SEMI EMPIRICAL MODELING OF THE STATIONARY STATE OF A REAL CAUSTICIZING SYSTEM IN A PULP MILL

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Abstract— **Causticizing system is an important part of the recuperation cycle of the Kraft pulp production process. In this system, the Na_2CO_3 in green liquor from the recovery boiler is converted in NaOH which is a component of the digester cooking liquor. The system is composed by one extinction reactor, where CaO is added to green liquor, followed by three reactors. Three semi-empirical models of CENIBRA's causticizing system are proposed to simulate the stationary state. The mass balance is developed considering three types of reaction rate equations, whose coefficients were estimated using industrial data. The following assumptions are used: CSTR reactors, instantaneous slaking reaction, constant temperature and rate reactions as functions of NaOH and Na_2CO_3 concentrations. The premise is that all non-modeled factors and the system specificities are included in the estimated coefficients. The obtained models were validated using new industrial data and good agreement was achieved.**

Keywords— **semi empirical modeling, real causticizing system, pulp mill.**

I. INTRODUCTION

The digester cooking liquor (or white liquor) used in the Kraft pulp production process is prepared in the recausticizing plant. In this plant, the smelt from the bottom of the recovery boiler is diluted with weak liquor in the dissolving tank. This solution, known as green liquor, is sent to tanks in series for removing recovery furnace impurities called dregs, and thus reducing variations in density and strength as well. The clarified green liquor is then mixed with lime in an agitated tank, known as slaker. In addition to providing intimate mixing of two reactants, which are the green liquor and the lime, the slaker also removes most of lime impurities, called grits. The reaction is then completed in a series of agitated tanks, known as causticizers. The white liquor contains a suspension of calcium carbonate, known as lime mud, which is formed during the causticizing reaction. The lime mud is separated from the white liquor in a white liquor clarifier. The obtained product is then sent to the digesting department. Figure 1 shows a diagram of the process.

The mill's economic viability depends on the capacity of its recausticizing system to convert recovered chemicals to a proper quality cooking liquor at demand flow to maintain a steady pulp production (Green and Hough, 1998). Three steady state semi-empirical models
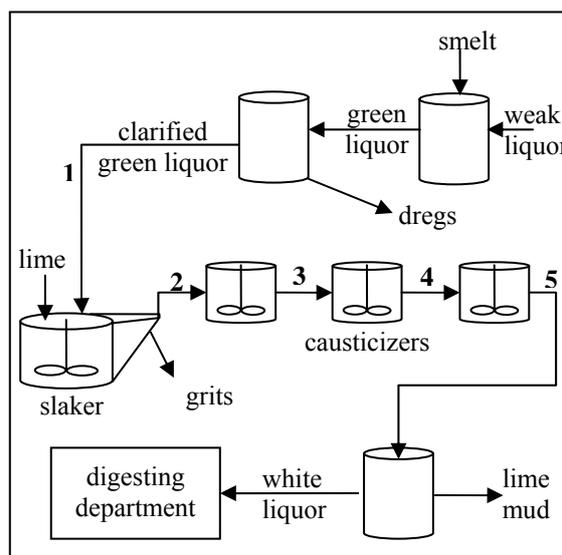

Figure 1: The recausticizing plant diagram.

that describe a real recausticizing plant are proposed in this work. The obtained models reproduce the real behavior of both the slaker and the causticizers of CENIBRA industry.

The studied process proceeds in two stages. The first reaction stage, known as slaking, involves the addition of quicklime (CaO) to the green liquor, where it reacts with the water to form calcium hydroxide $(Ca(OH)_2)$ (Eq. 1). The slaking reaction is exothermic. It releases 270kcal/kg CaO.

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)}, \qquad (1)$$
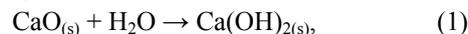
In the second stage, the $Ca(OH)_2$, which was formed in the slaker, reacts with sodium carbonate (Na_2CO_3) as written in Eq. (2).

$$Na_2CO_3 + Ca(OH)_{2(s)} \leftrightarrow CaCO_{3(s)} + 2NaOH, \qquad (2)$$
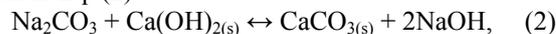
Although the reactions are written in two stages, they actually overlap because part of the causticizing occurs almost coincidentally with the slaking.

