SIMULATING A/D STAGE BLEACHING CHEMISTRY

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ABSTRACT

Comprehensive phenomena based models of kraft pulp bleaching were applied in the present simulation study. A process model for A/D pre-bleaching of oxygen delignified eucalyptus kraft pulp was built using a Flowbat simulator via its graphical user interface. The model was constructed according to literature on a recently build Fray Bentos pulp mill fiberline. Model input data regarding the chemical composition of fiber components was obtained from scientific articles. Tens of organic and inorganic components in total, however, relevant from the chemistry simulation point of view, were included in the simulation.
The model outputs e.g. simulated kappa, HexA and brightness were satisfyingly in line with the values reported in literature. The kappa reduction from 11 to 7 during the A stage contributed to 50% HexA reduction. During the /D delignification kappa decreased down to 4.1. In addition to the typical parameters (kappa, COD, AOX) monitored by process development personnel the simulation provides information e.g. on concentration of key in-situ formed chlorine species such as HOCl. The good agreement with the simulated values and the process measurements spurs to further apply the high fidelity pulp bleaching models in solving practical industrial problems.

I. INTRODUCTION

Bleached eucalyptus kraft pulps form the fastest growing global source of virgin papermaking fibers. Modern eucalyptus pulp bleaching lines are designed to produce pulps of high brightness with minimal consumption of bleaching chemicals. However, the current strive towards further reductions in mill fresh water usage and filtrate discharge with simultaneous need for cost reduction poses a challenge to process development. In this perspective, process modeling and simulation offers a valid means to further improve the process and cost efficiency while maintaining the pulp quality.
Since the early 2000's, a rather ambitious research has been conducted among Aalto University, VTT and Finnish P&P industry for creating phenomena based models for kraft pulp bleaching (Tarvo et al. 2008, Tarvo et al. 2010, Kuitunen et al. 2011). These models apply the concept of two liquid phases (Donnan model), include physico-chemical phenomena (mass transfer, chemical reactions) and delignifying and bleaching reactions taking place in pulp bleaching. The application of these models has recently become easy-to-use as a graphical user interface (GUI) in Simantics platform (Karhela et al. 2012) was combined to a Flowbat simulator (Jakobson et al.) in which the phenomena based models are implemented.
The objective of this study was to simulate oxygen delignified eucalyptus kraft pulp pre-bleaching in A/D stage using the created models in Flowbat simulator via the GUI. The process model was aimed to be constructed based on literature on a modern Fray Bentos pulp mill located in Uruguay, and utilizing mainly *Eucalyptus grandis* as raw material. However, as in case of a mill process there is not very detailed public information available, and thus the data was complemented with information obtained from articles concerning the bleaching chemistry of eucalyptus kraft pulps as well as from handbooks.

II. EXPERIMENTAL

A literature search was conducted to obtain data to form the basis of the simulated process. This data is presented in Tables 1, 2, 3, and 4. The Tables also include values that are estimates for those cases in which data was not available.
The process model i.e. balance area included A stage (for HexA removal) and D stage (ClO2 pre-bleaching) constructed without an intermediate washing followed by drum displacement (DD) washer (Saarela et al. 2008). A filtrate from the second D stage was used for pulp washing (see Fig 1). Process conditions (consistency, T, pH, etc.) and chemical doses were primarily adjusted according Saarela et al. 2008 (mill data) and Vehmaa et al. 2010 (laboratory study) (Table 1 and

2). The A and /D tower dimensions were set according to the reported retention times and nominal production. Prior to the DD washer pulp was diluted to a consistency of 3%. Thereafter, it was thickened and washed to produce outlet consistency of 13% (Krotscheck 2006). Design value for the effluent flow from the mill was reported to be 25 m3/Adt, and bleaching to form the main part of the effluent (Saarela et al. 2008). The bleach plant effluent in total was estimated to be 14.5 m3/Adt, and 60% of this volume was assumed be the volume of A/D stage effluent (8.8 m3/Adt). These assumptions quantified the volume of washing filtrate flow to DD washer (200 dm3/s).

