4.87 - 0.02*t)*(1 - x_ds)* x_ds^3; #heat capacity of BL according to
study
fcp_BL_amb: cp_BL_amb = 4.216*(1 - x_ds) + (1.675 - 0.00331*t_amb )* x_ds + (4.87 - 0.02*t_amb)*(1 - x_ds)* x_ds^3; #heat capacity
of BL according to study



#OPTION 2
#fcp_BL: cp_BL = 2.64; #Vakkilainen (2005)
#fcp_BL: cp_BL = 2.95; #Tan & Grace (2018)


#ENTHALPY

#Total enthalphy of BL at 80°C
fh_80: h_80 = -15865.96 + 105 * (2.718281828459^(x_ds/0.3) - 1);


#Enthalpy at input temperature t
fh: h = h_80  + cp_BL*(t-80);



tMass:      test (mass>=0.0) warning "mass flow negative";
```

Stream (connection)

```
#Shifting enthalpy from H-H0_tr to H

# H0_tr = Composition.fhf0


ft:         if blocksize() == 1.0 && isconverged(p) && isconverged(t) then

                        h0 = Composition.fhpt(p, t);
            else
                        t = Composition.ft(p, h0);

fh:  h = h0 + Composition.fhf0(); #from H-H0_tr to H; H0_tr = Composition.fhf0


fh_ambient: h_ambient = Composition.fhf0() + Composition.fhpt(1, t_amb);


ifl (boiler == off)then ft_amb: t_amb =0;
endifl


#standard
fs:         s = Composition.fs(p, h0);
fv:         v = Composition.fv(p,h0);

t1:          test (mass >=0.0) warning "mass flow negative";
```

KRB_stream / smelt (connection)

```
ftk: tk = t + 273.15; #shift from celcius to kelvin
ftk_amb: tk_amb = t_amb + 273.15; #used for h_ambient with smelt (KRB_stream) approach


#OPTION 1 -> total enthalphy of the stream calculated through the mass fraction of the various compositions


fh: h = h_S * KRB_Composition.m_S + h_SO3 * KRB_Composition.m_SO3 + h_Na2SO4 * KRB_Composition.m_Na2SO4 + h_K2CO3 *
KRB_Composition.m_K2CO3 + h_Na2S * KRB_Composition.m_Na2S + h_KCl * KRB_Composition.m_KCl + h_C *
KRB_Composition.m_C + h_NaCl * KRB_Composition.m_NaCl + h_Na2CO3 * KRB_Composition.m_Na2CO3 + h_NaOH *
KRB_Composition.m_NaOH + h_Na * KRB_Composition.m_Na + h_K2SO4 * KRB_Composition.m_K2SO4 + h_KOH *
KRB_Composition.m_KOH + h_K * KRB_Composition.m_K + h_Cl * KRB_Composition.m_Cl + KRB_Composition.m_Inerts* 0 ;

fh_ambient: h_ambient = h_S_amb * KRB_Composition.m_S + h_SO3_amb * KRB_Composition.m_SO3 + h_Na2SO4_amb *
KRB_Composition.m_Na2SO4 + h_K2CO3_amb * KRB_Composition.m_K2CO3 + h_Na2S_amb * KRB_Composition.m_Na2S +
h_KCl_amb * KRB_Composition.m_KCl + h_C_amb * KRB_Composition.m_C + h_NaCl_amb * KRB_Composition.m_NaCl +
h_Na2CO3_amb * KRB_Composition.m_Na2CO3 + h_NaOH_amb * KRB_Composition.m_NaOH + h_Na_amb *
KRB_Composition.m_Na + h_K2SO4_amb * KRB_Composition.m_K2SO4 + h_KOH_amb * KRB_Composition.m_KOH + h_K_amb *
KRB_Composition.m_K + h_Cl_amb * KRB_Composition.m_Cl + KRB_Composition.m_Inerts* 0 ;



#OPTION 2 -> Literature

#fh: h = (1350 + 1.67* (t - 850));

#fh_ambient: h_ambient = (1350 + 1.67* (t_amb - 850));



#S
fhm_S:    if t >= 25 && t < 115 then #solid
                    hm_S = 21.21978*(tk/1000) + 3.865858*(tk/1000)^2/2 + (22.27461)*(tk/1000)^3/3 + (-10.31908)*(tk/1000)^4/4 - (-
0.122518)/(tk/1000) + (-7.085604); # - (0);

          else if t == 115 then #mixture solid-liquid
                     hm_S = 2.13336;

          else if t < 159 && t > 115 then #liquid
                    hm_S = -4540.970*(tk/1000) + 26065.60*(tk/1000)^2/2 + (-55520.70)*(tk/1000)^3/3 + 42012.20*(tk/1000)^4/4 -
(54.58860)/(tk/1000) + (787.8070); #- (1.853781);

          else if t == 159 then #transition
                    hm_S = 5.73471;

          else if t > 159 && t < 609 then #liquid
                    hm_S = -37.93350*(tk/1000) + 133.2420*(tk/1000)^2/2 + (-95.32450)*(tk/1000)^3/3 + 24.00940*(tk/1000)^4/4 -
(7.654530)/(tk/1000) + (29.78810); # - (1.853781);

          else if t == 609 then
                    hm_S = 21.3138; #to 290.116

          else if t > 609 && t < 1127 then #gas
                    hm_S = 27.45968*(tk/1000) + (-13.32784) *(tk/1000)^2/2 + (10.06574)*(tk/1000)^3/3 + (-2.662381)*(tk/1000)^4/4 -
(-0.055851)/(tk/1000) + (269.1149); # - (276.9804);

          else if t == 1127 then
                    hm_S = 301.19;

          else if t > 1127 && t < 5727  then #gas
                    hm_S = 16.55345*(tk/1000) + (2.400266) *(tk/1000)^2/2 + (-0.255760)*(tk/1000)^3/3 + (0.005821)*(tk/1000)^4/4 -
(3.564793)/(tk/1000) + (278.4356); # - (276.9804);

          else hm_S = 0;


fh_S: h_S = (hm_S/32.065) * 1000; #h_S in kJ/kg  hm_S = molar enthalphy in kJ/mol  M = molar weight in g/mol


#SO3
```

```
fhm_SO3:
        if t >= 25 && t < 927 then
        hm_SO3 = 24.02503*(tk/1000) + 119.4607*(tk/1000)^2/2 + (-94.38686)*(tk/1000)^3/3 + 26.96237*(tk/1000)^4/4 - (-0.117517)/(tk/1000) + (-407.8526); # - (-395.7654);

        else if t == 927 then
                hm_SO3 = 100;

        else if t> 927 && t < 5727 then
                hm_SO3 = 81.99008*(tk/1000) + 0.622236*(tk/1000)^2/2 + (-0.122440)*(tk/1000)^3/3 + 0.008294*(tk/1000)^4/4 - (-6.703688)/(tk/1000) + (-437.6590); # - (-395.7654);
        else hm_SO3 = 0;

fh_SO3: h_SO3 = (hm_SO3/ 80.063) *1000;



#Na2SO4
fhm_Na2SO4:
        if t >= 25 && t < 185 then #solid; phase V
                hm_Na2SO4 = 96.97466*(tk/1000) + 149.5454*(tk/1000)^2/2 + (-44.51148)*(tk/1000)^3/3 + 14.24313*(tk/1000)^4/4 - (-0.874900)/(tk/1000) + (-1425.698);# - (-1387.561);

        else if t >= 185 && t < 241 then #solid; phase IV
                hm_Na2SO4 = 97.09767*(tk/1000) + 149.0676*(tk/1000)^2/2 + (-43.87886)*(tk/1000)^3/3 + (13.96711)*(tk/1000)^4/4 - (-0.877515)/(tk/1000) + (-1425.987);# - (-1387.816);

        else if t >= 241 && t < 884 then #solid; phase I
                hm_Na2SO4 = 154.1365*(tk/1000) + 12.24966*(tk/1000)^2/2 + (49.39296)*(tk/1000)^3/3 + (-15.42553)*(tk/1000)^4/4 - (-0.190212)/(tk/1000) + (-1428.447);# - (-1380.900);

        else if t >= 884 && t < 2727  then #liquid
                hm_Na2SO4 = 197.0330*(tk/1000) + -0.000028*(tk/1000)^2/2 + (0.000011)*(tk/1000)^3/3 + (-0.000001)*(tk/1000)^4/4 - (-0.000006)/(tk/1000) + (-1427.260);# - (-1356.380);
        else hm_Na2SO4 = 0;

fh_Na2SO4: h_Na2SO4= (hm_Na2SO4/142.042) *1000;


#K2CO3
fhm_K2CO3:
        if t >= 25 && t < 901 then #solid
                hm_K2CO3 = 97.08093*(tk/1000) + 94.22326*(tk/1000)^2/2 + (-2.053291)*(tk/1000)^3/3 + 0.709644*(tk/1000)^4/4 - (-0.947860)/(tk/1000) + (-1186.499);# - (-1150.182);
        else if t >= 901 && t < 2227 then #liquid
                hm_K2CO3 = 209.2000*(tk/1000) + (-1.629015*10^-7)*(tk/1000)^2/2 + (8.009850*10^-8)*(tk/1000)^3/3 + (-1.336428*10^-8)*(tk/1000)^4/4 - (-2.105289*10^-8)/(tk/1000) + (-1225.548);# - (-1130.609);
        else hm_K2CO3 = 0;

fh_K2CO3: h_K2CO3= (hm_K2CO3/138.206) *1000;


#Na2S
fhm_Na2S:

        if t >= 25 && t < 727 then #solid
                hm_Na2S = 78.38780*(tk/1000) + 13.94820*(tk/1000)^2/2 + (2.753281)*(tk/1000)^3/3 + (-2.347990)*(tk/1000)^4/4 - (0.008301)/(tk/1000) + (-390.0830);# - (-366.1000);

        else if t >= 727 && t < 1003 then #solid; #
                hm_Na2S = 58023.20*(tk/1000) + (-104689.0)*(tk/1000)^2/2 + (70037.20)*(tk/1000)^3/3 + (-16374.80)*(tk/1000)^4/4 - (-6903.890)/(tk/1000) + (-32139.00);# - (-366.1000);

        else if t >= 1003 && t < 1172  then #solid
                hm_Na2S = -542020.0*(tk/1000) + (789111.0)*(tk/1000)^2/2 + (-431902.0)*(tk/1000)^3/3 + (84244.40)*(tk/1000)^4/4 - (103416.0)/(tk/1000) + (373259.0);# - (-366.1000);

        else if t >= 1172 && t < 2727  then #liquid
                hm_Na2S = 92.04800*(t/1000) + (-0.000046)*(t/1000)^2/2 + (0.000018)*(t/1000)^3/3 + (-0.000002)*(t/1000)^4/4 - (-0.000011)/(t/1000) + (-354.3040);# - (-323.9400);
        else hm_Na2S = 0;

fh_Na2S: h_Na2S= (hm_Na2S/78.045) *1000;
```

```
#KCl
fhm_KCl:

		if t >= 25 && t < 627 then #solid
			hm_KCl = 35.41597*(tk/1000) + 70.03472*(tk/1000)^2/2 + (-91.38233)*(tk/1000)^3/3 + (52.52426)*(tk/1000)^4/4 - (0.153460)/(tk/1000) + (-449.1357);# - (-436.6841);

		else if t >= 627 && t < 771  then #solid
			hm_KCl  = -717.3845*(tk/1000) + (1247.861)*(tk/1000)^2/2 + (-708.5144)*(tk/1000)^3/3 + (141.4435)*(tk/1000)^4/4 - (103.6712)/(tk/1000) + (1.760084);# - (-436.6841);

		else if t >= 771 && t < 1727  then #liquid
			hm_KCl   = 73.59698*(tk/1000) + (0)*(tk/1000)^2/2 + (0)*(tk/1000)^3/3 + (0)*(tk/1000)^4/4 - (0)/(tk/1000) + (-443.7341);# - (-421.7932);
		else hm_KCl = 0;

fh_KCl: h_KCl= (hm_KCl/74.551) *1000;


