Modeling and Simulation of an Oxygen Delignification Industrial Process of Cellulosic Pulp using Kinetic Expressions and the software CADSIM Plus

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Abstract— The Brazilian productive sector of pulp and paper represents a relevant contribution for the development of Brazil. To increase the competitiveness of Brazilian companies to an international level, products must have high standards of quality and high added value. Thus, the mathematical modeling and simulation of industrial processes ensures the stability of production. This study presents the fit of mathematical models for the Oxygen Delignification process of eucalyptus pulp of the industry Klabin Monte Alegre. The mathematical model estimates the kappa number after the reactor, based on two kinetic models given by the literature, one of these models considers oxygen excess in the reaction medium. The models showed a mean relative error of 10 %. The adjustment of the kinetic parameters equations was done in Matlab software, using classical methods of optimization, such as BFGS, DFP, Steepest Descent, Gauss Newton, Simplex and Levenberg Marquardt. The models were incorporated in the commercial simulator CADSIM Plus to provide an optimization tool to the pulp industries. The simulator predicts the kappa number after the Oxygen Delignification reactor. The results of the phenomenological models indicate that possibly there is excess of oxygen in the reaction media. Only the model that considered the presence of the oxygen in the kinetic equation was able to be implemented in the simulator CADSIM Plus, generating consistent results, with an absolute error of ± 2 kappa number.

Application: The kinetic model applied to the CADSIM Plus software in this study may be used to optimize the Oxygen Delignification process either by reducing chemical consumptions or by testing different process conditions without changing production.

Keywords— Cellulosic Pulp, Kinetic Expressions, CADSIM Plus.

I.   INTRODUCTION

Klabin Papéis Monte Alegre increased the paper production capacity of the mill to 1,1 million tons/y. This project gave the company an excellent position in the global market with highly competitive production costs. The incorporation of mathematical models and process simulators helps the mill to optimize the pulp production assuring quality specifications that fit the clients demand with a safety and environmentally friend process.

After the Kraft cooking in the continuous digester # 1, the pulp goes to the oxygen delignification process that occurs in a medium consistency media with sodium hydroxide as alkali source. The pulp is washed and discharged into a tank where alkali and oxygen with medium pressure steam are applied. There are two parallel lines with two post oxygen washers in each line. At one line, the pulp is washed in a pressurized diffuser washer followed by a post oxygen filter washer. In the other line the washing is done with two presses. The washed pulp goes to the ECF bleaching. **Figure 1** illustrates the mill process.
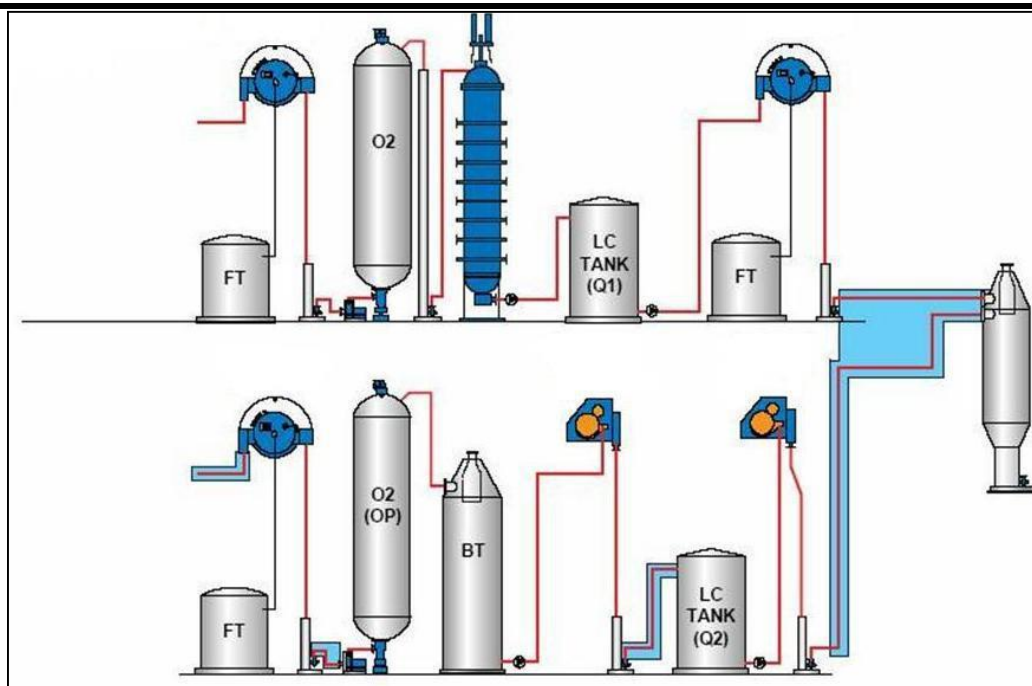
Fig.1: Oxygen delignification plant of Klabin Monte Alegre.

The oxygen delignification is the process which the pulp, suspended into an alkaline solution, is pressurized with oxygen which forms a stable dispersion in the pulp and is consumed in the lignin reactions. This stage removes 50% of the reminiscent lignin in the brown pulp, saving chemicals in the Bleach Plant and minimizing organic material in the effluents (COD and BOD). The process is controlled by a heterogeneous reaction that involves the solid fibers, liquid phase around and between the fibers and oxygen dispersed gas phase [1]. In general, delignification and the carbohydrates degradation reactions are mainly affected by temperature, sodium hydroxide concentration and dissolved oxygen concentration.