In this study, the causticizing efficiency (*CE*) is defined as the relation between the concentration of NaOH and the sum of the concentration of NaOH and Na_2CO_3 (Eq. 3).

$$CE = \frac{[NaOH]}{[NaOH] + [Na_2CO_3]}, \qquad (3)$$

The causticizing reaction is reversible and thus proceeds in either direction depending upon the relative concentrations of the reactants and the products (Eq. 2). According to Green and Hough (1998), this reaction, even under favorable conditions, does not get, a conver-

sion greater than 85% of Na_2CO_3 in NaOH. This amount depends on the total titratable alkali and the green liquor sulfidity.

According to Sethuraman *et al.* (1995), the causticizing system efficiency is affected by some factors such as quality and quantity of lime, concentration of green liquor constituents, temperature, and also intensity of the reaction in the slaker.

Lindberg and Ulmgren (1986) have showed that the temperature has great influence on the reaction rate. However, it doesn't affect the conversion of carbonate into caustic soda.

Because $CaCO_3$ is less soluble than $Ca(OH)_2$, the causticizing reaction happens mainly from the left to the right direction. However, due to the reversibility, Na_2CO_3 can't be completely converted into NaOH; and it doesn't depend on the amount of lime used. Less alkali concentration in green liquor produces greater conversion, because in more concentrated solutions, the NaOH progressively decreases the $Ca(OH)_2$ solubility. This phenomenon goes on until there are not enough calcium ions to exceed the $CaCO_3$ solubility limit (Green and Hough, 1998).

Maximum conversion is desired, because the carbonate that is not converted represents a dead load in the system, and this consequently results in more necessity of caustic soda make-up.

The causticizing reaction can be forced to the right by adding more lime. But it has an adverse effect on the equipment's performance due to the free lime $(Ca(OH)_2)$ presence. There is a limit for the causticizing efficiency in order to produce white liquor. Above this limit, the free lime becomes the greatest problem to operation, especially in the pressurized filter systems.

Some studies have been done into causticizing reaction and its equilibrium constant (K_e). Kobe and Wikinson (1953) concluded that K_e depends on the concentration of Na_2CO_3 in the green liquor. Rydin (1978) showed that the reaction rate could be represented as a function of the calcium oxide, the calcium hydroxide, and also the calcium carbonate concentrations. According to Rothrock (1958), the causticizing efficiency decreases as the green liquor concentration increases. It is affected by the lime quality and also by the size of the particles. Rydin *et al.* (1977) showed that the causticizing efficiency, in equilibrium condition, is a function of molar rate CaO/Na_2CO_3. The authors still analyzed the effect of the lime quality in the reaction equilibrium. The obtained results showed that the lime internal structure does not affect significantly the rate of the reaction. Theliander (1988) affirmed that the lime with larger porosity and smaller size causes a better performance to the causticizing efficiency.

Kojo (1979) proposed the Eq. (4) for calculating K_e, where C_{OH^-} is the concentration of OH$^-$, and $C_{CO_3^{2-}}$ is the concentration of CO_3^{-2}.

$$K_e = \frac{C_{OH^-}^2}{C_{CO_3^{2-}}}, \qquad (4)$$

Lindberg and Ulmgren (1985) determined the effects of the concentration, the composition and the temperature on the causticizing reaction. These authors concluded that the cations concentration was the most important variable in the equilibrium constant. The obtained result has also shown that the temperature has a small influence on the equilibrium. Lindberg and Ulmgren (1985) proposed the Eq. (5) for calculating K_e.

$$Log\ K_e\ =\ 2.95\ -0.62\left[\left(C_{Na^+}\right)+\left(C_{K^+}\right)\right]^{0.5}, \qquad (5)$$

Ransdell and Genco (1991) affirmed that the equilibrium constant depends mainly on the sodium cations concentration, and secondarily on the temperature. According to Ransdell and Genco (1991), the addition of sulfide ions to the green liquor decreases the reaction, and thus the value of the equilibrium constant is smaller.