All the organic and inorganic components, relevant from the chemistry simulation point of view were determined in the input steams of the process model. Important fiber wall components determined for the incoming two-stage oxygen delignified (OO) kraft pulp included lignin structures (phenolic lignin, -COOH groups, non-phenolic lignin - elucidated from kappa number, quinone i.e. chromophore structures - elucidated from brightness), carbohydrate polymer monomer (cellulose & hemicelluloses), hexenuronic and 4-O-methyl-glucuronic acids, fatty acids and sterols (Table 3). Aqueous organic components were determined in the model input according to COD (washing loss) reported by Saarela et al. 2008. This COD (8 kg/Adt) was assumed to be mainly (90%) lignin originated. Main inorganic compounds, such as Ca, Na, S, and Cl were adjusted in the model according to Doldan et al. (2011). The equilibrium reactions (acid-base reactions) of the organic and inorganic components and their reactions products were included in the computation.

The bleaching chemistry models covering the stoichiometry and kinetics of lignin structures (both fiber bound and aqueous) with the given chemicals and their various species were combined in the simulation by selecting a proper reaction kinetic library in the GUI's tower units (plug flow reactor).

Table 1. Fray Bentos pulp mill, utilizing mainly *Eucalyptus grandis* – OO-A/D delignification: kappa, brightness, chemical doses, and process conditions used in adjusting the process model.

	OO	A	/D	Eop
Kappa after, -	11	7	4.2	3
B'ness after, ISO-%	52.5-57.8	58	73.9	83
Chemicals, kg/Adt				
Tot. H_2SO_4 12.2		8.5*		
Tot. act Cl 19 – 20.5			13*	
Initial pH, -		3.5*	< 3.5*	
Final pH, -		< 3.5*	< 3*	
Consistency, w-%		10	10	
Temperature, °C		90	65	
Retention time, min	10 + 60	120	15	

*estimate

Table 2. Conditions and properties of oxygen delignified kraft pulp – model inputs.

	OO kraft	Reference
T, °C	90	Vehmaa et al. 2010
p, bar	1	
Water and fiber flow, Adt/d	2860	Saarela et al. 2008
Consistency, w-%	10	Vehmaa et al. 2010
FSP, kg water/kg fiber	1.5	Kuitunen 2011
External water pH, -	9*	
Kappa, mg/l	11	Saarela et al. 2008; Pikka, de Andrade 2011
Brightness, ISO-%	52*	
Scattering coefficient, m2/kg fibers	34.5	Kuitunen 2011
Intrinsic viscosity, ml/g	1080	Vehmaa et al. 2010

Table 3. Chemical composition of oxygen delignified kraft pulp – model inputs.

	OO kraft	Reference
Fraction of PLIG(f), mol fraction	0.11	Kuitunen 2011
FHA2(f), mol/kg fibers	0.02*	
MeGlc(f), mol/kg fibers	0.035	Monrroy et al. 2008
HEXA(f), mol/kg fibers	0.065	Vuorinen et al. 2007, Andrew et al. 2009
FATAC(f), mol/kg fibers	0.0018*	Saarela et al. 2008 (½ of total extractives)
STEROL(f), mol/kg fibers	0.0017*	Saarela et al. 2008 (½ of total extractives)

PLIG(f), phenolic lignin in fiber wall; FHA2(f), -COOH groups in lignin in fiber wall

III. RESULTS AND DISCUSSION

The flowsheet of the A/D stage process model is shown in Figure 1. Monitors (small text close to the streams) in the flowsheet present the model outputs i.e. the simulated values. Phenomena based simulation provides large amount of information. E.g. concentrations of all pseudo-structures of fiber compounds and their reaction products in different phases (fiber, fiber bound water, external water) can be monitored while they also have specific contribution to the sum parameters monitored by the mill personnel. Here, the simulation results of some of the sum parameters are presented and discussed.