Rubini [2] developed mathematical models based on the phenomenological and neural network models to predict the kappa number after the oxygen delignification reactor. The results achieved were very satisfactory regarding industrial simulation having an average error of 8,5%. By those results and the similarity of the data used in this study, the same kinetic models used at Rubini's [2] work were used given by Agarwal et al [3] and Violette [1]. The model proposed by Violette [1] is a single stage model that does not consider the oxygen pressure influence. Agarwal et al [3] suggested a homogeneous kinetic model considering the presence of the oxygen in the reaction media.

The goal of this study was to obtain models adapted from previous published kinetics equations by using classical optimization methods (like: BFGS, DFP, Steepest Descent, Gauss Newton, Levenberg-Marquardt and Simplex) to represent the industrial process. After identifying the kinetic parameters as the Arrhenius frequency factor, activation energy and the exponents of the chemicals concentrations involved in the reaction, the models were applied in the commercial simulator CADSIM Plus.The software represents the process with mass and energy balances being capable to predict the kappa number after the oxygen delignification reactor.

II. KINETIC MODELS

Several authors studied and proposed kinetic models to the oxygen delignification reaction rate considering the mass transfer phenomena. Usually the reaction is described into two phases, the initial is fast and the final is slow or nonexistent lignin reaction. The fast reaction represents the alkaline extraction of the soluble lignin instead of the oxygen reactions [1]. This can be represented by a mathematical model composed of two parallel first order ordinary differential equations related to the lignin [4]

The system can also be described by one equation representing the kappa number degradation in a potential form, usually having high reaction order related to the kappa number By using a simple reaction rate, the slow lignin degradation course during the final stage of the delignification can be mathematically described by the high reaction order. More slow the reaction, higher the exponent will be [4].

Agarwal et al [3] suggest representing the kinetic behavior as a series of parallel first order reactions occurring simultaneously and also consider the possibility of the nonexistent lignin presence characterizing the final slow reaction. The model is given by a one stage equation with a high reaction order related to the kappa number:

$$-\frac{dK}{dt} = k \cdot K^{7,7} \cdot [OH^-]^{0,92} \cdot P_{O_2}^{0,53} \qquad (1)$$

$$k = 2{,}368 \cdot 10^6 \exp(-\frac{107,2}{R \cdot T}) \qquad (2)$$

The authors believe that there is some kind of delay in the process due to the series of parallel first order reactions that leads to a high order equation. The parameters identification based on industrial data is easy to be done using this model because it is represented by the global kappa number, not being necessary to characterize the fast and slow reaction lignin. This model is also efficient to apply into process simulators to evaluate the kappa number variations caused by the oxygen because the kinetic model considers the presence of this chemical in the reaction media.

The objective of Violette's [1] study was to improve the selectivity of the delignification reaction using polymeric additives. The author evaluated the effects of these additives in the selectivity and reaction kinetic rate. Violette [1] suggested that oxygen radicals may be trapped with relatively low amounts of additive radical scavengers if they are concentrated at the cellulosic surfaces. To confirm his hypotheses, the researcher determined the change in the kappa number given by the alkaline extraction by measuring the kappa variations in a reaction media without oxygen.

The author tested seven models to evaluate the alkali consumption and he observed that the decrease in the alkali consumption was proportional to the kappa number decrease and independent of the process operational conditions:

$$\Delta[NaOH] = 0{,}168g/L \cdot \Delta K + 0{,}2g/L \qquad (3)$$

The model to predict the kappa number is represented by equation 4. As Violette [1] used nitrogen instead of oxygen in his work, the model is represented by a corrected kappa number. As this study is based on industrial data the correction is not applicable.

$$-\frac{dK}{dt} = k \cdot K^{3,12} \cdot [NaOH]^{0,588} \qquad (4)$$

$$k = 4{,}4 \cdot 10^3 \cdot \exp(\frac{-7140}{R \cdot T}) \qquad (5)$$

The parameter identification of Violette's model is also simple to apply regarding the use of the global kappa number and a linear model of alkali consumption. However, as the oxygen is not considered in the kinetic equation rate, this model cannot be represented in the simulator as this does not show the kappa-oxygen interaction.

III. PULP AND PAPER SIMULATORS

The process simulation is a useful tool to reduce operational costs and improve the efficiency of existent mills, it is also essential to project new systems and make the start-ups faster and more rentable. Testing different solutions in the simulator helps to indentify the potential problems and change control strategy.

During the 80's, the computational system started to be trustable enough to simulate processes. The Fortran language gave the opportunity to realize complex calculations quickly. The solution was given in the stationary state, by mass and pressure flows, valve opening and tank levels. Then the process parameters were calculated, as concentration, reaction rate and temperature. In this same period, Honeywell acquired the software SCADA (*Supervisory Control and Data Acquisition*) which included solutions to differential algebraic equations and interaction with the control system. This resulted in engineer tools as the MASSBAL [5].