Lindbergh and Ulgren (1986) showed that: (a) the temperature has a big influence on the causticizing reaction rate. However, it doesn't affect the conversion of carbonate into caustic soda; (b) the dosage of lime under the stoichiometric equilibrium curve decreases the process efficiency; and (c) the concentration of cations in the solution is of little consequence to the causticizing reaction rate.

Dorris and Allen (1985) studied the effect of the reburned lime structure on the rates of slaking, causticizing, and lime mud settling. The obtained results show that: (a) reburned limes with larger specific surface areas tended to slake and causticize at a higher rate than those with smaller surface areas; and (b) more reactive limes tended to produce slower settling lime mud than the less reactive ones.

Lewko and Blackwell (1991) showed that the use of recycling lime from rotative kilns improves the performance of causticizing process by decreasing the amount of $Ca(OH)_2$ in the mud, and so making the process of white liquor clarification easier.

Thus, the lime quality is an important parameter to the causticizing process. The lime produced from calcium carbonate burnt in a rotative limekiln tends to react slower than the lime that is bought in order to make-up the process. The reason is that recycled lime tends to sinter; and the sintering rate affects the causticizing reaction rate (Dorris and Allen, 1985).

Wang *et al.* (1994) presented a methodology, based on Pitzer's model, for the calculation of the equilibrium constant and the equilibrium composition of the recausticizing reaction in a Kraft pulp mill. They also proposed an empirical kinetic model using data from Canadian pulp mills.

Azgomi *et al.* (2007) investigated the influence of lime feeding on the mud settling rate and the causticizing efficiency. The results showed that overliming can be of little consequence to the mud settling rate, but it is not the only responsible for the reduction in the speed of this rate.

Azgomi *et al.* (2008) reported that the settling rate and filterability of lime mud decrease with an increase in liming ratio. The decrease is much more noticeable as liming ratio increases.

Ribeiro *et al.* (2007) investigated the main reasons of small proportion of solids within lime mud in a pulp mill. The obtained results indicated that this process characteristic is due to high SiO_2 concentration in the mud and the operation with high sulfidity liquor that causes reduction on the causticizing efficiency, hence promoting overliming.

Mao and Tran (2007) studied the effect of the proportion of $Ca(OH)_2$ on the lime mud. The obtained results show that the concentration of this substance decreases in the washed lime mud due to the continuity of the causticizing process.

Mao and Tran (2008) analyzed the free lime in mud samples in the causticizing plants of different pulp mills. The results show that all mud samples contain some free lime. The free lime content in the mud that was washed or diluted is lower than the content in the one that has not.

Grace and Tran (2007) studied the dead load consequence to the causticizing process. The obtained results show that an increase of 1% in the efficiency reaction has caused a substantial energy economy in the digesters, evaporators and recovery boiler.

The presented studies show the diversity of variables that affect the causticizing process and besides that there are some divergences between the obtained results. These characteristics illustrate that the process can be very specific, which indicates the use of an empiric methodology to describe the process.

II. PROCESS MODELING

Mathematical tools are often used to describe chemical process in the pulp mill (Oliveira *et al.* 2010; Silva *et al.*, 2008; Malmberg and Edwards, 2007; Rubini and Yamamoto, 2006; Costa *et al.*, 2005; Costanza and Zanuttini, 2004; Costa *et al.*, 2004; Constanza and Constanza, 2002).

Specifically, some studies have been developed on causticizing process mathematical modeling.

Williams and Holm (1975) proposed a model based on mass balance to describe the causticizing process. But they have not presented a validation for this model.

Lindbergh and Ulgren (1986) used an empiric equation to estimate the equilibrium constant (K_e) of the causticizing reaction. Their research was based on experimental data. The results were validated according to a bibliographic review and they proved to be satisfactory.

Sethuraman *et al.* (1995) proposed a hybrid model for calculating the kinetics parameters of the causticizing reaction. The results were validated by experimental data.

Swanda *et al.* (1997) developed a model based on mass end energy balances to describe the causticizing process. Experimental and industrial data were used to validate the obtained results.