#C
fhm_C:
		if t >= 25 && t < 1527 then #solid h = cp*deltaT; cp= 10.68 J/mol*K
			hm_C = 10.68/1000 *tk;
		else hm_C = 0;

fh_C: h_C = (hm_C/12.0107) *1000;


#NaCl
fhm_NaCl:

		if t >= 25 && t < 800 then #solid
			hm_NaCl = 50.72389*(tk/1000) + 6.672267*(tk/1000)^2/2 + (-2.517167)*(tk/1000)^3/3 + (10.15934)*(tk/1000)^4/4 - (-0.200675)/(tk/1000) + (-427.2115);# -(-411.1203);

		else if t >= 800 && t < 2227 then #solid
			hm_NaCl = -42.44780*(tk/1000) + (113.5260)*(tk/1000)^2/2 + (-43.64660)*(tk/1000)^3/3 + (5.896630)*(tk/1000)^4/4 - (39.13860)/(tk/1000) + (-305.5610);# - (-385.923);
		else hm_NaCl = 0;

fh_NaCl: h_NaCl= (hm_NaCl/58.443) *1000;


#Na2CO3
fhm_Na2CO3:

		if t >= 25 && t < 450 then #solid
			hm_Na2CO3 = 175.2010*(tk/1000) + (-348.0580)*(tk/1000)^2/2 + (743.0720)*(tk/1000)^3/3 + (-305.551)*(tk/1000)^4/4 - (-1.634221)/(tk/1000) + (-1178.98);# - (-1130.770);

		else if t >= 450 && t < 850 then #solid
			hm_Na2CO3 = -1067.000*(tk/1000) + (2469.340)*(tk/1000)^2/2 + (-1829.060)*(tk/1000)^3/3 + (505.7480)*(tk/1000)^4/4 - (100.1820)/(tk/1000) + (-607.124);# - (-1130.77);

		else if t >= 850 && t < 2227 then #liquid
			hm_Na2CO3 = 189.5350*(tk/1000) + (-0.000007)*(tk/1000)^2/2 + (0.000002)*(tk/1000)^3/3 + (-5.205100*10^-9)*(tk/1000)^4/4 - (-0.000003)/(tk/1000) + (-1183.060);# - (-1108.510);

		else hm_Na2CO3 = 0;

fh_Na2CO3: h_Na2CO3 = (hm_Na2CO3/105.988) *1000;


#NaOH
fhm_NaOH:

		if t >= 25 && t < 299 then #solid
			hm_NaOH = 419.4837*(tk/1000) + (-1717.754)*(tk/1000)^2/2 + (2953.573)*(tk/1000)^3/3 + (-1597.221)*(tk/1000)^4/4 - (-6.046884)/(tk/1000) + (-517.8662);# - (-425.9312);

		else if t >= 299 && t < 323 then #solid

			hm_NaOH = 86.02304*(tk/1000) + (0)*(tk/1000)^2/2 + (0)*(tk/1000)^3/3 + (0)*(tk/1000)^4/4 - (0)/(tk/1000) + (-448.8512);# - (-425.9312);