Since the early 90's, the necessity of dynamic simulations appeared. Nowadays the most used pulp and paper simulators are the WinGEMS from Mesto Automation, IDEAS from Andritz and CADSIM Plus from Aurel Systems.

CADSIM Plus allows a CAD draw to give the data source to the process simulation. It supports any drawing complexity, being especially adequate to P&ID diagrams. The dynamic simulation can be used to optimize process, to plan operations, to test DCS (Distributed Control System) control system and to develop control strategies. The software uses de 'C' code providing low execution time in commons computers. The user can also create particular modules of simulation called DLM (Dynamically Linked Modules). The streams of the process can indicate the fiber fraction and specific items as metallic ions, viscosity, brightness and kappa number [6].

The CADSIM Plus can use the function COM (Common Object Model) or DDE (Dynamic Data Change) to communicate with other applicative from Windows, as Microsoft Excel or Visual Basic. Once the communication is done, the software can send or receive data. The software can also Interact with distributes control systems (DCS) by the protocol OPC (OLE to process control) [6]. For example, in the Klabin Monte Alegre's case, the communication with the PI software is possible.

This simulator uses modules to represent the process. Each module is a mathematical representation of the process streams and equipment units. The software has a standard library that includes process equipments, control, integration, mathematical and logical modules.

There are optional libraries of fiber, utilities, hydrocarbons, data reconciliation and connection to other software and process controllers. The fiber library has modules for chip refinery, ion change, pressurized filters, pulp and reject refineries, washers and digesters washing zone.

IV. DATA ACQUISITION AND MODELING DEVELOPMENT

The data was collected from Klabin Papéis Monte Alegre industry The period was sufficient to recreate the process dynamics and generate the necessary amount of data to do trustable analyses. Statistical treatments were done to eliminate errors caused be production stops and variations, online analyzers wrong registered values and instruments out of operation.

A total of 470 process variables patterns of pulp volumetric flow entering the stage, pressure and mass flow of the oxygen, reactor temperature, pulp consistency and kappa number from the Digester and inlet of the Bleach Plant were used to do the modeling and the process simulation.

The kinetic parameters were adjusted based on the models given by Agarwal et al [3] and Violette [2]. The model to represent the alkali consumption is a linear model proportional do the kappa number decrease similar to the one proposed by Violette [2] given by equation 6.

$$\frac{d[OH^-]}{dt} = \alpha \cdot \frac{dK}{dt} \qquad (6)$$

The first order differential equation system composed by the kinetic equation rate (equation 7 or 8 referring to Violette and Agarwal's et al model respectively) and the alkali consumption model was solved with direct integration with the fourth order Runge-Kutta method with variable step on the average residence time of the reactor. The parameter fitting was done using the classical optimization routines: BFGS, DFP, Steepest Descent, Gauss Newton, Levenberg-Marquardt and Simplex

$$-\frac{dK}{dt} = k \cdot K^a \cdot [NaOH]^b \qquad (7)$$

$$-\frac{dK}{dt} = k \cdot K^a \cdot [OH^-]^b \cdot P_{O_2}{}^c \qquad (8)$$

To find the best equation to simulate the process the objective function was evaluated by the normalized quadratic error given by equation 9. A minimum value of the quadratic error implies that there is no need of a new adjusts of the parameters.

$$VV = \frac{\varepsilon^2}{N \cdot \overline{\overline{M}}} \qquad (9)$$

The criteria adopted in the optimization routines of Matlab were a normalized error related to the calculated variable of 10-3 or a maximum number of iterations of 750, what happened first. In all cases the test conjunct was 33% form the original data to validate the models.

The process simulation was created be drawing the industrial flowsheet with two main streams. One representing water, chemicals, organic and inorganic dissolved solids, fiber and lignin, the other is related to the steam line used in the process.

The pulp washing was characterized by the displacement ratio and dilution factors particularized to each type of washer. The reactor simulation mode was done by mass balance based on the kinetic equation rates obtained after the optimization step. The equation rate is an input to the software that considers perfect mixture in the reaction vase. The type of the reactor chosen to represent the industrial process was an upflow tubular reactor. The tanks were modeled to represent a perfect mixture behavior.

The software uses typical PID controllers to simulate de process control. The PID control varies the controlled variable until the measured variable reaches the set point which is a input to the simulation. CADSIM Plus tunes automatically the controllers but if the simulation shows oscillatory behavior or takes too long time to reach the set point it is possible to change the parameters values in order to avoid these disturbances.

First, equation 7 with the adjusted parameters was used as the kinetic equation rate, followed by equation 8 simulation. During the simulation, DDE communication protocols were created to make interactions between CADSIM Plus and Microsoft Excel. The simulator acts as data client or server, working as client the simulator imports the data to be utilized as inputs in the simulation. When working as server, the simulator exports the simulated data to the Microsoft Excel spreadsheets. Having the real process values and the simulated data, the relative error of the models was obtained.

V. RESULTS

To facilitate the comprehension of this work the models are nominated as Model 1, that is similar to Violette's model and represents de first delignification line. For this same process line, Model 2 represent the one based on Agawrall et al study. Regarding the second delignification line, Model 3 represents the one modeled based on Violette's proposition and Model 4 on

Agawrall's et al. The results shown in this section are normalized values to keep industrial confidential.

