REDUCTION EFFICIENCY PREDICTION OF CENIBRA'S RECOVERY BOILER BY DIRECT MINIMIZATION OF GIBBS FREE ENERGY

W. L. Silva[1], J. C. T. Ribeiro[1], E. F. da Costa Jr.[2] and A. O. S. da Costa[2*]

[1]CENIBRA, Celulose Nipo-Brasileira S.A., Belo Oriente - MG, Brazil.
[2]Centro de Ciências Agrárias, Universidade Federal do Espírito Santo, CCA/UFES,
Alto Universitário s/n, Caixa Postal 16, CEP: 29500-000,
Guararema, Alegre - ES, Brazil.
E-mail: andreaosc@yahoo.com.br

Abstract - The reduction efficiency is an important variable during the black liquor burning process in the Kraft recovery boiler. This variable value is obtained by slow experimental routines and the delay of this measure disturbs the pulp and paper industry customary control. This paper describes an optimization approach for the reduction efficiency determination in the furnace bottom of the recovery boiler based on the minimization of the Gibbs free energy. The industrial data used in this study were directly obtained from CENIBRA´s data acquisition system. The resulting approach is able to predict the steady state behavior of the chemical composition of the furnace recovery boiler, - especially the reduction efficiency when different operational conditions are used. This result confirms the potential of this approach in the analysis of the daily operation of the recovery boiler.
Keywords: Black liquor recovery boiler; Gibbs free energy; Combustion, Modeling; Optimization.

INTRODUCTION

In the pulp production process the Kraft recovery boiler has basically three functions: to convert the sodium sulfate (Na_2SO_4) present in the black liquor into sodium sulfide (Na_2S); to produce steam through the combustion of the black liquor organic components; and to eliminate undesirable by-products.

The main difference between recovery and classical boilers is the greater importance given, in the recovery boiler, to regenerate the Na_2S rather than to steam production during the black liquor combustion. Besides steam production, the recovery boiler should be capable of producing the maximum amount of Na_2S, a product of the burning process.

Basically, the recovery boilers can be divided into the following six parts: (1) furnace - where the black liquor is burned; (2) waterwall - where saturated steam is produced; (3) screen - where saturated and superheated steam are produced; (4) boiler bank - where the water that arrives from the economizer is distributed and saturated steam is separated; (5) superheater - where saturated steam is transformed into superheated steam; (6) economizer - where the feed water is heated.

One of the main difficulties that must be faced to study Kraft recovery boilers is due to the large diversity of physical and chemical transformations – often unknown – that take place during the black liquor burning process.

Although the black liquor burning process is similar to the combustion of any other combustible products in traditional boilers, the recovery of the inorganic salts from the black liquor complicates the process analysis in the furnace. In this case, the

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combustion products are not only carbonic gas and water, but also other chemical species (inorganic salts).

The black liquor burning process begins when this fluid is fed into the recovery boiler furnace through spray nozzles located on the furnace wall (Figure 1). Different physicochemical processes are involved in the black liquor particle burning phenomenon: drying, pyrolysis, char burning, oxidation and reduction of the inorganic salts (Grace, 1992; Smook, 1987).

During the drying process the particles lose their residual humidity (about 30%).

The pyrolysis begins when the black liquor particles reach 473K (Grace, 1992; Sricharoenchaikul et al., 2001). During this process the particle volume increases because of the generation of combustion gases: SO_2, CO_2, CO, CH_4, H_2O, and TRS (Total Reduced Sulfur). Due to the oxidation of these gases a visible flame surrounds the particles, which tends to follow the gas flow path. After the pyrolysis, the black liquor particles are composed of inorganic components (mainly Na_2CO_3, Na_2S and Na_2SO_4) and fixed carbon.

TRS gases are usually taken as H_2S for convenience though in practice they usually contain mercaptans (Adams, 1997). Lisa (1997) suggests that the TRS gases are composed of H_2S, CH_3SH, CH_3SCH_3 and $CH_3S_2CH_3$.