		else if t >= 323 && t < 2227 then #liquid
```

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                hm_NaOH = 88.34725*(tk/1000) + (-2.495103)*(tk/1000)^2/2 + (-3.013028)*(tk/1000)^3/3 +
(0.862607)*(tk/1000)^4/4 - (0.042216)/(tk/1000) + (-442.9350);# - (-416.8783);

        else if t >= 2227 && t < 4727 then #gas
                hm_NaOH = 49.46492*(tk/1000) + (7.000125)*(tk/1000)^2/2 + (-1.391757)*(tk/1000)^3/3 +
(0.095206)*(tk/1000)^4/4 - (-0.256928)/(tk/1000) + (-213.6706);# - (-197.7572);
        else hm_NaOH = 0;

fh_NaOH: h_NaOH = (hm_NaOH/39.9971) *1000;



#Na
fhm_Na:

        if t >= 25 && t < 97 then #solid
                hm_Na = 72.63675*(tk/1000) + (-9.491572)*(tk/1000)^2/2 + (-730.9322)*(tk/1000)^3/3 + (1414.518)*(tk/1000)^4/4 -
(-1.259377)/(tk/1000) + (-21.79467);# - (0);
        else if t >= 97 && t < 897 then #liquid
                hm_Na = 40.25707*(tk/1000) + (-28.23849)*(tk/1000)^2/2 + (20.69402)*(tk/1000)^3/3 + (-3.641872)*(tk/1000)^4/4 -
(-0.079874)/(tk/1000) + (-8.782300);# - (2.406001);
        else if t >= 897 && t < 5727 then #gas
                hm_Na = 20.80573*(tk/1000) + (0.277206)*(tk/1000)^2/2 + (-0.392086)*(tk/1000)^3/3 + (0.119634)*(tk/1000)^4/4 -
(-0.008879)/(tk/1000) + (101.0386);# - (107.2999);
        else hm_Na = 0;

fh_Na: h_Na = (hm_Na/22.9898) *1000;



#K2SO4
fhm_K2SO4:

        if t >= 25 && t < 927 then #solid; alpha phase
                hm_K2SO4 = 139.5050*(tk/1000) + (-1.199884)*(tk/1000)^2/2 + (136.808)*(tk/1000)^3/3 + (-
47.14322)*(tk/1000)^4/4 - (-1.663999)/(tk/1000) + (-1485.964);# - (-1437.706);

        else if t >= 927 && t < 1069 then #solid; beta phase
                hm_K2SO4 = 114.3424*(tk/1000) + (81.29554)*(tk/1000)^2/2 + (-0.000942)*(tk/1000)^3/3 + (-
0.016197)*(tk/1000)^4/4 - (0.000141)/(tk/1000) + (-1461.948);# - (-1424.246);


        else if t >= 897 && t < 5727 then #liquid
                hm_K2SO4 = 201.4604*(tk/1000) + (0)*(tk/1000)^2/2 + (0)*(tk/1000)^3/3 + (0)*(tk/1000)^4/4 - (0)/(tk/1000) + (-
1471.274);# - (-1393.669);

        else hm_K2SO4 = 0;

fh_K2SO4: h_K2SO4 = (hm_K2SO4/174.259) *1000;

#KOH
fhm_KOH:

        if t >= 25 && t < 243 then #solid
                hm_KOH = 80.78258*(tk/1000) + (-112.2329)*(tk/1000)^2/2 + (301.1543)*(tk/1000)^3/3 + (-
147.9923)*(tk/1000)^4/4 - (-0.468867)/(tk/1000) + (-447.7591);# - (-424.7178);

        else if t >=  243 && t < 409 then #solid
                hm_KOH = 78.65920*(tk/1000) + (0)*(tk/1000)^2/2 + (0)*(tk/1000)^3/3 + (0)*(tk/1000)^4/4 - (0)/(tk/1000) + (-
443.0814);# - (-424.7178);

        else if t >=  409 && t < 1727 then #liquid
                hm_KOH = 83.10721*(tk/1000) + (-2.329778*10^-9)*(tk/1000)^2/2 + (1.884198*10^9)*(tk/1000)^3/3 + (-
4.813735*10^-10)*(tk/1000)^4/4 - (-3.556267*10^-11)/(tk/1000) + (-437.4832);# - (-412.7056);

        else if t >= 1727 && t < 5727 then #gas
                hm_KOH = 49.48500*(tk/1000) + (7.051337)*(tk/1000)^2/2 + (-1.41254)*(tk/1000)^3/3 + (0.097243)*(tk/1000)^4/4 -
(-0.245887)/(tk/1000) + (-248.5150);# - (-232.6304);

        else hm_KOH = 0;

fh_KOH: h_KOH= (hm_KOH/56.1056) *1000;


#K
fhm_K:
```

```
          if t >= 25 && t < 63 then #solid
                    hm_K = -63.47410*(tk/1000) + (-3226.34)*(tk/1000)^2/2 + (14644.6)*(tk/1000)^3/3 + (-16229.5)*(tk/1000)^4/4 -
(16.2941)/(tk/1000) + (119.648);# - (0);


          else if t >=  63 && t < 766 then #liquid
                    hm_K = 40.27113*(tk/1000) + (-30.54542)*(tk/1000)^2/2 + (26.49505)*(tk/1000)^3/3 + (-5.727854)*(tk/1000)^4/4 -
(-0.063477)/(tk/1000) + (-8.812467);# - (2.270005);


          else if t >=  766 && t < 1527  then #gas
                    hm_K = 20.66122*(tk/1000) + (0.391869)*(tk/1000)^2/2 + (-0.417344)*(tk/1000)^3/3 + (0.145582)*(tk/1000)^4/4 -
(0.003764)/(tk/1000) + (82.83860);# - (88.99996);


          else if t >= 1527 && t < 5727 then #gas
                    hm_K = 58.70570*(tk/1000) + (-27.38277)*(tk/1000)^2/2 + (6.730509)*(tk/1000)^3/3 + (-0.420844)*(tk/1000)^4/4 -
(-25.87921)/(tk/1000) + (32.37931);# - (88.99996);

          else hm_K = 0;

fh_K: h_K = (hm_K/39.0983) *1000;


#Cl
fhm_Cl:

          if t >= 25 && t < 327 then #gas
                    hm_Cl = 13.38298*(tk/1000) + (42.33999)*(tk/1000)^2/2 + (-64.74656)*(tk/1000)^3/3 + (32.99532)*(tk/1000)^4/4 -
(0.063319)/(tk/1000) + (116.1491);# - (121.3021);

          else if t >=  327 && t < 5727  then #gas
                    hm_Cl = 23.26597*(tk/1000) + (-1.555939)*(tk/1000)^2/2 + (0.34691)*(tk/1000)^3/3 + (-0.025961)*(tk/1000)^4/4 -
(0.153212)/(tk/1000) + (114.6604);# - (121.3021);
          else hm_Cl = 0;

fh_Cl: h_Cl = (hm_Cl/35.453) *1000;



#h_ambient calculation through NIST Polinomials:


#S
fhm_S_amb: if t_amb >= 25 && t_amb < 115 then #solid
                    hm_S_amb  =  21.21978*(tk_amb/1000)  +  3.865858*(tk_amb/1000)^2/2  +  (22.27461)*(tk_amb/1000)^3/3  +  (-
10.31908)*(tk_amb/1000)^4/4 - (-0.122518)/(tk_amb/1000) + (-7.085604); # - (0);

          else if t_amb == 115 then #mixture solid-liquid
                     hm_S_amb = 2.13336;

          else if t_amb < 159 && t_amb > 115 then #liquid
                    hm_S_amb  =  -4540.970*(tk_amb/1000)  +  26065.60*(tk_amb/1000)^2/2  +  (-55520.70)*(tk_amb/1000)^3/3  +
42012.20*(tk_amb/1000)^4/4 - (54.58860)/(tk_amb/1000) + (787.8070); #- (1.853781);

          else if t_amb == 159 then #transition
                    hm_S_amb = 5.73471;

          else if t_amb > 159 && t_amb < 609 then #liquid
                    hm_S_amb  =  -37.93350*(tk_amb/1000)  +  133.2420*(tk_amb/1000)^2/2  +  (-95.32450)*(tk_amb/1000)^3/3  +
24.00940*(tk_amb/1000)^4/4 - (7.654530)/(tk_amb/1000) + (29.78810); # - (1.853781);

          else if t_amb == 609 then
                    hm_S_amb = 21.3138; #to 290.116

          else if t_amb > 609 && t_amb < 1127 then #gas
                    hm_S_amb  = 27.45968*(tk_amb/1000)  + (-13.32784)  *(tk_amb/1000)^2/2  + (10.06574)*(tk_amb/1000)^3/3  + (-
2.662381)*(tk_amb/1000)^4/4 - (-0.055851)/(tk_amb/1000) + (269.1149); # - (276.9804);

          else if t_amb == 1127 then
                    hm_S_amb = 301.19;

          else if t_amb > 1127 && t_amb < 5727  then #gas
                    hm_S_amb  =  16.55345*(tk_amb/1000)  +  (2.400266)  *(tk_amb/1000)^2/2  +  (-0.255760)*(tk_amb/1000)^3/3  +
(0.005821)*(tk_amb/1000)^4/4 - (3.564793)/(tk_amb/1000) + (278.4356); # - (276.9804);
```

```
        else hm_S_amb = 0;


fh_S_amb: h_S_amb = (hm_S_amb/32.065) * 1000; #h_S in kJ/kg  hm_S = molar enthalpy in kJ/mol  M = molar weight in g/mol



#SO3
fhm_SO3_amb:
        if t_amb >= 25 && t_amb < 927 then
                hm_SO3_amb = 24.02503*(tk_amb/1000) + 119.4607*(tk_amb/1000)^2/2 + (-94.38686)*(tk_amb/1000)^3/3 +
26.96237*(tk_amb/1000)^4/4 - (-0.117517)/(tk_amb/1000) + (-407.8526); # - (-395.7654);

        else if t_amb == 927 then
                hm_SO3_amb = 100;

        else if t_amb > 927 && t_amb < 5727 then
                hm_SO3_amb = 81.99008*(tk_amb/1000) + 0.622236*(tk_amb/1000)^2/2 + (-0.122440)*(tk_amb/1000)^3/3 +
0.008294*(tk_amb/1000)^4/4 - (-6.703688)/(tk_amb/1000) + (-437.6590); # - (-395.7654);
        else hm_SO3_amb = 0;

fh_SO3_amb: h_SO3_amb = (hm_SO3_amb/ 80.063) *1000;




#Na2SO4
fhm_Na2SO4_amb:
        if t_amb >= 25 && t_amb < 185 then #solid; phase V
                hm_Na2SO4_amb = 96.97466*(tk_amb/1000) + 149.5454*(tk_amb/1000)^2/2 + (-44.51148)*(tk_amb/1000)^3/3 +
14.24313*(tk_amb/1000)^4/4 - (-0.874900)/(tk_amb/1000) + (-1425.698);# - (-1387.561);

        else if t_amb >= 185 && t_amb < 241 then #solid; phase IV
                hm_Na2SO4_amb = 97.09767*(tk_amb/1000) + 149.0676*(tk_amb/1000)^2/2 + (-43.87886)*(tk_amb/1000)^3/3 +
(13.96711)*(tk_amb/1000)^4/4 - (-0.877515)/(tk_amb/1000) + (-1425.987);# - (-1387.816);

        else if t_amb >= 241 && t_amb < 884 then #solid; phase I
                hm_Na2SO4_amb = 154.1365*(tk_amb/1000) + 12.24966*(tk_amb/1000)^2/2 + (49.39296)*(tk_amb/1000)^3/3 + (-
15.42553)*(tk_amb/1000)^4/4 - (-0.190212)/(tk_amb/1000) + (-1428.447);# - (-1380.900);

        else if t_amb >= 884 && t_amb < 2727  then #liquid
                hm_Na2SO4_amb = 197.0330*(tk_amb/1000) + -0.000028*(tk_amb/1000)^2/2 + (0.000011)*(tk_amb/1000)^3/3 + (-
0.000001)*(tk_amb/1000)^4/4 - (-0.000006)/(tk_amb/1000) + (-1427.260);# - (-1356.380);
        else hm_Na2SO4_amb = 0;

fh_Na2SO4_amb: h_Na2SO4_amb = (hm_Na2SO4_amb/142.042) *1000;


#K2CO3
fhm_K2CO3_amb:
        if t_amb >= 25 && t_amb < 901 then #solid
                hm_K2CO3_amb = 97.08093*(tk_amb/1000) + 94.22326*(tk_amb/1000)^2/2 + (-2.053291)*(tk_amb/1000)^3/3 +
0.709644*(tk_amb/1000)^4/4 - (-0.947860)/(tk_amb/1000) + (-1186.499);# - (-1150.182);
        else if t_amb >= 901 && t_amb < 2227 then #liquid
                hm_K2CO3_amb = 209.2000*(tk_amb/1000) + (-1.629015*10^-7)*(tk_amb/1000)^2/2 + (8.009850*10^-
8)*(tk_amb/1000)^3/3 + (-1.336428*10^-8)*(tk_amb/1000)^4/4 - (-2.105289*10^-8)/(tk_amb/1000) + (-1225.548);# - (-1130.609);
        else hm_K2CO3_amb = 0;

fh_K2CO3_amb: h_K2CO3_amb= (hm_K2CO3_amb/138.206) *1000;


#Na2S
fhm_Na2S_amb:

        if t_amb >= 25 && t_amb < 727 then #solid
                hm_Na2S_amb = 78.38780*(tk_amb/1000) + 13.94820*(tk_amb/1000)^2/2 + (2.753281)*(tk_amb/1000)^3/3 + (-