The results obtained from Model 1 are shown by equations 10 and 11. The adjusted parameters were given by the BFGS optimization method that presented the lowest error. The kinetic constant model is the same one obtained by Rubini but the exponents of the chemicals concentrations changed. The difference between this and Rubini's work is the raw material utilized in the delignification process.

$$-\frac{dK}{dt} = k \cdot K^{4,620} \cdot [NaOH]^{-0,029} \qquad (10)$$

$$k = 11610 \cdot \exp(\frac{-72,5 \cdot 10^3}{R \cdot T}) \qquad (11)$$

Figure 2 (A) and **(B)** illustrate the simulated results and the real industrial values. The first figure shows the values across the data quantity. The second one is the plotting of the calculated data by the real values, more the curve is close to the 45 line better the modeling prediction is.

(A)

(B)
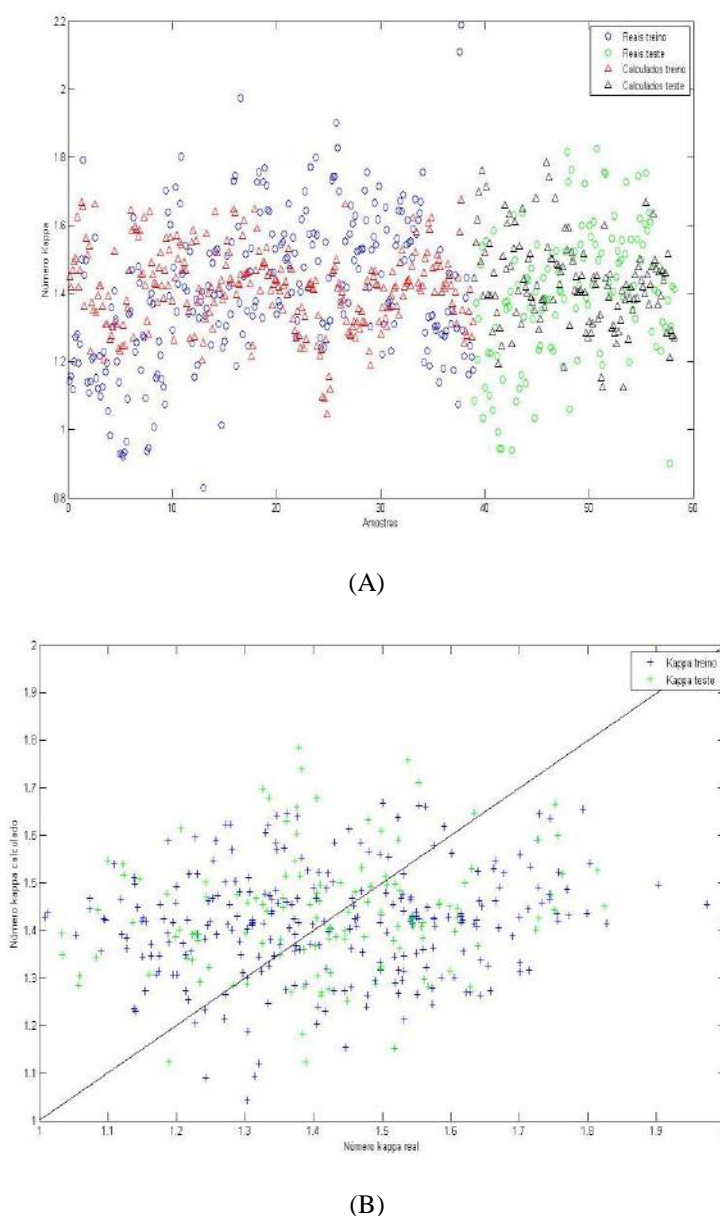
Fig.2: Kappa number comparison between simulated and real values for Model 1.

The simulated values follow the real values tendency even not considering the oxygen presence in the reaction media. Only for high kappa numbers the model was not accurate, however these are not usual operational values as they seldom occurs in the process. It can be concluded also that there is oxygen in excess because Violette's model describes well the data pattern.

The absolute error (difference between real and calculated values) is ± 2,5 kappa number and the relative error is 20%, the most part is due to process variations. The model is able to represent accurately normalized kappa numbers between 1,3 and 1,7.

The kappa number decrease and the alkali consumption trough the reactor are illustrated on Figure 4. All optimization routines resulted in values close to 6 to the proportional constant that describes these profile, as given by equation 12, same result obtained by Rubini [2].