When the particles reach the furnace bottom, they get in contact with the char bed and the primary and secondary air fed (Figure 1). The char bed consists of carbon, partially pyrolyzed black liquor solids and melted inorganic salts, called smelt. The oxidation and reduction reactions of the inorganic salts occur in the char bed region. These chemical reactions take place simultaneously in the char bed (Grace, 2001). The exothermic oxidation reaction of Na_2S with air oxygen forming $Na2SO4$, takes place in the solid char bed surface. Because Na_2S is an active agent of the wood digestion process in the pulp industry, it is desirable to recover it at the end of the black liquor burning process. The relationship between the recovered sulphur mass as Na_2S and the total sulphur mass in the smelt is called reduction efficiency.

Although the inorganic salt oxidation causes a decrease of the reduction efficiency, the energy liberated during the exothermic reaction allows the fusion and the endothermic reduction of the salts, with the Na_2SO_4 reacting with carbon to form new Na_2S. Usually, the smelt is composed of one-third of Na_2S and two-thirds of Na_2CO_3 (Adams, 1997).

Grace and Frederick (1997) suggest that the temperature of the bed surface decreases with distance into the bed; from 1273 – 1473K on the bed surface to the point where smelt is solidified, at approximately 1033K. The smelt is removed from the furnace bottom and taken to a dissolution stage.

Besides, particulate material- composed of not burned liquor particles and inorganic salts (chemical dust) – is formed during the black liquor burning process and are carried by the combustion gases. These carried substances cause a deposit on the surfaces of the boiler and reduce heat transfer efficiency. Electrostatic precipitators pick up the particulates remaining in the recovery boiler outlet. The formation mechanism of the chemical dust is not completely known (Jokiniemi et al., 1996). Empirical models are usually used in the description of the particulate formation phenomenon (Costa et al., 2004) which it is not considered in this work.

This paper describes an optimization approach for the chemical composition determination in the furnace bottom of the recovery boiler (char bed region - Figure 1) based on the minimization of the Gibbs free energy. The resulting approach is able to predict the steady state behavior of the chemical composition in the furnace recovery boiler - especially the reduction efficiency - when different operational conditions are used.

METHODOLOGY

The black liquor burning process involves unknown chemical reactions in solid, liquid and gas phases. Moreover, the reagents of this combustion vary depending on the digestion process used. In order to overcome this difficulty we have considered an optimization approach that allows the calculation of the chemical composition of the system minimizing the Gibbs free energy. This methodology has been frequently used to describe closed multiphase systems (Faungnawakih et al., 2007; Faungnawakih et al., 2006; Solórzano et al., 2004; Nichita et al. 2002; Lee et al., 1999; Ansari and Pandis, 1999; Soares et al., 1982) and is based on the fact that Gibbs free energy of these systems must be minimum at the equilibrium.

In a closed system with F phases and N different chemical species the Gibbs free energy is calculated by a combination of the chemical potentials of each component in each phase, expressed by equation (1) (Zeggeren and Storey, 1970).

$$G = \sum_{j=1}^{F} \sum_{i=1}^{N} \mu_{i,j} n_{i,j} \qquad (1)$$

Where G is the total Gibbs free energy of the closed system, $\mu_{i,j}$ is the chemical potential of component i in phase j, $n_{i,j}$ is the mole number of component i in phase j, F is the phases number in the closed system, N is the number of chemical components in the closed system. The chemical potential of specie i in phase j is described by equation (2).

$$\mu_{i,j} = G^o_{f_{i,j}} + RT\ln\left(\frac{f_{i,j}}{f^o{}_{i,j}}\right) \qquad (2)$$

where $G^o_{f\ i,j}$ is Gibbs free formation energy of component i in phase j at an average temperature of the closed system (T), R is the gas constant, $f_{i,j}$ is the fugacity of component i in phase j, $f^o{}_{i,j}$ is the fugacity of pure component i in phase j at the standard state. For condensed (liquid and solid) ideal phase the partial fugacity is expressed by,

$$\frac{f_{i,j}}{f^o{}_{i,j}} = \frac{n_{i,j}}{\sum\limits_{k=1}^{N} n_{k,j}} \qquad (3)$$

and for the ideal gas phase by,

$$\frac{f_{i,j}}{f^o{}_{i,j}} = P\frac{n_{i,j}}{\sum\limits_{k=1}^{N} n_{k,j}} \qquad (4)$$

where P is the pressure of the closed system.