2.347990)*(tk_amb/1000)^4/4 - (0.008301)/(tk_amb/1000) + (-390.0830);# - (-366.1000);

        else if t_amb >= 727 && t_amb < 1003 then #solid; #
                hm_Na2S_amb = 58023.20*(tk_amb/1000) + (-104689.0)*(tk_amb/1000)^2/2 + (70037.20)*(tk_amb/1000)^3/3 + (-
16374.80)*(tk_amb/1000)^4/4 - (-6903.890)/(tk_amb/1000) + (-32139.00);# - (-366.1000);

        else if t_amb >= 1003 && t_amb < 1172  then #solid
                hm_Na2S_amb = -542020.0*(tk_amb/1000) + (789111.0)*(tk_amb/1000)^2/2 + (-431902.0)*(tk_amb/1000)^3/3 +
(84244.40)*(tk_amb/1000)^4/4 - (103416.0)/(tk_amb/1000) + (373259.0);# - (-366.1000);
```

```
            else if t_amb >= 1172 && t_amb < 2727 then #liquid
                        hm_Na2S_amb = 92.04800*(t_amb/1000) + (-0.000046)*(t_amb/1000)^2/2 + (0.000018)*(t_amb/1000)^3/3 + (-
0.000002)*(t_amb/1000)^4/4 - (-0.000011)/(t_amb/1000) + (-354.3040);# - (-323.9400);
            else hm_Na2S_amb = 0;

fh_Na2S_amb: h_Na2S_amb = (hm_Na2S_amb/78.045) *1000;


#KCl
fhm_KCl_amb:

            if t_amb >= 25 && t_amb < 627 then #solid
                        hm_KCl_amb = 35.41597*(tk_amb/1000) + 70.03472*(tk_amb/1000)^2/2 + (-91.38233)*(tk_amb/1000)^3/3 +
(52.52426)*(tk_amb/1000)^4/4 - (0.153460)/(tk_amb/1000) + (-449.1357);# - (-436.6841);

            else if t_amb >= 627 && t_amb < 771 then #solid
                        hm_KCl_amb = -717.3845*(tk_amb/1000) + (1247.861)*(tk_amb/1000)^2/2 + (-708.5144)*(tk_amb/1000)^3/3 +
(141.4435)*(tk_amb/1000)^4/4 - (103.6712)/(tk_amb/1000) + (1.760084);# - (-436.6841);

            else if t_amb >= 771 && t_amb < 1727 then #liquid
                        hm_KCl_amb = 73.59698*(tk_amb/1000) + (0)*(tk_amb/1000)^2/2 + (0)*(tk_amb/1000)^3/3 +
(0)*(tk_amb/1000)^4/4 - (0)/(tk_amb/1000) + (-443.7341);# - (-421.7932);
            else hm_KCl_amb = 0;

fh_KCl_amb: h_KCl_amb = (hm_KCl_amb/74.551) *1000;


#C
fhm_C_amb:
            if t_amb >= 25 && t_amb < 1527 then #solid h = cp*deltaT; cp= 10.68 J/mol*K
                        hm_C_amb = 10.68/1000 *tk_amb;
            else hm_C_amb = 0;

fh_C_amb: h_C_amb = (hm_C_amb/12.0107) *1000;


#NaCl
fhm_NaCl_amb:

            if t_amb >= 25 && t_amb < 800 then #solid
                        hm_NaCl_amb = 50.72389*(tk_amb/1000) + 6.672267*(tk_amb/1000)^2/2 + (-2.517167)*(tk_amb/1000)^3/3 +
(10.15934)*(tk_amb/1000)^4/4 - (-0.200675)/(tk_amb/1000) + (-427.2115);# -(-411.1203);

            else if t_amb >= 800 && t_amb < 2227 then #solid
                        hm_NaCl_amb = -42.44780*(tk_amb/1000) + (113.5260)*(tk_amb/1000)^2/2 + (-43.64660)*(tk_amb/1000)^3/3 +
(5.896630)*(tk_amb/1000)^4/4 - (39.13860)/(tk_amb/1000) + (-305.5610);# - (-385.923);
            else hm_NaCl_amb = 0;

fh_NaCl_amb: h_NaCl_amb= (hm_NaCl_amb/58.443) *1000;


#Na2CO3
fhm_Na2CO3_amb:

            if t_amb >= 25 && t_amb < 450 then #solid
                        hm_Na2CO3_amb = 175.2010*(tk_amb/1000) + (-348.0580)*(tk_amb/1000)^2/2 + (743.0720)*(tk_amb/1000)^3/3 +
(-305.551)*(tk_amb/1000)^4/4 - (-1.634221)/(tk_amb/1000) + (-1178.98);# - (-1130.770);

            else if t_amb >= 450 && t_amb < 850 then #solid
                        hm_Na2CO3_amb = -1067.000*(tk_amb/1000) + (2469.340)*(tk_amb/1000)^2/2 + (-1829.060)*(tk_amb/1000)^3/3 +
(505.7480)*(tk_amb/1000)^4/4 - (100.1820)/(tk_amb/1000) + (-607.124);# - (-1130.77);

            else if t_amb >= 850 && t_amb < 2227 then #liquid
                        hm_Na2CO3_amb = 189.5350*(tk_amb/1000) + (-0.000007)*(tk_amb/1000)^2/2 + (0.000002)*(tk_amb/1000)^3/3 +
(-5.205100*10^-9)*(tk_amb/1000)^4/4 - (-0.000003)/(tk_amb/1000) + (-1183.060);# - (-1108.510);

            else hm_Na2CO3_amb = 0;

fh_Na2CO3_amb: h_Na2CO3_amb = (hm_Na2CO3_amb/105.988) *1000;


#NaOH
fhm_NaOH_amb:

            if t_amb >= 25 && t_amb < 299 then #solid
```

```
		hm_NaOH_amb = 419.4837*(tk_amb/1000) + (-1717.754)*(tk_amb/1000)^2/2 + (2953.573)*(tk_amb/1000)^3/3 + (-
1597.221)*(tk_amb/1000)^4/4 - (-6.046884)/(tk_amb/1000) + (-517.8662);# - (-425.9312);

	else if t_amb >= 299 && t_amb < 323 then #solid

		hm_NaOH_amb = 86.02304*(tk_amb/1000) + (0)*(tk_amb/1000)^2/2 + (0)*(tk_amb/1000)^3/3 +
(0)*(tk_amb/1000)^4/4 - (0)/(tk_amb/1000) + (-448.8512);# - (-425.9312);

	else if t_amb >= 323 && t_amb < 2227 then #liquid
		hm_NaOH_amb = 88.34725*(tk_amb/1000) + (-2.495103)*(tk_amb/1000)^2/2 + (-3.013028)*(tk_amb/1000)^3/3 +
(0.862607)*(tk_amb/1000)^4/4 - (0.042216)/(tk_amb/1000) + (-442.9350);# - (-416.8783);

	else if t_amb >= 2227 && t_amb < 4727 then #gas
		hm_NaOH_amb = 49.46492*(tk_amb/1000) + (7.000125)*(tk_amb/1000)^2/2 + (-1.391757)*(tk_amb/1000)^3/3 +
(0.095206)*(tk_amb/1000)^4/4 - (-0.256928)/(tk_amb/1000) + (-213.6706);# - (-197.7572);
	else hm_NaOH_amb = 0;

fh_NaOH_amb: h_NaOH_amb = (hm_NaOH_amb/39.9971) *1000;



#Na
fhm_Na_amb:

	if t_amb >= 25 && t_amb < 97 then #solid
		hm_Na_amb = 72.63675*(tk_amb/1000) + (-9.491572)*(tk_amb/1000)^2/2 + (-730.9322)*(tk_amb/1000)^3/3 +
(1414.518)*(tk_amb/1000)^4/4 - (-1.259377)/(tk_amb/1000) + (-21.79467);# - (0);
	else if t_amb >= 97 && t_amb < 897 then #liquid
		hm_Na_amb = 40.25707*(tk_amb/1000) + (-28.23849)*(tk_amb/1000)^2/2 + (20.69402)*(tk_amb/1000)^3/3 + (-
3.641872)*(tk_amb/1000)^4/4 - (-0.079874)/(tk_amb/1000) + (-8.782300);# - (2.406001);
	else if t_amb >= 897 && t_amb < 5727 then #gas
		hm_Na_amb = 20.80573*(tk_amb/1000) + (0.277206)*(tk_amb/1000)^2/2 + (-0.392086)*(tk_amb/1000)^3/3 +
(0.119634)*(tk_amb/1000)^4/4 - (-0.008879)/(tk_amb/1000) + (101.0386);# - (107.2999);
	else hm_Na_amb = 0;

fh_Na_amb: h_Na_amb = (hm_Na_amb/22.9898) *1000;



#K2SO4
fhm_K2SO4_amb:

	if t_amb >= 25 && t_amb < 927 then #solid; alpha phase
		hm_K2SO4_amb = 139.5050*(tk_amb/1000) + (-1.199884)*(tk_amb/1000)^2/2 + (136.808)*(tk_amb/1000)^3/3 + (-
47.14322)*(tk_amb/1000)^4/4 - (-1.663999)/(tk_amb/1000) + (-1485.964);# - (-1437.706);

	else if t_amb >= 927 && t_amb < 1069 then #solid; beta phase
		hm_K2SO4_amb = 114.3424*(tk_amb/1000) + (81.29554)*(tk_amb/1000)^2/2 + (-0.000942)*(tk_amb/1000)^3/3 + (-
0.016197)*(tk_amb/1000)^4/4 - (0.000141)/(tk_amb/1000) + (-1461.948);# - (-1424.246);

	else if t_amb >= 897 && t_amb < 5727 then #liquid
		hm_K2SO4_amb = 201.4604*(tk_amb/1000) + (0)*(tk_amb/1000)^2/2 + (0)*(tk_amb/1000)^3/3 +
(0)*(tk_amb/1000)^4/4 - (0)/(tk_amb/1000) + (-1471.274);# - (-1393.669);

	else hm_K2SO4_amb = 0;

fh_K2SO4_amb: h_K2SO4_amb = (hm_K2SO4_amb/174.259) *1000;

#KOH
fhm_KOH_amb:

	if t_amb >= 25 && t_amb < 243 then #solid
		hm_KOH_amb = 80.78258*(tk_amb/1000) + (-112.2329)*(tk_amb/1000)^2/2 + (301.1543)*(tk_amb/1000)^3/3 + (-
147.9923)*(tk_amb/1000)^4/4 - (-0.468867)/(tk_amb/1000) + (-447.7591);# - (-424.7178);

	else if t_amb >=  243 && t_amb < 409 then #solid
		hm_KOH_amb = 78.65920*(tk_amb/1000) + (0)*(tk_amb/1000)^2/2 + (0)*(tk_amb/1000)^3/3 +
(0)*(tk_amb/1000)^4/4 - (0)/(tk_amb/1000) + (-443.0814);# - (-424.7178);

	else if t_amb >=  409 && t_amb < 1727 then #liquid
		hm_KOH_amb = 83.10721*(tk_amb/1000) + (-2.329778*10^-9)*(tk_amb/1000)^2/2 +
(1.884198*10^9)*(tk_amb/1000)^3/3 + (-4.813735*10^-10)*(tk_amb/1000)^4/4 - (-3.556267*10^-11)/(tk_amb/1000) + (-437.4832);# - (-
412.7056);

	else if t_amb >= 1727 && t_amb < 5727 then #gas
```

```
                    hm_KOH_amb = 49.48500*(tk_amb/1000) + (7.051337)*(tk_amb/1000)^2/2 + (-1.41254)*(tk_amb/1000)^3/3 + (0.097243)*(tk_amb/1000)^4/4 - (-0.245887)/(tk_amb/1000) + (-248.5150);# - (-232.6304);

          else hm_KOH_amb = 0;

fh_KOH_amb: h_KOH_amb = (hm_KOH_amb/56.1056) *1000;


#K
fhm_K_amb:

          if t_amb >= 25 && t_amb < 63 then #solid
                    hm_K_amb = -63.47410*(tk_amb/1000) + (-3226.34)*(tk_amb/1000)^2/2 + (14644.6)*(tk_amb/1000)^3/3 + (-16229.5)*(tk_amb/1000)^4/4 - (16.2941)/(tk_amb/1000) + (119.648);# - (0);

          else if t_amb >=  63 && t_amb < 766 then #liquid
                    hm_K_amb = 40.27113*(tk_amb/1000) + (-30.54542)*(tk_amb/1000)^2/2 + (26.49505)*(tk_amb/1000)^3/3 + (-5.727854)*(tk_amb/1000)^4/4 - (-0.063477)/(tk_amb/1000) + (-8.812467);# - (2.270005);


          else if t_amb >=  766 && t_amb < 1527  then #gas
                    hm_K_amb = 20.66122*(tk_amb/1000) + (0.391869)*(tk_amb/1000)^2/2 + (-0.417344)*(tk_amb/1000)^3/3 + (0.145582)*(tk_amb/1000)^4/4 - (0.003764)/(tk_amb/1000) + (82.83860);# - (88.99996);


          else if t_amb >= 1527 && t_amb < 5727 then #gas
                    hm_K_amb = 58.70570*(tk_amb/1000) + (-27.38277)*(tk_amb/1000)^2/2 + (6.730509)*(tk_amb/1000)^3/3 + (-0.420844)*(tk_amb/1000)^4/4 - (-25.87921)/(tk_amb/1000) + (32.37931);# - (88.99996);

          else hm_K_amb = 0;

fh_K_amb: h_K_amb = (hm_K_amb/39.0983) *1000;


#Cl
fhm_Cl_amb:

          if t_amb >= 25 && t_amb < 327 then #gas
                    hm_Cl_amb = 13.38298*(tk_amb/1000) + (42.33999)*(tk_amb/1000)^2/2 + (-64.74656)*(tk_amb/1000)^3/3 + (32.99532)*(tk_amb/1000)^4/4 - (0.063319)/(tk_amb/1000) + (116.1491);# - (121.3021);

          else if t_amb >=  327 && t_amb < 5727  then #gas
                    hm_Cl_amb = 23.26597*(tk_amb/1000) + (-1.555939)*(tk_amb/1000)^2/2 + (0.34691)*(tk_amb/1000)^3/3 + (-0.025961)*(tk_amb/1000)^4/4 - (0.153212)/(tk_amb/1000) + (114.6604);# - (121.3021);
          else hm_Cl_amb = 0;

fh_Cl_amb: h_Cl_amb = (hm_Cl_amb/35.453) *1000;



t1:          test (mass >=0.0) warning "mass flow negative";
```