$$\frac{d[OH^-]}{dt} = 6 \cdot \frac{dK}{dt} \qquad (12)$$

With this information, it is possible to evaluate the alkali amount consumed in the reaction and the possibility to reduce its concentration or flow in the process. These results are also normalized values.
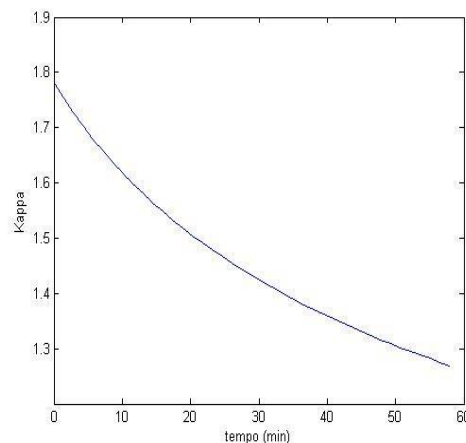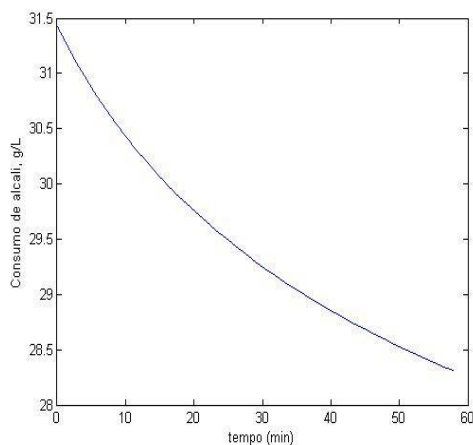

Fig.3: Alkali consumption and kappa number decrease profiles for Model 1.

These profiles allow establishing quality limits to the reaction, i.e., find the optimum sodium hydroxide concentration to get the desired kappa number within the specifications [2]. The results show that the alkali consumption profile has similar behavior to the one propose by Violette [1].

Regarding Model 2, the optimization routines that gave the best results were Gauss Newton and Levenberg Marquardt. By choice, the results below are given by the Gauss Newton method. Equation 13 is the kinetic equation for this model, the kinetic constant is also represented by equation 11 because the results are the same as Model 1. The alkali consumption is the same as Model 1.

$$-\frac{dK}{dt} = k \cdot K^{3,330} \cdot [NaOH]^{0,751} \qquad (13)$$

The absolute error is into the interval of ± 2,5 kappa number and the relative error is 15%, proving the model accuracy. **Figure 4 (A)** and **(B)** illustrate the simulated results and the real industrial values.
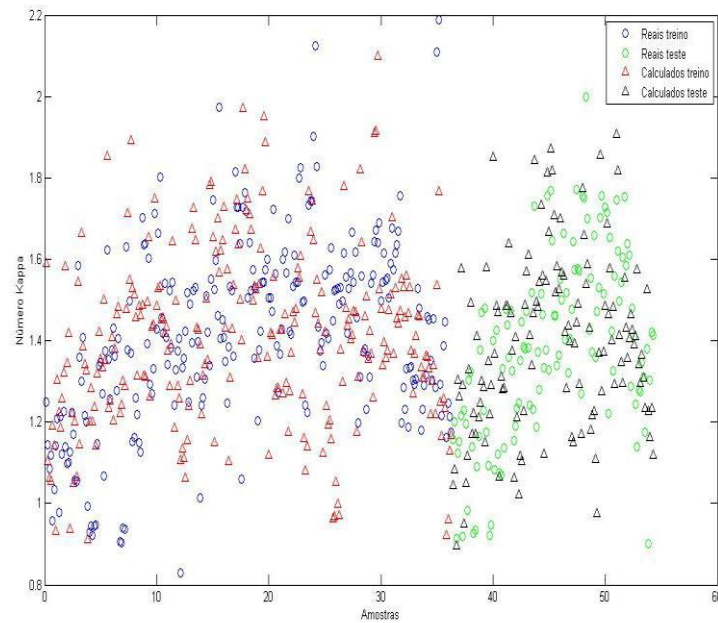
(A)
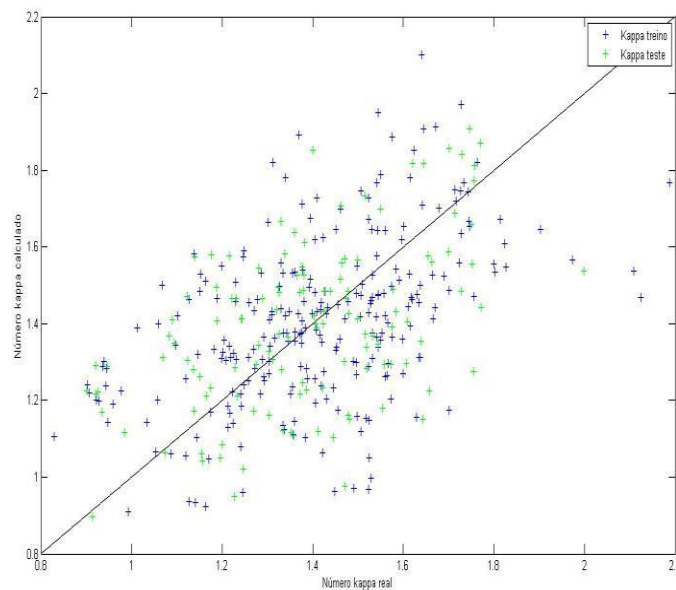
(B)

Fig.4: Kappa number comparison between simulated and real values for Model 2.