Figueirêdo (2006) developed a model based on artificial neural network. For this, experimental laboratorial data were used to train and to validate the proposed model.

Saeidi *et al.* (2006) used a commercial program to predict the effects of minor components within white liquor and liming on the causticizing efficiency (CE). Simulation results showed that chloride, potassium and sulfate have insignificant effects on CE. Besides, the obtained results prove that overliming does not change the maximum attainable CE. When the mixture of lime and Na_2CO_3 is formed in the liquor, it is noticeable that the CE increases with time until a plateau is reached. The maximum CE obtainable is usually lower than the predicted value.

Andreola *et al.* (2007) studied the loss of water caused by evaporation and chemical reaction in a slaker. The simulated results showed that the water being consumed by slaking reaction and evaporation have an influence on the volumetric flow rate of limed liquor, which impose a decrease of 4.6% on the amount of water in the reactor outlet.

Although some researchers have been carrying out studies concerning mathematical modeling of causticizing process, few of them developed such studies based on industrial data and none of these studies could be reproduced on a satisfactory way to be applied at CENIBRA's plant. These aspects were a special motivation for developing this research.

In this study, a steady state mass balance has been used to describe a real causticizing process. The slaker and the causticizers of CENIBRA (plant 2), located in the State of Minas Gerais, in Brazil, are taken into consideration.

The studied pieces of equipment (the slaker with $62m^3$; and the three causticizing tanks with $112m^3$ each) are considered as ideal CSTR reactors.

At CENIBRA, on-line sensors (Kajaani alkali analyzer) are used at points 1, 2 and 5, showed in Fig. 1. Some samples were obtained at point 4 (Fig. 1) to validate the proposed model. Therefore, the concentration of NaOH, Na_2S and Na_2CO_3 is known in these points. The system temperature was constant and equal to 373K.

The kinetic rate expressions, presented in the Eqs. 6 and 7, are required to describe the reaction rate of the causticizing process (Eq. 2). Equation 6 represents the formation reaction rate (r_1) of $CaCO_3$ and NaOH (or the consumption reaction rate of Na_2CO_3 and $Ca(OH)_2$). Equation (7) represents the inverse reaction (the formation reaction rate (r_2) of Na_2CO_3 and $Ca(OH)_2$ or the consumption reaction rate of $CaCO_3$ and NaOH). The kinetic parameters are represented by m_1, k_1, m_2 and k_2.

$$r_1 = -k_1 C_1^{m_1}, \qquad (6)$$

$$r_2 = k_2 C_2^{m_2}, \qquad (7)$$

where C_1 and C_2 are the concentrations of Na_2CO_3 and NaOH respectively.

Using Eqs. (6) and (7) and a static mass balance, it is possible to describe the concentration of Na_2CO_3 and NaOH by the Eqs. (8) and (9) respectively.

$$\frac{F}{V}\left(C_1 - C_1^{(e)}\right) - k_2 C_2^{m_2} + k_1 C_1^{m_1} = 0, \qquad (8)$$

$$\frac{F}{V}\left(C_2 - C_2^{(e)}\right) - 2k_1C_1^{m_1} + 2k_2C_2^{m_2} = 0, \qquad (9)$$

where F is the liquor flow rate; V is the reactor volume; $C_1^{(e)}$ is the Na_2CO_3 concentration that feeds the reactor; $C_2^{(e)}$ is the NaOH concentration that feeds the reactor.

Equations (8) and (9) are used to describe each studied reactor. Therefore, the flow of liquor that leaves a reactor feeds the next equipment. By solving the resultant equations, it is possible to describe the concentration of Na_2CO_3 and NaOH from point 2 to 5 presented in Fig. 1.

In this study, three semi empirical models are proposed and analyzed.