Water stream (connection)

```
#Shifting enthalpy from H-H0_tr to H
# H0_tr = Composition.fhf0

ft:         if blocksize() == 1.0 && isconverged(p) && isconverged(t) then
                        h0 = Composition.fhpt(p, t);
            else
                        t = Composition.ft(p, h0);


fh:  h = h0 ;


ifl (boiler == off)then ft_amb: t_amb =0;
endifl


fh_ambient: h_ambient = Composition.fhf0() + Composition.fhpt(1, t_amb);



#standard
fs:         s = Composition.fs(p, h0);
fv:         v = Composition.fv(p,h0);
fx:         x = fx(p, h0, 1, 0,0,0,0,0,0,0,0,0,0,0,0,0);



t1:          test (mass >=0.0) warning "mass flow negative";
```

KRB unit V2 external sootblowing

```
fh_reduction: h_reduction = 12900; #Tran & Grace (2018)  /  in Vakkilainen (2005) h_reduction = 13099
fh_Cu: h_Cu = 32800; #in Vakkilainen (2005): n.A.
fh_formation_SO2: h_formation_SO2 = 5506; #Tran & Grace (2018) / in Vakkilainen (2005) = 5531
fh_formation_CO: h_formation_CO = 10110; #in Vakkilainen (2005): n.A.

fh_evap_w: h_evap_w = 2442; #heat of evaporation of water
fcp_wv: cp_wv = 1.88; #heat capacity of water vapor
#________________________________________________________________________________


#BLOWDOWN:
#absolute blowdown stream in kg/kg
fstream_blowdown: stream_blowdown = blowdown.mass;
fstream_blowdown_pct:stream_blowdown_pct = stream_blowdown*100/water.mass;



#SOOTBLOWING:
fsootblowing_steam: sootblowing_steam = sootblowing.mass/BL.mass;



#in kg/kg BLS
fH2O_total: H2O_total = sootblowing_steam + BL.BL_H2O; #H2O_total = sootblowing steam + H2O in BL



#smelt:
#mass flows:             -> variables defined as "mass fraction" bc of dimension kg/kg (BLS)

#reduction
fNa2S_smelt: Na2S_smelt = (BL.BL_Composition.myS/32 - SO2_fg/64) * R/100 * 78;

#no reduction
fNa2SO4_smelt: Na2SO4_smelt = Na2S_smelt/78 * (100/R -1)*142;

fNaCl_smelt: NaCl_smelt = 117/71 * BL.BL_Composition.myCl;

fNa2CO3_smelt: Na2CO3_smelt = (BL.BL_Composition.myNa - (46* Na2S_smelt/78 + 46*Na2SO4_smelt/142 +
23*NaCl_smelt/58.5))*106/46;

fK2CO3_smelt: K2CO3_smelt = BL.BL_Composition.myK*138.2/78.2;

fInerts_smelt: Inerts_smelt = BL.BL_Composition.Inerts;

#fCu_smelt:  Cu_smelt = Cu;

#above in kg/kg BLS therefore multipyling by BL.mass gives total mass flow of smelt

fsmelt_sum: smelt.mass = BL.mass*(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt + Na2CO3_smelt + Cu + K2CO3_smelt);


#composition/mass fractions of smelt stream in kg/kg:

fmNa2S_smelt: smelt.KRB_Composition.m_Na2S = Na2S_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNa2SO4_smelt: smelt.KRB_Composition.m_Na2SO4 = Na2SO4_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNaCl_smelt: smelt.KRB_Composition.m_NaCl = NaCl_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNa2CO3_smelt: smelt.KRB_Composition.m_Na2CO3 = Na2CO3_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmK2CO3_smelt: smelt.KRB_Composition.m_K2CO3 = K2CO3_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmInerts_smelt: smelt.KRB_Composition.m_Inerts = Inerts_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);
```

```
#Sulphidity of smelt:
fsulfidity_smelt: sulfidity_smelt = (smelt.KRB_Composition.m_Na2S/78)/(smelt.KRB_Composition.m_Na2S/78 +
smelt.KRB_Composition.m_Na2CO3/106 + smelt.KRB_Composition.m_K2CO3/138.2) *100;


#Number of Moles in flue gas [kmol/kgBLS]:

fFG_moles: FG_moles = (4.86/12 * (BL.BL_Composition.myC - Cu) + 2.93 * BL.BL_Composition.myH/2 + H2O_total/18 - 3.86 *
BL.BL_Composition.myO /32 +0.93* (BL.BL_Composition.myNa/46 + BL.BL_Composition.myK/78 + BL.BL_Composition.myCl/71) +
(6.79 - 7.72 * R/100) * BL.BL_Composition.myS/32)/(1-4.76*O2_wvb/100);


#CO, SO2 and O2 in FG in kg/kg BLS

fCO_ppmv:  CO_fg = CO_ppmv/(10^6)*28*FG_moles;

fSO2_ppmv:SO2_fg = SO2_ppmv/(10^6)*64*FG_moles;

fO2_fg: O2_fg = O2_wvb/100 * FG_moles *32;


#Combustion products in kg/kg BLS

fCO2_fg: CO2_fg = 44/12*(BL.BL_Composition.myC - Cu - CO_fg*12/28- Na2CO3_smelt*12/106 - K2CO3_smelt*12/138);

fH2O_comb: H2O_comb = 18/2* BL.BL_Composition.myH; #H2O content in FG from combustion

fO2_total: O2_total = (16/28)* CO_fg + 32/64* SO2_fg + 48/106* Na2CO3_smelt + 64/142 * Na2SO4_smelt + 48/138 * K2CO3_smelt +
32/44* CO2_fg +16/18*H2O_comb; #O2 in smelt and gas

fO2_theo: oxy_theo =  O2_total - BL.BL_Composition.myO;

fair_theo: air_theo = oxy_theo/0.232;


fair_infiltration: air_infiltration = air_theo * 3/100;

ftotal_dry_air_to_boiler: air_total = (oxy_theo + O2_fg)/0.232; #total dry air to boiler

fN2_fg: N2_fg = 0.768 * air_total;

fdry_fg_total: dry_fg_total = CO_fg + SO2_fg + O2_fg + CO2_fg + N2_fg;

fair_moisture: air_moisture = air_total * humidity_comb_air;

fH2O_fg: H2O_fg = air_moisture + BL.BL_H2O + H2O_comb; #total H2O in FG

fdry_air_fan: dry_air_fan = air_total - air_infiltration;

fH2O_KRB: H2O_KRB = H2O_fg + sootblowing_steam;

fN2_KRB: N2_KRB = air_theo*0.768; #N2 theoretical

fCO_KRB: CO_KRB = CO_fg;

fSO2_KRB: SO2_KRB = SO2_fg;


#total air to boiler -> multiplying with BL.mass (from kg/kg BLS/s to kg/s)

fmassflowair: air.mass = air_total * (1+humidity_comb_air)*BL.mass;


#flue gas in kg/kg BLS

ffg_wo_excess_air: fg_wo_excess_air = H2O_KRB + N2_KRB +CO_KRB + SO2_KRB; #FG without excess air

fexcess_air: excess_air = (FG_moles - (H2O_KRB/18 + CO2_fg/44 + N2_KRB/28 + CO_fg/28 +  SO2_fg/64 )) * 28.84;

fexcess_air_pct: excess_air_pct = 100* excess_air/air_theo; # excess air as pct of theoretical air

fH2O_excess_air: H2O_excess_air = excess_air * humidity_comb_air ;

fO2_excess_air: O2_excess_air = O2_fg;
```

```
fN2_excess_air: N2_excess_air = excess_air*0.767;

fflue_gas_wet: flue_gas_wet = dry_fg_total + H2O_KRB; #mass flow of fg per kg BLS


#g/mol

fmol_weight_fg_wet: mol_weight_fg_wet = flue_gas_wet/FG_moles;  #wet molecular weight of fg


#flue gas total mass flow:
fmb_fg: flue_gas_default.mass = flue_gas_wet * BL.mass; #mass flow FG


#flue gas composition
#wet mass basis
fwm_H2O_fg: flue_gas_default.Composition.H2O = H2O_KRB/flue_gas_wet;
fwm_CO2_fg: flue_gas_default.Composition.CO2 = CO2_fg/flue_gas_wet;
fwm_N2_fg:  flue_gas_default.Composition.N2 = (N2_KRB+N2_excess_air)/flue_gas_wet;
fwm_O2_fg: flue_gas_default.Composition.O2 =  O2_excess_air/flue_gas_wet;
fwm_CO_fg:  flue_gas_default.Composition.CO = CO_KRB/flue_gas_wet;
fwm_SO2_fg: flue_gas_default.Composition.SO2 = SO2_KRB/flue_gas_wet;

fFG_moles_wet:FG_moles_wet = (flue_gas_default.Composition.H2O/18 + flue_gas_default.Composition.CO2/44 +
flue_gas_default.Composition.N2/28 + flue_gas_default.Composition.O2/32 + flue_gas_default.Composition.CO/28 +
flue_gas_default.Composition.SO2/64)*10;


#Heavy (Virgin) Black Liquor
#Chloride and potassium

fmoles_pct_Cl:  moles_pct_Cl = (BL.BL_Composition.myCl /35.5)/(BL.BL_Composition.myNa/23+BL.BL_Composition.myK/39.1)*100;
        #mole% Cl/(Na+K)

fmoles_pct_K:  moles_pct_K = (BL.BL_Composition.myK/39.1)/(BL.BL_Composition.myNa/23+BL.BL_Composition.myK/39.1)*100;
        #mole% K/(Na+K)

#fenrich_Cl: enrich_Cl = ; #Chloride enrichment factor  = C64/C163 -> input data from dust
#fenrich_K: enrich_K = ; #Potassium enrichment factor  = C65/C164 -> input data from dust

fratio_S_Na2_K2:  ratio_S_Na2_K2 = (BL.BL_Composition.myS/32)/(BL.BL_Composition.myNa/46+BL.BL_Composition.myK/78.2);
        #S/(Na2+K2) molar ratio



#__________________________________________

#HEAT-INPUT:

#BL
fheat_LHV:heat_LHV = BL.mass*BL.LHV_wet;


#fheat_BL_sensible: heat_BL_sensible =  BL.mass*(BL.t-BL.t_amb)*BL.cp_BL*(1+BL.BL_H2O);

fheat_BL_sensible: heat_BL_sensible =  BL.mass*(BL.cp_BL*BL.t-BL.t_amb*BL.cp_BL_amb)*(1+BL.BL_H2O);


#air
fheat_air: heat_air = (air.h - air.h_ambient)* air.mass;


#SOOTBLOWING:

#internal sootblowing: input = 0* ...

#fheat_sootblowing: heat_sootblowing = sootblowing.mass* (sootblowing.h -2500.9); #approach Vakkilainen(2005): h_sootblowing and
h_steam?

fheat_sootblowing: heat_sootblowing = sootblowing.mass*(sootblowing.h-sootblowing.h_ambient);


#BLOWDOWN:

#NEW
```

```
#Changes due to new blowdown input stream:
fheat_blowdown: heat_blowdown =  (blowdown.h-blowdown.h_ambient) * blowdown.mass; #only used if HX is used for transfering heat from blowdownstream to feedwater


fsum_heat_input: sum_heat_input = heat_LHV + heat_BL_sensible + heat_air  + heat_sootblowing + heat_blowdown;


#_____________________________________________________________________________________


#HEAT LOSSES:

#Flue Gas
floss_fg: loss_fg = (flue_gas_default.mass*(flue_gas_default.h - flue_gas_default.h_ambient));



#Reductions / Formation
floss_Na2S: loss_Na2S = BL.mass* Na2S_smelt*h_reduction;
floss_K2S: loss_K2S = 0;
floss_SO2: loss_SO2 = BL.mass*SO2_KRB*h_formation_SO2;

#Smelt
floss_smelt: loss_smelt = smelt.mass*(smelt.h - smelt.h_ambient); #enthalpy of smelt at ambient temp


#sootblowing loss: according to Tran & Grace (2018)-> no difference between INT/EXT


#TRAN:
floss_sootblowing: loss_sootblowing = sootblowing.mass*(h_evap_w+cp_wv*(flue_gas_default.t - flue_gas_default.t_amb)); #2442 =h_evap, 1.88 =cp_wv




#Other losses
floss_radi: loss_radi = rad_heat_loss/100 *sum_heat_input;
floss_unaccounted: loss_unaccounted = unac_loss/100*sum_heat_input;
floss_margin:loss_margin = margin_loss/100 *sum_heat_input;

#additional cf Tran & Grace (2018)
#Unburned carbon in smelt
fheat_cu_smelt: loss_cu_smelt = BL.mass*Cu*h_Cu; #not used assumed to be part of enthalpy of smelt


#CO formation
fheat_formation_CO: loss_formation_CO = BL.mass*CO_KRB*h_formation_CO;


#NEW
#floss_blowdown: loss_blowdown =  (blowdown.h-blowdown.h_ambient) * blowdown.mass; #used if no HX implemented / used -> input_heat = heat_loss
floss_blowdown: loss_blowdown =  0;




#Sum

fsum_heat_output: sum_heat_output = loss_blowdown + loss_fg + loss_sootblowing  + loss_Na2S + loss_K2S + loss_SO2 + loss_smelt + loss_formation_CO + loss_cu_smelt + loss_radi + loss_unaccounted + loss_margin;

#+ loss_blowdown; before w/o now with


#___________________________________________________________________________

#STEAM GENERATION

#Heat to steam
fheat_to_steam: heat_to_steam = sum_heat_input - sum_heat_output;

#Steam generation efficiency
```

```
fsteam_efficiency: steam_efficiency =  heat_to_steam/sum_heat_input *100;


#Steam production
fsteam_production: steam_production = (1- stream_blowdown_pct/100) * water.mass;


#______________________________________________________________________

#Tran & Grace (2018)
#feedwater:

#ffeedwater_to_boiler:  water.mass  =  (heat_to_steam/((1-stream_blowdown_pct/100)*steam.h  +  stream_blowdown_pct/100*  1423.3  - water.h ));

ffeedwater_to_boiler: water.mass = (steam.mass*steam.h + blowdown.h * blowdown.mass - heat_to_steam)/ water.h;



#steam to mill

#external sootblowing:
fsteamtomill: steam.mass = water.mass - blowdown.mass;



#TESTs

t1:         test (blowdown.x == 0) warning "gaseous blowdown stream";
```