The simulated values follow the real process values mainly in the range between 1,2 and 1,6 normalized kappa numbers, even not considering the oxygen presence in the reaction media. Again, it can be seen that the model is capable of predicting the process values as shown by **Figure 4 (A).**

Model 3 was obtained by the Steepest Descent optimization method, having an relative error of 20% and an absolute error of ± 2,0 kappa number. Equation 14 represents the alkali consumption and equations 15 and 16 show the kinetic rate.
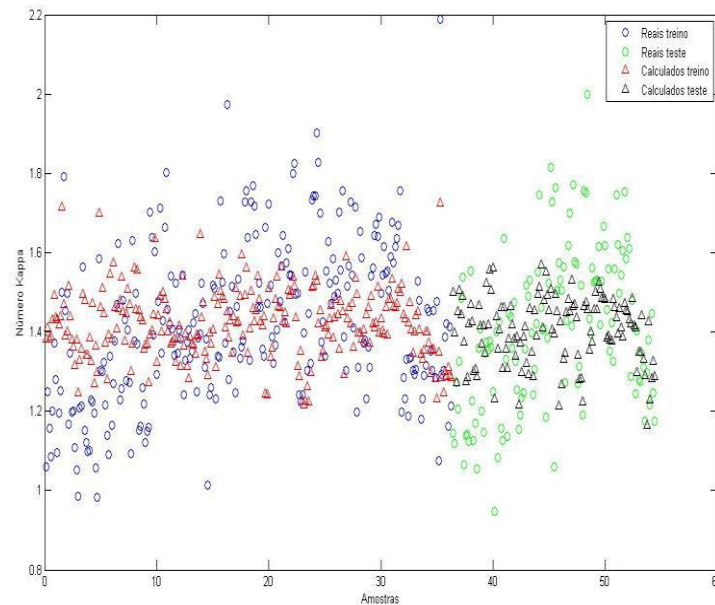
$$\frac{d[OH^-]}{dt} = 6,706 \cdot \frac{dK}{dt} \tag{14}$$

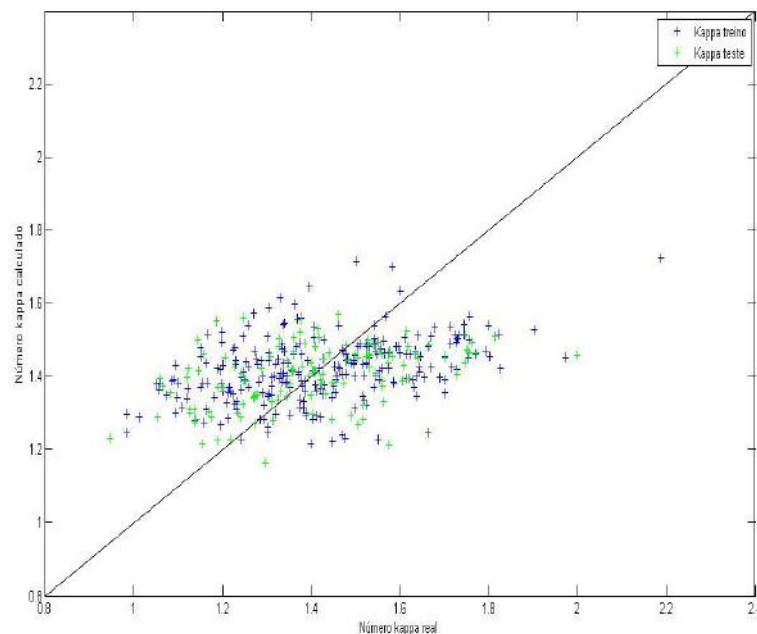$$-\frac{dK}{dt} = k \cdot K^{9,231} \cdot [OH^-]^{5,839} \cdot P_{O_2}{}^{-11,986} \tag{15}$$

$$k = 2,3 \cdot 10^6 \cdot \exp(\frac{-107,20}{R \cdot T}) \tag{16}$$

Figure 5 (A) and **(B)** illustrate this model is able to predict normalized kappa number values in the range of 1,2 and 1,6, only high kappa numbers were not well represented but they are not usual in the process.

(A)

(B)

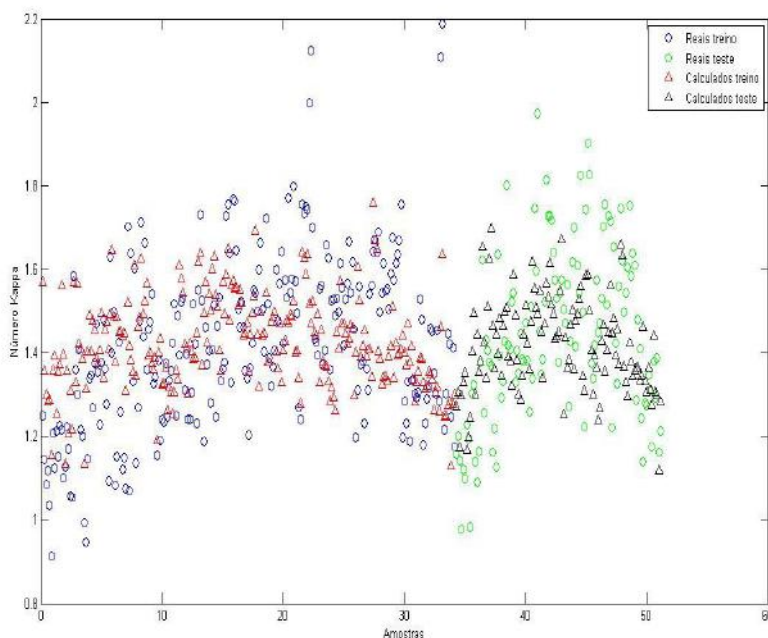*Fig.5: Kappa number comparison between simulated and real values for Model 3.*