As presented in Eq. (4), in literature, the assumed orders of the direct and inverse causticizing reactions are generally: first order to direct reaction ($m_1 = 1$) and second order to inverse reaction ($m_2 = 2$). This assumption is used in Model 1 and, for this reason, the Eqs. (8) and (9) are a nonlinear system with two analytical solutions. However, one of these solutions has a negative value for C_2 and has no physical meaning. Then there is only one physical solution of Model 1:

$$C_2 = \frac{-\frac{F}{V} + \sqrt{\Delta}}{4k_2}\left(1 - \frac{k_1}{\frac{F}{V} + k_1}\right)^{-1}, \qquad (10)$$

where $\Delta = \frac{F^2}{V^2} + 8k_2\frac{F}{V}\left[1 - \frac{k_1}{\left(\frac{F}{V} + k_1\right)}\right]\left[C_2^{(e)} + \frac{2k_1C_1^{(e)}}{\left(\frac{F}{V} + k_1\right)}\right]$

$$C_1 = \frac{k_2}{\left(\frac{F}{V} + k_1\right)}C_2^2 + \frac{\frac{F}{V}}{\left(\frac{F}{V} + k_1\right)}C_1^{(e)}, \qquad (11)$$

In Model 2, it is used first orders for both, direct and inverse causticizing reactions ($m_1 = m_2 = 1$). Then, the Eqs. (8) and (9) are a linear system whose solution is:

$$C_2 = \left(\frac{2k_1C_1^{(e)}\frac{F}{V}}{\left(\frac{F}{V} + k_1\right)} + \frac{F}{V}C_2^{(e)}\right)\left(\frac{F}{V} + 2k_2 - \frac{2k_1k_2}{\left(\frac{F}{V} + k_1\right)}\right)^{-1}, \quad (12)$$

$$C_1 = \frac{k_2}{\left(\frac{F}{V} + k_1\right)}C_2 + \frac{\frac{F}{V}}{\left(\frac{F}{V} + k_1\right)}C_1^{(e)}, \qquad (13)$$

In Model 3, the orders of the direct and inverse causticizing reactions are parameters, whose values must be empirically estimated. Using arbitrary values of m_1 and m_2, there is not any analytical solution for the Eqs. (8-9). For this reason, the solution of Model 3 is obtained through the numerical solution of the Eqs. (8) and (9).

III. RESULTS

In order to solve the obtained models it is necessary to know the kinetic parameters values (m_1, k_1, m_2 and k_2). For each model, a subset of these parameters was esti-

mated using the previously mentioned real data that describe the points 1, 2, 4 and 5. Therefore, the objective function, described by the Eq. (14), was proposed.

$$SSE(X) = \sum_{i=1}^{n} (X_i - X)^2, \qquad (14)$$

where SSE stands for Sum Squared Errors; n is the data number; X_i represents the calculated values for the concentration of Na_2CO_3 and NaOH; and X is the real values for the concentration of Na_2CO_3 and NaOH.

All programs used in this work were implemented in Matlab language. The Nelder and Mead Simplex Search Method was used to solve the non-linear unconstrained multivariable optimization problem. For the solution of the Model 3, whose objective function depends on the numerical solution of the Eqs. (8) and (9), the performance of this method (that uses only the value of the objective function) is better than the performance of the other used methods (gradient methods and Newton's methods of Matlab), that use, besides the value of the objective function, the values of first derivatives (and second order derivatives in the case of Newton's methods). Using the Nelder and Mead Simplex Search Method, even using different initial guess for the values of the parameters, the obtained optimum values are always the same. Using the others optimization methods, different solutions, with greater Sum Squared Errors, were achieved for each initial guess used. It is possible that the unavoidable numerical errors, presented in the solution of Model 3, are amplified in the numerical calculations of the derivatives in Matlab optimization methods.

The used data set has 120 values for the concentration of each chemical species at points 1, 2, 4 and 5 presented in Fig. 1, totalizing 480 samples. These data were collect during the normal operation of the CENIBRA's causticizing system. The obtained results of the optimization problem are shown in Table 1.

The expected orders of the direct and inverse causticizing reactions are used in Model 1 ($m_1 = 1$ and $m_2 = 2$). However, the values of SSE presented in Table 2 show that the better fit is obtained with Model 2, whose reaction orders are $m_1 = m_2 = 1$. This result confirms the premise that non-modeled factors, inherent to CENIBRA's causticizing system, have influence on the obtained values of the estimated parameters.