KRB unit V2 internal sootblowing

```
fh_reduction: h_reduction = 12900; #Tran & Grace (2018)  /  in Vakkilainen (2005) h_reduction = 13099
fh_Cu: h_Cu = 32800; #in Vakkilainen (2005): n.A.
fh_formation_SO2: h_formation_SO2 = 5506; #Tran & Grace (2018) / in Vakkilainen (2005) = 5531
fh_formation_CO: h_formation_CO = 10110; #in Vakkilainen (2005): n.A.

fh_evap_w: h_evap_w = 2442; #heat of evaporation of water
fcp_wv: cp_wv = 1.88; #heat capacity of water vapor
#___________________________________________________________________________


#BLOWDOWN:
#absolute blowdown stream in kg/kg
fstream_blowdown: stream_blowdown = blowdown.mass;
fstream_blowdown_pct:stream_blowdown_pct = stream_blowdown*100/water.mass;


#SOOTBLOWING:
#fsootblowing_steam: sootblowing_steam = sootblowing.mass/BL.mass;
fmass_sootblowing: mass_sootblowing = sootblowing_steam*BL.mass; #entire mass flow of sootblowing



#in kg/kg BLS
fH2O_total: H2O_total = sootblowing_steam + BL.BL_H2O; #H2O_total = sootblowing steam + H2O in BL



#smelt:
#mass flows:             -> variables defined as "mass fraction" bc of dimension kg/kg (BLS)

#reduction
fNa2S_smelt: Na2S_smelt = (BL.BL_Composition.myS/32 - SO2_fg/64) * R/100 * 78;

#no reduction
fNa2SO4_smelt: Na2SO4_smelt = Na2S_smelt/78 * (100/R -1)*142;

fNaCl_smelt: NaCl_smelt = 117/71 * BL.BL_Composition.myCl;

fNa2CO3_smelt: Na2CO3_smelt = (BL.BL_Composition.myNa - (46* Na2S_smelt/78 + 46*Na2SO4_smelt/142 +
23*NaCl_smelt/58.5))*106/46;

fK2CO3_smelt: K2CO3_smelt = BL.BL_Composition.myK*138.2/78.2;

fInerts_smelt: Inerts_smelt = BL.BL_Composition.Inerts;


#above in kg/kg BLS therefore multipyling by BL.mass gives total mass flow of smelt

fsmelt_sum: smelt.mass = BL.mass*(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt + Na2CO3_smelt + Cu + K2CO3_smelt);


#composition/mass fractions of smelt stream in kg/kg:

fmNa2S_smelt: smelt.KRB_Composition.m_Na2S = Na2S_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNa2SO4_smelt: smelt.KRB_Composition.m_Na2SO4 = Na2SO4_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNaCl_smelt: smelt.KRB_Composition.m_NaCl = NaCl_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmNa2CO3_smelt: smelt.KRB_Composition.m_Na2CO3 = Na2CO3_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmK2CO3_smelt: smelt.KRB_Composition.m_K2CO3 = K2CO3_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);

fmInerts_smelt: smelt.KRB_Composition.m_Inerts = Inerts_smelt/(Inerts_smelt + Na2S_smelt + Na2SO4_smelt + NaCl_smelt +
Na2CO3_smelt + Cu + K2CO3_smelt);


#Sulphidity of smelt:
```

```
fsulfidity_smelt: sulfidity_smelt = (smelt.KRB_Composition.m_Na2S/78)/(smelt.KRB_Composition.m_Na2S/78 +
smelt.KRB_Composition.m_Na2CO3/106 + smelt.KRB_Composition.m_K2CO3/138.2) *100;


#Number of Moles in flue gas [kmol/kgBLS]:

fFG_moles: FG_moles = (4.86/12 * (BL.BL_Composition.myC - Cu) + 2.93 * BL.BL_Composition.myH/2 + H2O_total/18 - 3.86 *
BL.BL_Composition.myO /32 +0.93* (BL.BL_Composition.myNa/46 + BL.BL_Composition.myK/78 + BL.BL_Composition.myCl/71) +
(6.79 - 7.72 * R/100) * BL.BL_Composition.myS/32)/(1-4.76*O2_wvb/100);


#CO, SO2 and O2 in FG in kg/kg BLS

fCO_ppmv:  CO_fg = CO_ppmv/(10^6)*28*FG_moles;

fSO2_ppmv:SO2_fg = SO2_ppmv/(10^6)*64*FG_moles;

fO2_fg: O2_fg = O2_wvb/100 * FG_moles *32;


#Combustion products in kg/kg BLS

fCO2_fg: CO2_fg = 44/12*(BL.BL_Composition.myC - Cu - CO_fg*12/28- Na2CO3_smelt*12/106 - K2CO3_smelt*12/138);

fH2O_comb: H2O_comb = 18/2* BL.BL_Composition.myH; #H2O content in FG from combustion

fO2_total: O2_total = (16/28)* CO_fg + 32/64* SO2_fg + 48/106* Na2CO3_smelt + 64/142 * Na2SO4_smelt + 48/138 * K2CO3_smelt +
32/44* CO2_fg +16/18*H2O_comb; #O2 in smelt and gas

fO2_theo: oxy_theo =  O2_total - BL.BL_Composition.myO;

fair_theo: air_theo = oxy_theo/0.232;

fair_infiltration: air_infiltration = air_theo * 3/100;


ftotal_dry_air_to_boiler: air_total = (oxy_theo + O2_fg)/0.232; #total dry air to boiler

fN2_fg: N2_fg = 0.768 * air_total;

fdry_fg_total: dry_fg_total = CO_fg + SO2_fg + O2_fg + CO2_fg + N2_fg;

fair_moisture: air_moisture = air_total * humidity_comb_air;

fH2O_fg: H2O_fg = air_moisture + BL.BL_H2O + H2O_comb; #total H2O in FG

fdry_air_fan: dry_air_fan = air_total - air_infiltration;

fH2O_KRB: H2O_KRB = H2O_fg + sootblowing_steam;

fN2_KRB: N2_KRB = air_theo*0.768; #N2 theoretical

fCO_KRB: CO_KRB = CO_fg;

fSO2_KRB: SO2_KRB = SO2_fg;


#total air to boiler -> multiplying with BL.mass (from kg/kg BLS/s to kg/s)

fmassflowair: air.mass = air_total * (1+humidity_comb_air)*BL.mass;


#flue gas in kg/kg BLS

ffg_wo_excess_air: fg_wo_excess_air = H2O_KRB + N2_KRB +CO_KRB + SO2_KRB; #FG without excess air

fexcess_air: excess_air = (FG_moles - (H2O_KRB/18 + CO2_fg/44 + N2_KRB/28 + CO_fg/28 +  SO2_fg/64 )) * 28.84;

fexcess_air_pct: excess_air_pct = 100* excess_air/air_theo; # excess air as pct of theoretical air

fH2O_excess_air: H2O_excess_air = excess_air * humidity_comb_air ;

fO2_excess_air: O2_excess_air = O2_fg;

fN2_excess_air: N2_excess_air = excess_air*0.767;
```

```
fflue_gas_wet: flue_gas_wet = dry_fg_total + H2O_KRB; #mass flow of fg per kg BLS


#g/mol

fmol_weight_fg_wet: mol_weight_fg_wet = flue_gas_wet/FG_moles;  #wet molecular weight of fg


#flue gas total mass flow:
fmb_fg: flue_gas_default.mass = flue_gas_wet * BL.mass; #mass flow FG


#flue gas composition
#wet mass basis
fwm_H2O_fg: flue_gas_default.Composition.H2O = H2O_KRB/flue_gas_wet;
fwm_CO2_fg: flue_gas_default.Composition.CO2 = CO2_fg/flue_gas_wet;
fwm_N2_fg:  flue_gas_default.Composition.N2 = (N2_KRB+N2_excess_air)/flue_gas_wet;
fwm_O2_fg: flue_gas_default.Composition.O2 =  O2_excess_air/flue_gas_wet;
fwm_CO_fg:  flue_gas_default.Composition.CO = CO_KRB/flue_gas_wet;
fwm_SO2_fg: flue_gas_default.Composition.SO2 = SO2_KRB/flue_gas_wet;

fFG_moles_wet:FG_moles_wet = (flue_gas_default.Composition.H2O/18 + flue_gas_default.Composition.CO2/44 +
flue_gas_default.Composition.N2/28 + flue_gas_default.Composition.O2/32 + flue_gas_default.Composition.CO/28 +
flue_gas_default.Composition.SO2/64)*10;


#Heavy (Virgin) Black Liquor
#Chloride and potassium

fmoles_pct_Cl:  moles_pct_Cl  = (BL.BL_Composition.myCl  /35.5)/(BL.BL_Composition.myNa/23+BL.BL_Composition.myK/39.1)*100;
        #mole% Cl/(Na+K)

fmoles_pct_K:   moles_pct_K   =  (BL.BL_Composition.myK/39.1)/(BL.BL_Composition.myNa/23+BL.BL_Composition.myK/39.1)*100;
        #mole% K/(Na+K)

#fenrich_Cl: enrich_Cl = ; #Chloride enrichment factor  = C64/C163 -> input data from dust
#fenrich_K: enrich_K = ; #Potassium enrichment factor  = C65/C164 -> input data from dust

fratio_S_Na2_K2:  ratio_S_Na2_K2  =  (BL.BL_Composition.myS/32)/(BL.BL_Composition.myNa/46+BL.BL_Composition.myK/78.2);
        #S/(Na2+K2) molar ratio



#________________________________________________

#HEAT-INPUT:

#BL
fheat_LHV:heat_LHV = BL.mass*BL.LHV_wet;


#fheat_BL_sensible: heat_BL_sensible =  BL.mass*(BL.t-BL.t_amb)*BL.cp_BL*(1+BL.BL_H2O);

fheat_BL_sensible: heat_BL_sensible =  BL.mass*(BL.cp_BL*BL.t-BL.t_amb*BL.cp_BL_amb)*(1+BL.BL_H2O);



#air
fheat_air: heat_air = (air.h - air.h_ambient)* air.mass; #h_air at 25°C = -134.32

#SOOTBLOWING:
#INTERNAL
#internal sootblowing: input = 0* ...

fheat_sootblowing: heat_sootblowing = 0;


#BLOWDOWN
#NEW
#Changes due to new blowdown input stream:
fheat_blowdown: heat_blowdown =  (blowdown.h-blowdown.h_ambient) * blowdown.mass; #only used if HX is used for transfering heat
from blowdownstream to feedwater

#only used if HX is used for transfering heat from blowdownstream to feedwater
#fheat_blowdown: heat_blowdown =  0;
```

```
fsum_heat_input: sum_heat_input = heat_LHV + heat_BL_sensible + heat_air + heat_sootblowing + heat_blowdown;


#____________________________________________________________________________________________


#HEAT LOSSES:

#Flue Gas
floss_fg: loss_fg = (flue_gas_default.mass* (flue_gas_default.h - flue_gas_default.h_ambient));


#Reductions / Formation
floss_Na2S: loss_Na2S = BL.mass* Na2S_smelt*h_reduction;
floss_K2S: loss_K2S = 0;
floss_SO2: loss_SO2 = BL.mass*SO2_KRB*h_formation_SO2;

#Smelt
floss_smelt: loss_smelt = smelt.mass*(smelt.h - smelt.h_ambient); #enthalpy of smelt at ambient temp


#according to Tran & Grace (2018) no difference between INT/EXT
#sootblowing loss:

floss_sootblowing:  loss_sootblowing  =  (BL.mass*sootblowing_steam)*(h_evap_w+cp_wv*(flue_gas_default.t  -  flue_gas_default.t_amb));
#2442 =h_evap, 1.88 =cp_wv



#Other losses
floss_radi: loss_radi = rad_heat_loss/100 *sum_heat_input;
floss_unaccounted: loss_unaccounted = unac_loss/100*sum_heat_input;
floss_margin:loss_margin = margin_loss/100 *sum_heat_input;

#additional cf Tran & Grace (2018)
#Unburned carbon in smelt
fheat_cu_smelt: loss_cu_smelt = BL.mass*Cu*h_Cu; #not used assumed to be part of enthalpy of smelt

#CO formation  = C112*10110
fheat_formation_CO: loss_formation_CO = BL.mass*CO_KRB*h_formation_CO;

#NEW
#floss_blowdown: loss_blowdown =  (blowdown.h-blowdown.h_ambient) * blowdown.mass;
floss_blowdown: loss_blowdown =  0; #neither in Tran & Grace (2018) nor Vakkilainen (2005) blowdownloss


#Sum
fsum_heat_output: sum_heat_output = loss_blowdown + loss_fg + loss_sootblowing  + loss_Na2S + loss_K2S + loss_SO2 + loss_smelt +
loss_formation_CO + loss_cu_smelt + loss_radi + loss_unaccounted + loss_margin;

#+ loss_blowdown; before w/o now with


#___________________________________________________________________________________

#STEAM GENERATION

#Heat to steam
fheat_to_steam: heat_to_steam = sum_heat_input - sum_heat_output;

#Steam generation efficiency
fsteam_efficiency: steam_efficiency =  heat_to_steam/sum_heat_input *100;


#Steam production
fsteam_production: steam_production = (1- stream_blowdown_pct/100) * water.mass;


#___________________________________________________________________________________

#Tran & Grace (2018)
#feedwater:
ffeedwater_to_boiler: water.mass = (steam.mass*steam.h +(BL.mass*sootblowing_steam)* h_sootblowing +blowdown.h * blowdown.mass
- heat_to_steam)/(water.h);
```

```
#steam to mill
#internal sootblowing:
fsteamtomill: steam.mass = water.mass - blowdown.mass - BL.mass*sootblowing_steam;




#TESTs

t1:         test (blowdown.x == 0) warning "gaseous blowdown stream";
```