Model 4 was better represented by the BFGS method as this was the one with the lowest error conjunct data. Equations 17, 18 and 19 represent the kinetic rate and the alkali consumption model respectively with accuracy of ± 2,0 kappa number and 15% of relative error.

$$-\frac{dK}{dt} = k \cdot K^{7,144} \cdot [OH^-]^{2,694} \cdot P_{O_2}^{-3,343} \qquad (17)$$

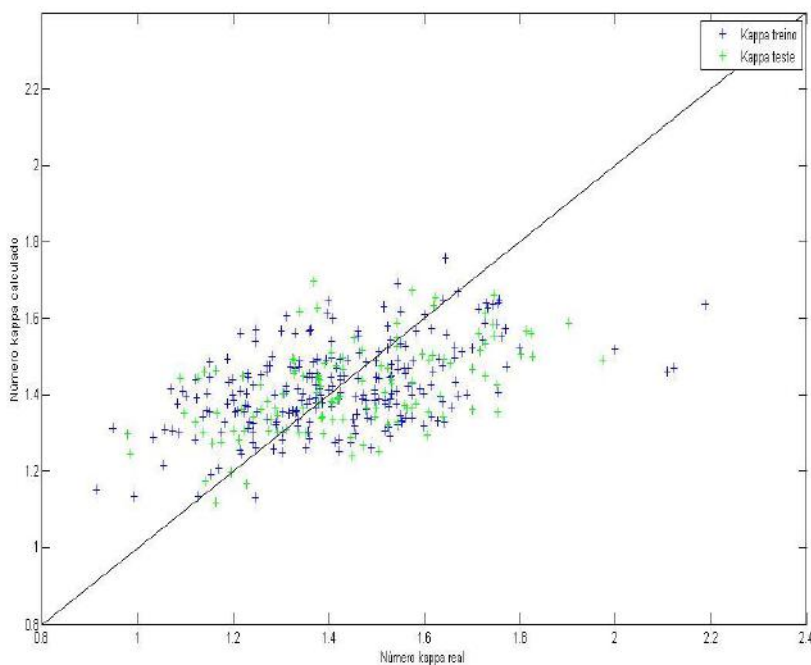$$k = 11610 \cdot \exp(\frac{-72,5 \cdot 10^3}{R \cdot T}) \qquad (18)$$

$$\frac{d[OH^-]}{dt} = 6,612 \cdot \frac{dK}{dt} \qquad (19)$$

As shown by the figures below, this model has a good performance between the range of 1,2 and 1,6 normalized kappa number. The alkali consumption profile is similar to the one from Model 1.

(A)

(B)

Fig.6: Kappa number comparison between simulated and real values for Model 4.

Only Models 3 and 4 gave coherent result when applied to the CADSIM Plus simulator, also these models had short simulation time.

In the first simulation, the software acted as client receiving the inputs, as chemical flows and concentrations

from excel. It presented an average absolute error of 1,3 kappa number after the delignification reactor. **Figure 7** is a tendency chart of the real and simulated kappa number.
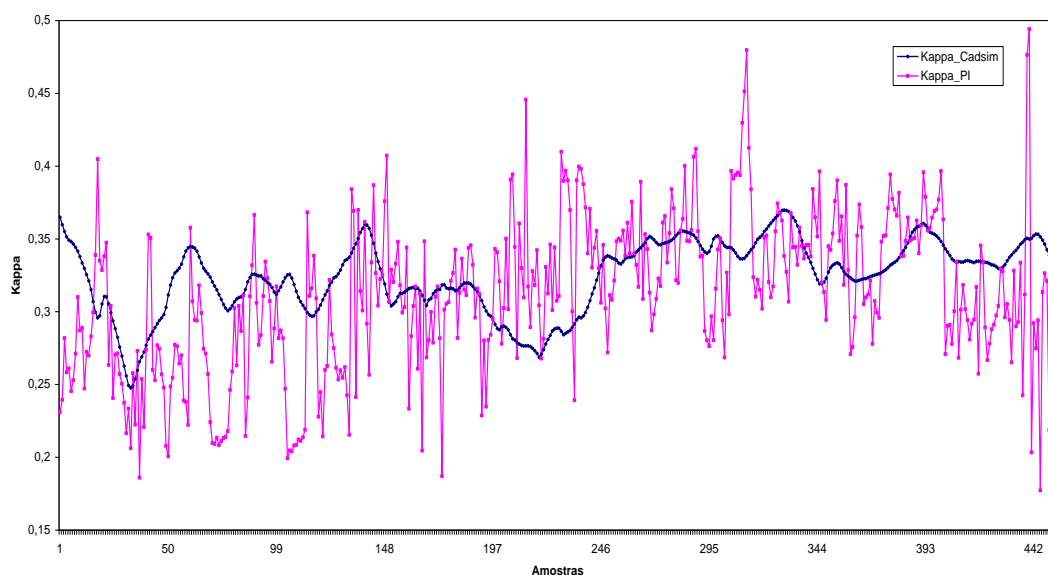

Fig.7: Caparison between real and simulated kappa number values simulated on CADSIM Plus with Model 3.