Minimization of equation (1) produces the equilibrium composition of F phases at one condition of pressure and temperature as a function of the mole number of each chemical species in each phase ($n_{i,j}$). Moreover, the mass relations in the closed system must be satisfied during the solution of the optimization problem. Although the M chemical elements in a close system are distributed between different chemical species, the elementary chemical composition must remain fixed. This behavior described by equation (5) - for each chemical element – restricts the optimization problem.

$$b_k = \sum_{i=1}^{N}\sum_{j=1}^{F} a_{k,i} n_{i,j} \quad k = 1,\cdots,M \qquad (5)$$

Where b_k is the total number of gram-atoms of chemical element k in the closed system, $a_{k,i}$ is the gram-atoms number of the chemical element k in component i.

Finally, additional restrictions must be considered as the mole number of each species in each phase ($n_{i,j}$) is positive or equal to zero (equation (6)).

$$n_{i,j} \geq 0 \qquad (6)$$

The optimization problems are solved for a deterministic optimization method, which is Sequential Quadratic Programming (SQP) (Edgar and Himmelblau, 1988). Random values are used for the initial mole number of the chemical species in each phase, thus satisfying the restrictions described by equations (5) and (6).

The industrial data used in this study were directly obtained from CENIBRA´s data acquisition system and describe the operation of the recovery boiler between September 2004 and March 2005. To analyze each operating condition, some process operation variables must be specified to properly define the constrained equations of the optimization problem. They are:
1) the black liquor elementary chemical composition;
2) the black liquor feed flow rate (Vlu);
3) the black liquor solids concentration (X);
4) the air feed flow rates (the sum of the primary (Var1) and secondary (Var2) air flow rates).

The following assumptions are adopted in order to solve the proposed optimization problem:
1) CENIBRA's black liquor has the elementary chemical composition presented in Table 1;
2) the system is at chemical equilibrium for a given constant average furnace gas temperature equal to 1273K;
3) the pressure in the furnace is 101.3 kPa;
4) the different phases present ideal behavior;
5) good control of black liquor droplets diameters assure that only dry black liquor particles reach the studied region (Figure 1).;
6) combustion reactions only take place in the studied region (Figure 1).;
7) N_2 is inert.

Costa et al. (2005), Costa et al. (2004) and Costa et al. (2003) report that the oxidation and reduction reactions take place simultaneously in the solid phase. Then, the chemical species only melt, forming the smelt, after the chemical equilibrium has been reached. Thus, two phases are considered in this work to obtain the concentration of chemical species in the furnace bottom (Figure 1): a gaseous one and a condensed one.
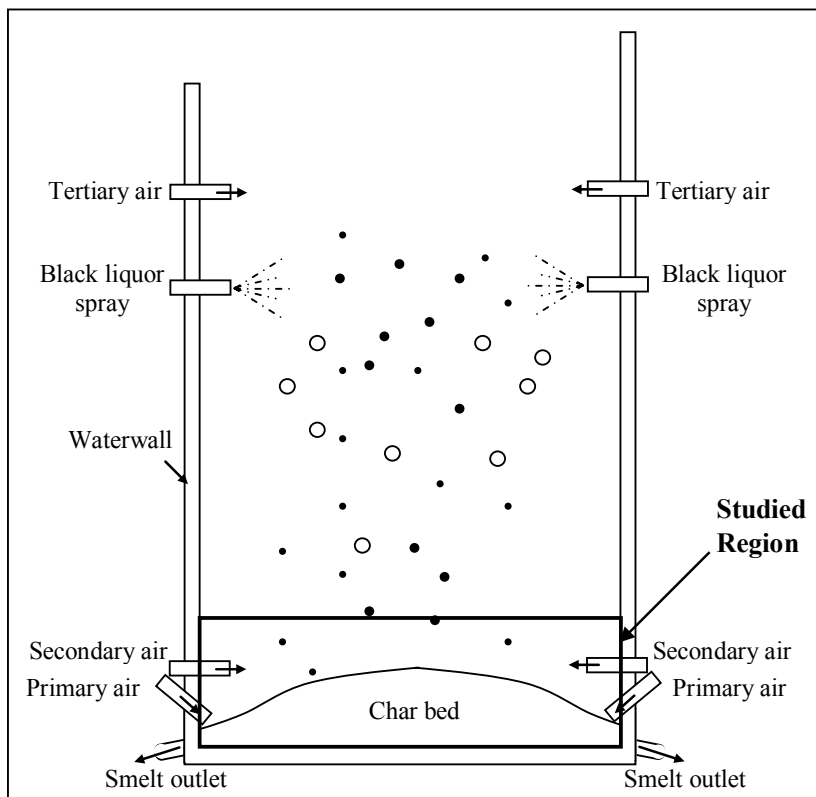
Figure 1: Burning process of black liquor in a typical recovery boiler and identification of the studied region.