Excel worksheet Validation Base Model V1

INPUTS	**Tran & Grace**	
Boiler Operating Data		
Heavy (virgin) black liquor mass	1.00	kg BLS
Heavy BL gross heating value (HHV)	14000.00	kJ/kg BLS
Heavy BL solids content	70.00	% ds
Smelt reduction efficiency	92.00	%
Unburned C in smelt	0.002	kg/kg BLS
Excess O2 (as % wet gas)	2.00	vol. %
CO concentration in wet flue gas	100.00	ppmv
SO2 concentration in wet flue gas	10.00	ppmv
Humidity (H2O) in combustion air	0.013	kg/kg air
Sootblowing steam consumption	0.110	kg/kg BLS
Recycled ash/dust	0.00	% BLS
Makeup salt cake (as Na2SO4)	0.000	kg/kg BLS
Precipitator dust removal efficiency	0.00	%
BL temperature before indirect	125.00	C
BL temperature after indirect heater	130.00	C
Ambient air temperature	25.00	C
FD fan preheat air temperature	150.00	C
Economizer gas exit temperature	210.00	C
Smelt temperature	850.00	C
Feed water to econo. Temperature	120.00	C
Sootblowing steam source	Internal	
Sootblowing steam temperature	315.00	C
Superheater outlet steam	482.00	C
Sootblowing steam pressure	17.30	bar
Steam drum pressure	65.50	bar
Superheater outlet steam pressure	62.00	bar
Feedwater blowdown steam	2.00	%
Radiation heat loss	0.24	%
Unaccounted heat loss	1.00	%
Heat Capacity Data		
Water	4.18	kJ/kg.C
Dry air	1.01	kJ/kg.C
Dry flue gas	1.02	kJ/kg.C
Water vapor	1.88	kJ/kg.C
Black liquor	2.95	kJ/kg.C
Smelt	1.72	kJ/kg.C
Enthalpy data		
Smelt	1350	kJ/kg
Sulfide formation	12900	kJ/kg
Water evaporation	2442	kJ/kg
Sootblowing steam	3068	kJ/kg
Economizer feed water	508	kJ/kg

Steam drum blowdown water	1244	kJ/kg
Superheater outlet steam	3377	kJ/kg
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	34.70	% BLS
Hydrogen (H)	3.50	% BLS
Sulfur (S)	4.20	% BLS
Sodium (Na)	19.50	% BLS
Potassium (K)	1.80	% BLS
Chlorine (Cl)	0.50	% BLS
Inerts (N, Si, Mg, Ca, Mn, etc.)	0.20	% BLS
Oxygen (O)	35.60	% BLS
Precipitator Dust Analysis		
Sodium (Na)	0.00	wt%
Potassium (K)	0.00	wt%
Chlorine (Cl)	0.00	wt%
Sulfate (SO_4)	0.00	wt%
Carbonate (CO_3)	0.00	wt%
Impurities	0.00	wt%
Anions-to-cations mole ratio	0.0	
mole% Cl/(Na+K)	0.0	
mole% K/(Na+K)	0.0	
OUTPUTS	**SI Unit**	
MATERIAL BALANCE		
H_2O In heavy black liquor	0.4286	kg/kg BLS
H_2O from sootblowing	0.1100	kg/kg BLS
Total	0.5386	kg/kg BLS
Na in HBL with makeup salt cake	0.1950	kg/kg BLS
S in HBL with makeup salt cake	0.0420	kg/kg BLS
O in HBL with makeup salt cake	0.3560	kg/kg BLS
Moles of flue gas	0.2009	kmol/kg BLS
CO in flue gas	0.0006	kg/kg BLS
SO_2 in flue gas	0.0001	kg/kg BLS
O_2 in flue gas	0.1286	kg/kg BLS
Smelt Mass Flow		
Na_2S	0.0940	kg/kg BLS
Na_2SO_4	0.0149	kg/kg BLS
NaCI	0.0082	kg/kg BLS
Na_2CO_3	0.3030	kg/kg BLS
K_2CO_3	0.0318	kg/kg BLS
lnerts	0.0020	kg/kg BLS
Unburned carbon (char)	0.0020	kg/kg BLS
Total	0.4559	kg/kg BLS
Smelt Composition		
Na_2S	20.6253	wt%
Na_2SO_4	3.2651	wt%
NaCl	1.8071	wt%

Na2CO3	66.4484	wt%
K2CO3	6.9768	wt%
Inerts	0.4386	wt%
Unburned carbon (char)	0.4386	wt%
Total	100.0000	wt%
Smelt sulfidity	28.08	% on TTA
Combustion Products		
CO2 in flue gas	1.128	kg/kg BLS
H2O from combustion	0.315	kg/kg BLS
O2 in smelt and gases	1.256	kg/kg BLS
Theoretical O2	0.900	kg/kg BLS
Theoretical air	3.879	kg/kg BLS
Infiltration air (assumed)	0.116	kg/kg BLS
Total dry air to boiler	4.433	kg/kg BLS
N2 in flue gas	3.405	kg/kg BLS
Total dry flue gas	4.662	kg/kg BLS
Moisture in air	0.058	kg/kg BLS
Total H2O in flue gas (excluding SB)	0.801	kg/kg BLS
Dry air to FD fan	4.317	kg/kg BLS
H2O	0.911	kg/kg BLS
N2 (theoretical)	2.979	kg/kg BLS
CO	0.0006	kg/kg BLS
SO2	0.00013	kg/kg BLS
Flue gas with 0% excess air	3.891	kg/kg BLS
Excess air	0.526	kg/kg BLS
Excess air,% of theoretical air	13.6	%
H2O in excess air	0.007	kg/kg BLS
Excess O2	0.129	kg/kg BLS
N2 in excess air	0.404	kg/kg BLS
Flue gas (wet)	5.573	kg/kg BLS
Molecular weight of flue gas (wet)	27.74	g/mol
Molecular weight of flue gas (dry)	30.98	g/mol
Flue gas (wet) volume	4.50	Nm3/kg BLS
Flue gas (dry) volume	3.37	Nm3/kg BLS
Dust loss to stack	0.00000	IWkg
Dust conc. at ESP inlet, @ 8%O2	0.00	g/dNm3
Particulate emissions from stack	0.00	mg/dNm3
Flue Gas Composition		
Wet mass basis		
H2O	16.350	wt%
CO2	20.243	wt%
N2	60.691	wt%
O2	2.307	wt%
CO	100.941	ppm
SO2	23.072	ppm
Total	99.6032	wt%