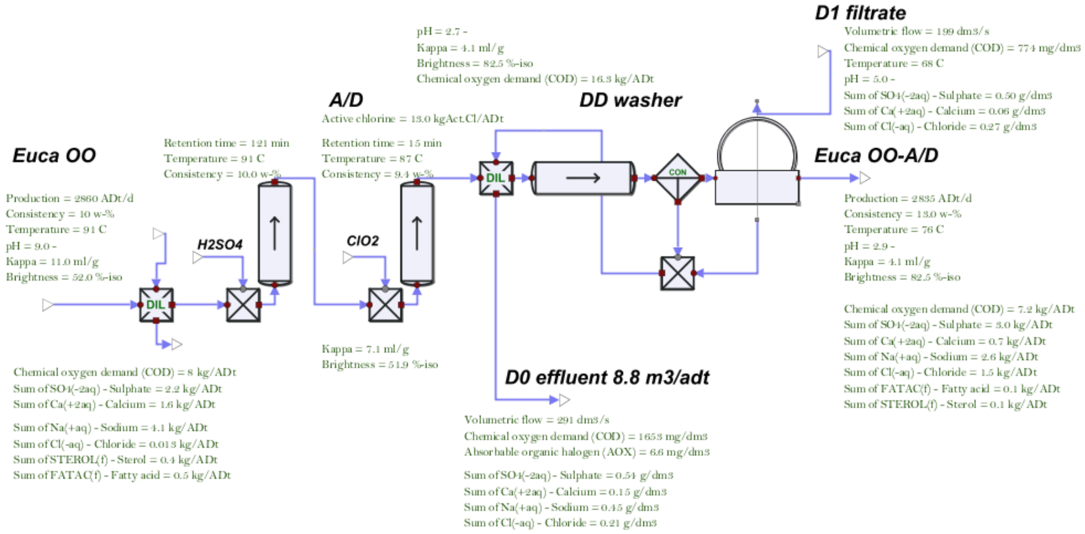

Figure 1. Flowsheet of A/D stage process model. Monitors present the model outputs.

Figure 2 presents the A/D profiles i.e. the simulated and measured kappa and HexA as a function of A tower and /D tower height. Kappa reduction from 11 to 7 during the acid treatment was solely due to HexA removal. When comparing to independent data, the 50% HexA reduction is less than 63% reported by Andrew et al. (2009), who conducted the acid treatment (in laboratory) to fairly similar pulp at similar conditions except at 95 °C (in this study 91 °C). During the /D pre-bleaching, the kappa decreased from 7 to 4.1. In the laboratory study by Vehmaa et al. (2010) the kappa after /D was 4.2. All together 65% of the initial HexA content was removed in the A/D stage. Based on the aforesaid comparison, the simulation succeeded well. Figure 3 shows the COD evolvement as a function of A tower and /D tower height. The simulated value of COD after A/D pre-bleaching was 16.3 kg/Adt. DD washing reduced the value down to 7.2 kg/Adt.

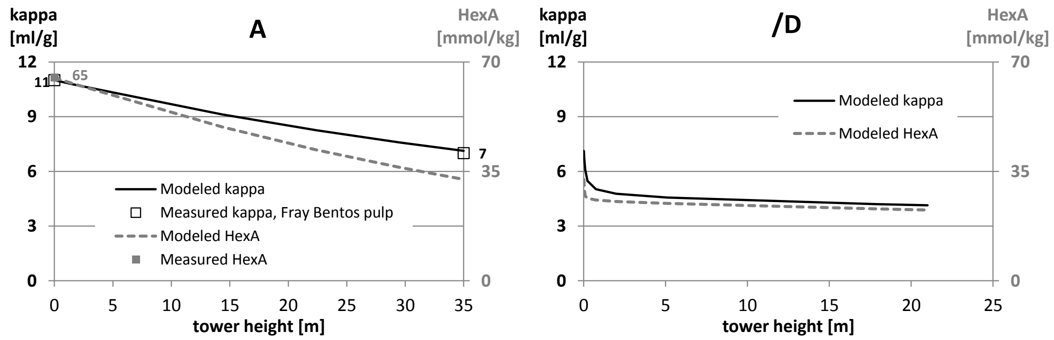

Figure 2. Simulated and measured kappa and HexA during A/D pre-bleaching.