Table 1: CENIBRA's black liquor elementary composition.

Chemical Element	Concentration
C	34.4%
H	3.7%
O	31.6%
Na	21.4%
S	5.4%
K	2%
Cl	1.5%

RESULTS AND DISCUSSION

The average operation condition is directly obtained by industrial data set (Table 2).

Table 3 presents the chemical species considered to obtain the results and the respective values of $a_{k,i}$ (equation 5).

Using the operation conditions presented in Table 2, the values of b_k (equation 5) are calculated and the obtained results are presented in Table 4.

Table 5 presents the Gibbs free formation energy $(G^o_{f\ i,j})$ at 1273K of each chemical component considered in this study.

Different values for Vlu are analyzed and the results are presented in Table 6 (test 1 to 7). The model reproduces the behavior reported in literature and that is expected for the system (Costa et al., 2005; Adams, 1997; Grace, 1992). Na_2CO_3 and Na_2S are the principal chemical species of the obtained smelt (condensed phase) as reported by Adams (1997) and Grace (1992). Grace (1992) affirms that the furnace bottom of the recovery boiler is poor in oxygen and this information is shown in Table 6. Costa et al. (2005) studied a different recovery boiler and reported that the increase of black liquor feed promotes an increase of the reduction efficiency

since the oxygen concentration is fixed. This behavior is observed in Table 6.

Table 6 shows the chemical composition of the studied region obtained when the real average operating condition is considered (test 5). The average reduction efficiency of the mill is 93.3% (Table 2) and the proposed model can reproduce this variable within an error of 0.6%.

The reduction efficiency value is obtained at CENIBRA by experimental procedures. Therefore, the value of this variable is not known for all industrial data but only for few sampling times. This characteristic of the system disturbs the control of the recovery boiler operation. Sometimes the influence of different operational conditions in the reduction efficiency is known after a long time.

The operational variables are controlled during the recovery boiler operation. Then, small variations can be observed during a significant time of operation. To illustrate this behavior, nine real and different operational conditions that describe eight hours of the recovery boiler operation were analyzed. Table 7 shows the simulated reduction efficiency to each case. The real values are known only for two conditions (Table 7). The proposed model can reproduce these real values with a maximum error of 1.1%.

The results presented in Table 7 confirm that small changes in the operating conditions do not affect significantly the reduction efficiency. However, the operation of the recovery boiler can be drastically modified, causing important alterations in the chemical composition of the system. Thereby, the challenge is not to describe the standard operating conditions of the equipment, but to describe the recovery boiler behavior during its operation time.

Table 8 shows the results obtained when real different operating conditions are considered for CENIBRA's recovery boiler. The studied data were chosen randomly. The maximum error obtained is 5.3% (operational conditions 5). The results presented in Table 8 justify the use of this methodology in addition to the usual experimental routines to predict the reduction efficiency of the recovery boiler.

Table 2: CENIBRA's average operation condition.

Variables	Values
Vlu	109.88 m^3/h
X	70%
Var1	162.02 t/h
Var2	164.65 t/h
Reduction efficiency	93.3%

Table 3: Atom number of the chemical element k in component i ($a_{k,i}$) to the studied system.