Moles of wet flue gas	36.084	moles/kg
Dry mass basis		
CO2	24.2	wt%
N2	72.6	wt%
O2	2.8	wt%
CO	121	oom
SO2	27.6	ppm
Total	99.5	wt%
Moles of dry flue gas	32.28	moles/kg flue gas
Wet volume basis		
H2O	25.2	vol%
CO2	12.8	vol%
N2	60.1	vol%
O2	2.0	vol%
CO	99.9	ppmv
SO2	10.0	ppmv
Total	100.0	vol%
Dry volume basis		
CO2	17.0	vol%
N2	80	vol%
O2	2.7	vol%
CO	134	ppmv
SO2	13	ppmv
Total	100.0	vol%
Heavy (Virgin) Black Liquor		
Chloride and potassium		
mole% Cl/(Na+K)	1.58	
mole% K/(Na+K)	5.15	
Chloride enrichment factor	0.00	
Potassium enrichment factor	0.00	
S/(Na2+K2) molar ratio	0.29	
As-fired Black Liquor		
Mass flow	1.000	kg BLS
Solids content	70.00	%
Higher heating value	14,000	kJ/kg BLS
Composition		
Carbon (C)	34.70	% ds
Hydrogen (H)	3.50	% ds
Sulfur (S)	4.20	% ds
Sodium (Na)	19.50	% ds
Potassium (K)	1.80	% ds
Chlorine (Cl)	0.50	% ds
Inerts (Si, Mg, Ca, Mn, etc)	0.20	% ds
Oxygen (O)	35.60	% ds
Total	100.00	% ds
Chloride and potassium		
mole% Cl/(Na+K)	1.58	

mole% K/(Na+K)	5.15	
Chloride enrichment factor	0.00	
Potassium enrichment factor	0.00	
S/(Na2+K2) molar ratio	0.29	
ENERGY BALANCE		
Heat Input		
Heat from liquor combustion	14000.000	kJ/kg BLS
Sensible heat of heavy black liquor	421.429	kJ/kg BLS
Sensible heat from liquor heating	20.000	kJ/kg BLS
Sensible heat in combustion air	552.253	kJ/kg BLS
Sensible heat in sootblowing steam	0.000	kJ/kg BLS
Heat in fw for blowdown steam	26.234	kJ/kg BLS
Total Heat Input	15019.915	kJ/kg BLS
Heat Output		
Sensible heat of dry flue gas	879.728	kJ/kg BLS
Sensible heat of water vapor	281.037	kJ/kg BLS
Evaporation of combustion water	769.230	kJ/kg BLS
Evaporation of water in liquor	1046.571	kJ/kg BLS
Sootblowing steam in flue gas	306.878	kJ/kg BLS
Sensible heat of smelt	615.531	kJ/kg BLS
Smelt reduction (Na2S formation)	1213.127	kJ/kg BLS
Unburned carbon in smelt	65.600	kJ/kg BLS
CO formation	5.688	kJ/kg BLS
SO2 formation	0.708	kJ/kg BLS
Radiaton loss	36.048	kJ/kg BLS
Unaccounted losses	150.199	kJ/kg BLS
Total Heat Loss	5370.345	kJ/kg BLS
Steam Generation		
Heat to steam	9649.571	kJ/kg
Steam generation efficiency	64.25	%
Feedwater to boiler flow	3.4142	kg/kg BLS
Blowdown steam	0.068283	kg/kg BLS
Steam production	3.345875	kg/kg BLS

Excel Worksheet Validation Vakkilainen (2005) calculation example

INPUTS	SI Unit	
Boiler Operating Data		
Heavy (virgin) black liquor mass	1.00	kg BLS
Heavy BL gross heating value (HHV)	13000.00	kJ/kg ds
Heavy BL solids content	85.00	% ds
Smelt reduction efficiency	96.00	%
Excess O2 (as % wet gas)	3.00	vol. %
Sootblowing steam consumption	0.150	kg/kg BLS
Recycled ash/dust	0.00	% BLS
Air ratio (~3% O2 in flue gas)	1.1625	
Humidity(H2O) in combustion air	0.0135	kg/kg air
SO2 emissions	0.052	mg/kgds
HCl emissions	0.010	mg/kgds
Main steam temperature	490.0	°C
Main steam pressure	91.0	bar
Feedwater temperature	115.0	°C
Feedwater pressure	110.0	bar
Flue gas outlet temperature	155.0	°C
Air inlet temperatire	30.0	°C
Air preheating temperature	108.8	°C
Blowdown	0.10	kg/kgds
Drum pressure	1036.0	bar
BL inlet temperature	140.0	°C
Sootblowing enthalpy	3054.8	kJ/kg
Radiation and convection losses	0.283	%
Unaccounted losses	0.300	%
Margin losses	0.500	%
Hydrogen enthalpy in BL	21806.300	kJ/kg
LHV of dry BL	12280.400	kJ/kg ds
Water enthalpy in BL	2440.000	kJ/kg
LHV of wet BL	11849.800	kJ/kg ds
BL sensible	2.640	kJ/kg.K
Air	1.034	kJ/kg.K
Enthalpy of steam (9.1MPa, 490°C)	3360.7	kJ/kg
Enthalpy of water (11MPa, 115°C)	490.3	kJ/kg
Enthalpy of sat. water (103.6 MPa)	1423.3	kJ/kg
Enthalpy of sootbl.steam (155°C)	2792.0	kJ/kg
Heavy (Virgin) Black Liquor Analysis		
Carbon (C)	32.50	% BLS
Hydrogen (H)	3.30	% BLS
Sulfur (S)	6.10	% BLS
Sodium (Na)	20.00	% BLS
Potassium (K)	3.00	% BLS
Chlorine (Cl)	0.25	% BLS
Nitrogen (N)	0.09	% BLS

Boron (B)	0.00	% BLS
Inerts	0.60	% BLS
Oxygen (O)	34.16	% BLS
Water content		
Precipitator Dust Analysis		
Sodium (Na)	0.0000	g/kgds
Potassium (K)	0.0000	g/kgds
Chlorine (Cl)	0.0000	g/kgds
Sulfate (SO4)	0.0000	g/kgds
Carbonate (CO3)	0.0000	g/kgds
Sulfide (S)	0.0000	g/kgds
Boride (B)	0.0000	g/kgds
Sum	0.0000	g/kgds
Ash Analysis		
Sodium (Na)	0	g/kgds
Potassium (K)	0	g/kgds
Chlorine (Cl)	0	g/kgds
Sulfate (SO4)	0	g/kgds
Carbonate (CO3)	0	g/kgds
Sulfide (S)	0	g/kgds
Boride (B)	0	g/kgds
	0	g/kgds
OUTPUTS	**SI Unit**	
Heavy (Virgin) Black Liquor Analysis in Mols		
Carbon (C)	27.059	mol/kgds
Hydrogen (H)	16.369	molH2/kgds
Sulfur (S)	1.903	mol/kgds
Sodium (Na)	4.350	molNa2/kgds
Potassium (K)	0.384	molK2/kgds
Chlorine (Cl)	0.071	mol/kgds
Nitrogen (N)	0.032	molN2/kgds
Boron (B)	0.000	mol/kgds
Inerts		mol/kgds
Oxygen (O)	10.675	molO2/kgds
Water content	9.796	molH2O/kgds
MATERIAL BALANCE		
Sulfur Balance		
Availbale sulfur	1.903	molS/kgds
In non-condensable gas (NCG)	0.333	molS/kgds
SO2	0.000	molS/kgds
dust as SO4	0.000	molS/kgds
dust as S (-2)	0.000	molS/kgds
ash as SO4	0.000	molS/kgds
ash as S (-2)	0.000	molS/kgds
SUM (S in smelt)	2.236	molS/kgds
SO4 in smelt	0.089	molS/kgds

Sulfide (s) in smelt	2.146	molS/kgds
Cloride Balance		
Available chloride	0.071	molCl/kgds
NaCl and KCl in dust	0.000	molCl/kgds
NaCl and KCl in ash	0.000	molCl/kgds
HCl in flue gas	0.000	molCl/kgds
SUM (Cl in smelt)	0.071	molCl/kgds
Borate Balance		
Available boron	0.000	molB/kgds
loss in dust	0.000	molB/kgds
lost in ash	0.000	molB/kgds
SUM (boron in smelt)	0.000	molB/kgds
Na3BO3 in smelt	0.000	molB/kgds
NaBO2 in smelt	0.000	molB/kgds
Sodium Balance		
Available sodium	4.350	molNa2/kgds
Na2SO4, Na2CO3 and NaCl in dust	0.000	molNa2/kgds
Na2SO4, Na2CO3 and NaCl in ash	0.000	molNa2/kgds
SUM (sodium in smelt)	4.350	molNa2/kgds
Potassium Balance		
Available potassium	0.384	molK2/kgds
K2SO4, K2CO3 and KCl in ash	0.000	molK2/kgds
K2SO4, K2CO3 and KCl in dust	0.000	molK2/kgds
SUM (potassium in smelt)	0.384	molK2/kgds
mole% Na/(Na+K)	91.9	mol%
mole% K/(Na+K)	8.1	mol%
H2O In heavy black liquor	0.17647	kg/kg BLS
H2O from sootblowing	0.1500	kg/kg BLS
Total	0.3265	kg/kg BLS
Smelt Composition		
Na2SO4	0.082	molNa2/kgds
Na2S	1.972	molNa2/kgds
Na3BO3	0.000	molNa2/kgds
NaBO2	0.000	molNa2/kgds
NaCI	0.032	molNa2/kgds
Na2CO3	2.263	molNa2/kgds
K2SO4	0.007	molK2/kgds
K2S	0.174	molK2/kgds
KCI	0.003	molK2/kgds
K2CO3	0.200	molK2/kgds
Available carbon	27.059	mol/kgds
Na2CO3 and K2CO3 in dust	0.000	mol/kgds
Na2CO3 and K2CO3 in ash	0.000	mol/kgds
Na2CO3 and K2CO3 in smelt	-2.462	mol/kgds
CO2 (burned carbon)	24.596	mol/kgds
Available oxygen	10.675	mol/kgds

CO2	-24.596	mol/kgds
CO3 and SO4 in dust	0.000	mol/kgds
CO3 and SO4 in ash	0.000	mol/kgds
SO2	0.000	mol/kgds
Na2SO4 and K2SO4 in smelt	-0.179	mol/kgds
Na2CO3 and K2CO3 in smelt	-3.694	mol/kgds
Na3BO3 in smelt	0.000	mol/kgds
NaBO2 in smelt	0.000	mol/kgds
H2O formed after combustion	-8.185	mol/kgds
O2 in air supply	-25.978	mol/kgds
Humid air demand	4.215	kg/kgds
Smelt Balance flow		
K2S	0.174	mol/kgds
Na2S	1.972	mol/kgds
Na2SO4	0.082	mol/kgds
K2SO4	0.007	mol/kgds
NaCI	0.065	mol/kgds
KCI	0.006	mol/kgds
Na2CO3	2.263	mol/kgds
K2CO3	0.200	mol/kgds
Na3BO3	0.000	mol/kgds
NaBO2	0.000	mol/kgds
Other inorganics		mol/kgds
Sum		
Flue Gas balance flow		
Dry BL	1000.0	g/kgds
water with BL	176.5	g/kgds
Air	4215.4	g/kgds
Sootblowing steam	150.0	g/kgds
Loss in dust	0.0	g/kgds
Ash recycle	0.0	g/kgds
Smelt	-463.7	g/kgds
Wet flue gas	5078.2	g/kgds
Water with air	-0.1	g/kgds
Water from hydrogen in BL	-294.6	g/kgds
Dry flue gas	4457.0	g/kgds
Steam mass flow	3.107	kg/kgds
Feedwater massflow	3.207	kg/kgds
ENERGY BALANCE		
Heat Input		
HHV dry BL	13000.0	kJ/kg
Hydrogen enthalpy in BL	-719.6	kJ/kg
LHV of dry BL	12280.4	kJ/kg
Water enthalpy in BL	-430.6	kJ/kg
LHV of wet BL	11849.8	kJ/kg
Sensible heat BL	434.8	kJ/kg
Sensible heat in combustion air	130.7	kJ/kg

Sensible heat in combustion air preheat	343.3	kJ/kg
Sensible heat from infiltration	6.9	kJ/kg
Sensible heat in sootblowing steam	83.1	kJ/kg
Sum	12848.6	kJ/kg
Heat Losses		
Wet flue gas	871.3	kJ/kg
Reduction to Na2S	2016.2	kJ/kg
Reduction to K2S	184.7	kJ/kg
Reduction to SO2	0.3	kJ/kg
Autocausticizion of Na3BO3	0.0	kJ/kg
Loss in smelt sensible	625.9	kJ/kg
Radiation & convection	36.4	kJ/kg
Unaccounted losses	38.5	kJ/kg
Margin	64.2	kJ/kg
Total Losses	3837.6	kJ/kg
Net heat available	9011.0	kJ/kg
Steam generation efficiency	70.1	%