The figure above shows that this model is able to follow the process tendency, excepting for some points, probably from transient periods in the operation or conditions that were not used in the data fitting. Even with the data treatment to assure stationary simulation, some data should be characteristic of process variations. This is because this is a new operation in the mill, resulting in some instability

With CADSIM Plus it was possible to evaluate de chemical consumption inside the delignification reactor,

simulating the mass balance to the oxygen with mass flow into the process and the residual oxygen after the reaction, the same was done referring to alkali. The result showed oxygen in excess while the alkali was all consumed in the reaction corroborating with the results obtained from the alkali consumption modeling.

Model 4 simulation gave an average absolute error of 1,2 kappa number. **Figure 8** shows the tendency chart of the real and simulated kappa number.
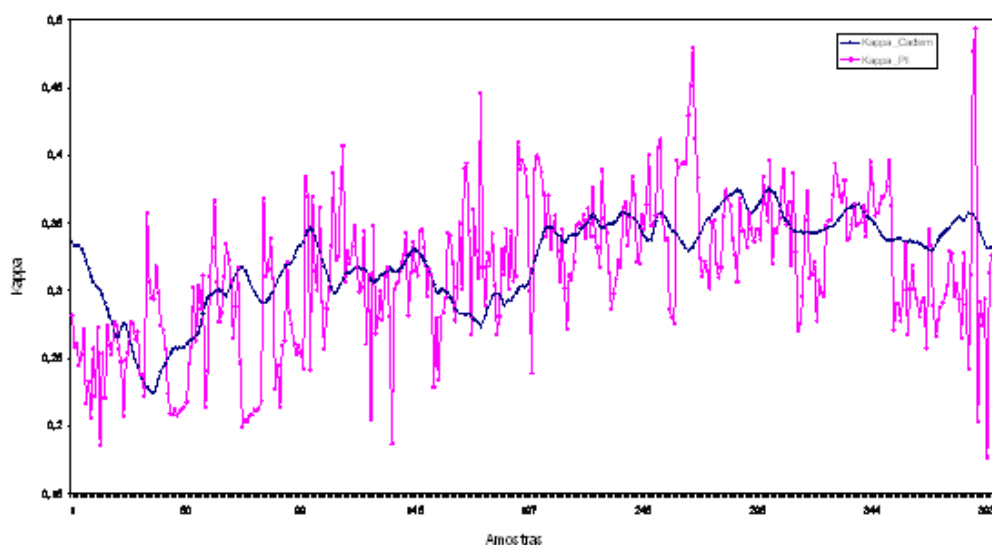

Fig.8: Caparison between real and simulated kappa number values simulated on CADSIM Plus with Model 4.

Again, this model is able to follow the behavior of the process excepting for unusual data. When analyzing the mass balance for oxygen and alkali, it ca be seen that this line also operates with excess oxygen while practically all the alkali is consumed.

In the second type of simulation for both models, the software worked as server, with fixed usual process conditions as inputs, providing the analyses of the kappa number behavior when changing operational conditions.

VI. CONCLUSIONS

To represent the kinetic of the chemical reactions two adapted phenomenological models based on literature study were used. Both models were able to predict the kappa number after the delignification reactor and it was possible to obtain profiles for the kappa number decrease and the alkali consumption inside the reactor. However only the model that considered the oxygen presence in the reaction media was able to be implemented in the CADSIM Plus simulator generating reliable results.

The vantage of the phenomenological modeling is that, once the models are validated, they become a methodology potentially useful to investigate the behavior of the reaction in many operational conditions.

The models showed an average relative error of 13% to one delignification line and 10% to the other. The models are applicable to predict normalized kappa numbers in the range of 1,2 to 1,6 kappa number units. Rubini's model presented an average relative error of 8,5%, these values are in agreement with the errors given by the literature, about 8 to 20% [2].

This shows that the models obtained in this study have good accuracy to represent the real process as they are in the same level of the errors obtained by other authors in the literature. The deviations were slightly higher from another works because this is a new process in the mill operation what results in process variations and non stationary operation. Even with cautiously analyses to assure the stationary state, some data still can have errors from instrument calibration, data acquisition, or signal processing for PI software.

REFERENCES

[1] Violette, S. M., (2003) *Oxygen delignification kinetics and selectivity improvement*. PhD Thesis. University of Maine.

[2] Rubini, B. R., (2006).*Desenvolvimento de Modelos Matemáticos para uma Planta de Deslignificação de Polpa Celulósica com Oxigênio*. Master's Dissertation. Universidade Federal do Paraná.

[3] Agarwal, S. B., Genco, J. M.,Cole, B. J. M., Miller, W., (1999) Kinetics of oxygen delignification. *Journal of Pulp and Paper Science*, 25 (10).

[4] Sixta, H., (2006) *Handbook of pulp, Pulp Bleaching*. Wiley-VCH Verlag GmbH & Co, Weinhein.

[5] Dahlquist, E. (2008), Process Simulation for Pulp and Paper Industries: Current Practice and Future Trend. *Chemical Product and Process Modeling*, 3 (18), University of Malardalen, Sweden

[6] Aurel Systems Inc. Chemical Process Simulation Software Tools & Services. (2008) http://www.aurelsystems.com.