$a_{k,i}$	Chemical element (k)							
	C	H	O	Na	S	K	Cl	N
Substance (i)								
C	1	0	0	0	0	0	0	0
Na_2CO_3	1	0	3	2	0	0	0	0
Na_2SO_4	0	0	4	2	1	0	0	0
K_2SO_4	0	0	4	0	1	2	0	0
Na_2S	0	0	0	2	1	0	0	0
K_2S	0	0	0	0	1	2	0	0
NaOH	0	1	1	1	0	0	0	0
NaCl	0	0	0	1	0	0	1	0
KCl	0	0	0	0	0	1	1	0
O_2	0	0	2	0	0	0	0	0
H_2	0	2	0	0	0	0	0	0
CO_2	1	0	2	0	0	0	0	0
CO	1	0	1	0	0	0	0	0
H_2O	0	2	1	0	0	0	0	0
SO_2	0	0	2	0	1	0	0	0
H_2S	0	2	0	0	1	0	0	0
CH_3SH	1	4	0	0	1	0	0	0
CH_3SCH_3	2	6	0	0	1	0	0	0
$CH_3S_2CH_3$	2	6	0	0	2	0	0	0
CH_4	1	4	0	0	0	0	0	0
N_2	0	0	0	0	0	0	0	2

Table 4: Total number of gram-atoms (b_k) of chemical element k in the closed system considering the average operating condition (Table 2).

Chemical Element k	b_k
C	889.12
H	1298.3
O	1987.6
Na	289
S	52.3
K	15.9
Cl	13.1
N	4897.1

Table 5: Gibbs free formation energy of component i in phase j at T = 1273K.

$G^o_{f i,i}$ (J.mol^{-1})	
The condensed phase substances	
C	-1.29×10^4
Na_2CO_3	-8.62×10^5
Na_2SO_4	-1.03×10^6
K_2SO_4	-1.07×10^6
Na_2S	-3.73×10^5
K_2S	-3.82×10^5
NaOH	-2.81×10^5
NaCl	-3.43×10^5
KCl	-3.67×10^5
The gaseous phase substances	
O_2	-3.04×10^4
H_2	-2.55×10^4
CO_2	-4.37×10^5
CO	-2.51×10^5
H_2O	-2.17×10^5
SO_2	-3.52×10^5
H_2S	-1.09×10^5
CH_3SH	-2.97×10^4
CH_3SCH_3	3.91×10^4
$CH_3S_2CH_3$	3.21×10^4
CH_4	-1.52×10^4
N_2	-2.63×10^4

Table 6: Chemical composition at the furnace bottom obtained by minimizing Gibbs free energy considering the average operating condition and different values of Vlu.

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
Vlu (m^3/h)	87.90	92.30	95.92	100.28	109.88*	120.87	131.86
X (%)	70	70	70	70	70*	70	70
Var1 (t/h)	162.02	162.02	162.02	162.02	162.02*	162.02	162.02
Var2 (t/h)	164.65	164.65	164.65	164.65	164.65*	164.65	164.65
Substances	**Molar chemical composition of the condensed phase (%)**						
C	0.03	0.04	0.06	0.08	0.16	0.27	0.40
Na_2CO_3	58.09	58.06	58.00	57.94	57.80	57.66	57.51
Na_2SO_4	2.33	0.78	0.29	0.12	0.03	0.01	0.00
K_2SO_4	1.81	0.96	0.43	0.20	0.05	0.01	0.00
Na_2S	27.12	28.90	29.54	29.78	29.93	29.99	30.01
K_2S	0.93	1.56	1.97	2.17	2.29	2.32	2.32
NaOH	1.50	1.51	1.52	1.52	1.56	1.57	1.60
NaCl	3.77	3.32	3.10	3.01	2.97	2.96	2.95
KCl	4.42	4.87	5.09	5.18	5.21	5.21	5.21

Continuation Table 6

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
Substances	Molar chemical composition of the gaseous phase (%)						
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	1.82	2.40	3.04	3.70	5.03	6.66	8.23
CO_2	14.20	13.79	13.30	12.79	11.79	10.64	9.61
CO	3.39	4.41	5.49	6.57	8.67	11.10	13.32
H_2O	12.92	12.74	12.49	12.21	11.60	10.82	10.05
SO_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_3SH	0.02	0.02	0.01	0.01	0.01	0.01	0.01
CH_3SCH_3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$CH_3S_2CH_3$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	67.65	66.64	65.67	64.72	62.90	60.77	58.78
Reduction efficiency (%)	84.2	89.8	91.7	92.3	92.7	92.7	92.8

*Average operating condition

Table 7: Predicted reduction efficiency obtained by the minimization of the Gibbs free energy in a serial of operating conditions.