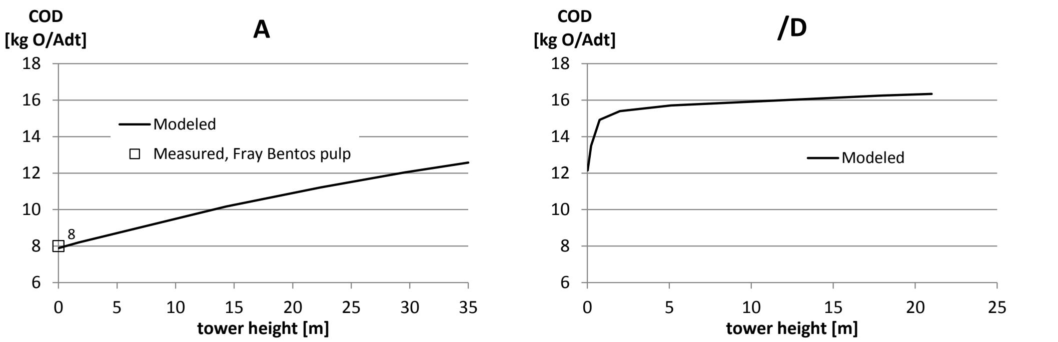

Figure 3. Simulated and measured COD content during A/D pre-bleaching.

Pulp brightness did not increase during the acid treatment at all, since the model only considers HexA reactions during the acid hydrolysis (no lignin reactions). During the /D pre-bleaching brightness gain was from 52% to 82.5% (Figure 4, left). Fray Bentos mill measurement data of pulp brightness after /D was not available, yet, it was reported that brightness after Eop is 83%. When comparing the simulated value to a measured value, 73.9 % obtained from a laboratory study by Vehmaa et al. (2010), there is no agreement. One advantage of simulation is that the concentration of key in-situ formed chlorine species in ClO2 delignification, e.g. HOCl can be interpreted (Figure 4, right).

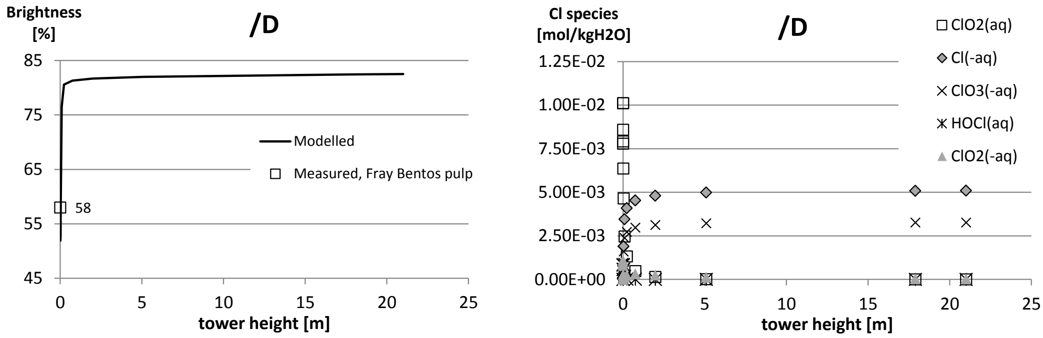

Figure 4. Simulated and measured brightness during /D pre-bleaching. Evolvement of Cl species.

IV. CONCLUSIONS

A process model of A/D pre-bleaching of oxygen delignified eucalyptus kraft pulp was built using Flowbat simulator via its GUI. The model was based on public data. In building the model, there was also partly freedom to choose some of the input quantities/values to adjust the model outputs on a desired level. The simulation results were satisfyingly in line with the values reported in literature, which spurs these phenomenon based pulp bleaching models to be further utilized in solving practical industrial problems.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

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