	Operating Conditions - Date:10/24/04								
	1	2	3	4	5	6	7	8	9
	6 hr	7 hr	8 hr	9 hr	10 hr	11 hr	12 hr	13 hr	14 hr
Vlu (m^3/h)	125.0	127.8	128.7	128.4	128.1	126.3	125.0	124.9	124.8
X (%)	68.2	68.4	69.3	70.3	70.4	70.7	71.0	70.5	71.0
Var1 (t/h)	173.5	180.5	181.4	180.3	179.4	180.0	180.7	177.7	179.2
Var2 (t/h)	169.6	178.3	177.1	176.7	175.6	175.8	176.6	176.8	176.6
Reduction efficiency (simulated) (%)	92.73	92.72	92.73	92.74	92.75	92.74	92.73	92.72	92.73
Reduction efficiency (real) (%)	93.8	-	-	-	-	-	-	-	92.7

Table 8: Predicted reduction efficiency obtained by the minimization of the Gibbs free energy considering real different operating conditions.

	Operational Conditions							
	1	2	3	4	5	6	7	8
Date	09/01/04 06 hr	09/01/04 22 hr	10/06/04 22 hr	11/30/04 14 hr	01/12/05 22 hr	01/25/05 22 hr	02/07/05 06 hr	02/22/05 22 hr
Vlu (m^3/h)	121.58	124.28	122.53	119.05	120.15	114.9	110.20	99.96
X (%)	70.5	70.0	71.0	70.3	70.0	71.4	70.5	70.0
Var1 (t/h)	173.64	175.83	180.05	170.01	180.50	175.67	176.77	178.64
Var2 (t/h)	174.44	168.32	219.05	177.20	180.50	183.72	169.63	188.86
Reduction efficiency (simulated) (%)	92.7	92.8	92.2	92.6	89.2	92.6	92.4	87.9
Reduction efficiency (real) (%)	95.6	93.2	92.2	93.8	84.7	92.8	91.3	89.8
Error (%)	3.0	0.4	0	1.3	5.3	0.2	1.2	2.1

CONCLUSION

The methodology of minimizing the Gibbs free energy has been used satisfactorily in this study to describe the chemical composition of the furnace bottom of the recovery boiler. By this approach it is possible to reproduce the industrial behavior of this equipment, specially the reduction efficiency.

The obtained results are validated by industrial data and information reported by literature. Few variables involved in the black liquor burning process are monitored in the industry. Only the recovery boiler outputs are traditionally analyzed. Variables that describe the chemical composition of the furnace are frequently unknown by the industry, since it is difficult to install sensors in this part of the

equipment. Therefore, all information reported by the literature has been important to validate the obtained results.

To obtain the chemical composition of the studied region (for each operational condition) a small computational time is requested. This result confirms the potential of this approach in the analysis of the daily operation of the recovery boiler, since the reduction efficiency value is usually obtained through slow experimental routines.

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NOMENCLATURE

$a_{k,i}$	Gram-atoms number of the chemical element k in component i	(-)
b_k	Total number of gram-atoms of chemical element k in the closed system	(-)
$f_{i,j}$	fugacity of component i in phase j	(-)
$f^o_{i,j}$	fugacity of pure component i in phase j at the standard state	(-)
F	phases number in the closed system	(-)
G	Total Gibbs free energy of the closed system	$J.mol^{-1}$
$G^o_{f\,i,j}$	Gibbs free formation energy of component i in phase j at T	$J.mol^{-1}$
M	number of chemical elements in the closed system	(-)
$n_{i,j}$	mole number of component i in phase j	mol
N	number of chemical components in the closed system	(-)
P	pressure of the closed system	atm
R	gas constant	8.314 $J.K^{-1}.mol^{-1}$
T	average temperature of the closed system	K

Var1	primary air feeds	$t.hr^{-1}$
Var2	secondary air feeds	$t.hr^{-1}$
Vlu	black liquor feed	$m^3.h^{-1}$
X	black liquor solids concentration	%

Greek Letters

$\mu_{i,j}$	chemical potential of component i in phase j	$J.mol^{-1}$

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