In Model 3, the orders of the direct and reverse reactions are given by the estimated values of m_1 and m_2, respectively. Since this model possesses two more parameters than Model 1 and Model 2, the value of SSE for Model 3 must be lower, or at least equal, than the obtained value for Model 2 (that is lower than Model 1). As expected, there is a significant difference between the values of SSE of Models 2 and 3.

Table 1: Parameters and SSE of each model.

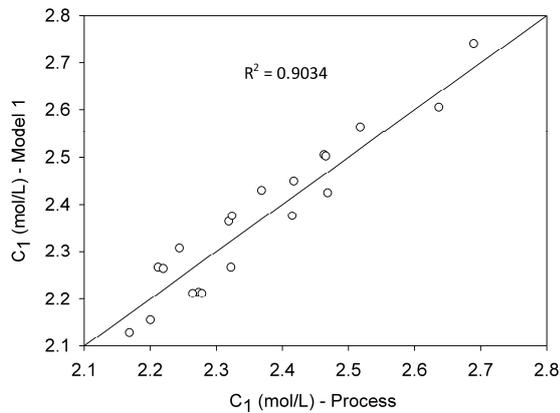|	Model 1	Model 2	Model 3
m_1	1*	1*	0.4097
m_2	2*	1*	2.3172
k_1	22.9028	21.3344	13.667
k_2	0.8678	1.9943	0.9349

| *SSE* | 7.2841 | 7.0029 | 6.2007 |

*values fixed before the estimation of m_1 and m_2.

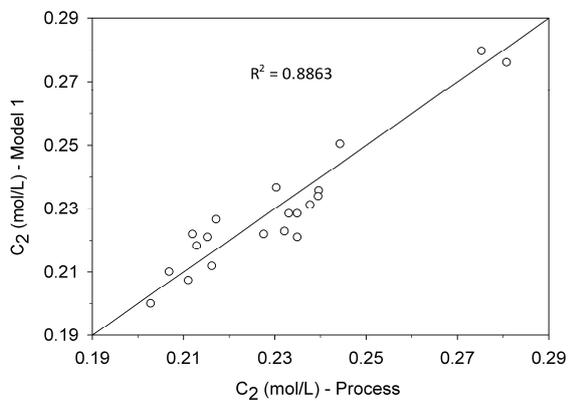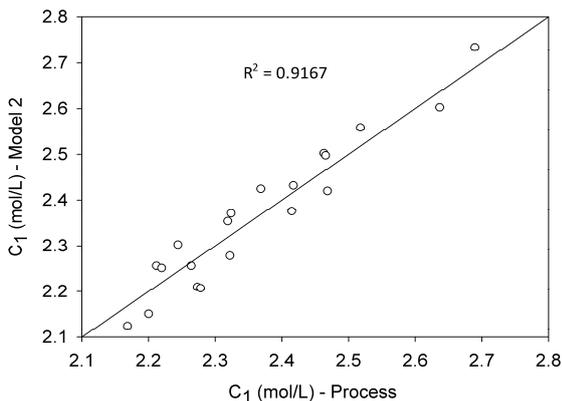Figure 2: Model 1 validation results for NaOH concentration in the outlet of the causticizing system.

Figure 3: Model 1 validation results for Na_2CO_3 concentration in the outlet of the causticizing system.

Figure 4: Model 2 validation results for NaOH concentration in the outlet of the causticizing system.

Although the number of parameters is low for all tested models, when compared with the number of experimental data, an over adjustment could be obtained, especially in Model 3. To verify that possibility, some new data, not used in the parameter estimation, are used to validate the models. The results are presented in Figs. 2 to 7.

Although Model 1 possess the greater value of SSE, when it is compared to the others, it is possible to observe in Figs. 2 and 3 that there is a good concordance between the predicted and measured values in the validation process. It must be emphasized that the expected orders of the causticizing reactions are used in Model 1.

Figures 4 and 5 show that Model 2 is better than Model 1, in both analysis: SSE value and validation performance. Since the opposite behavior is expected, as previously discussed, this result indicates that factors not considered in the modeling process are presented in the estimated parameters. Moreover, this result indicates that the reaction orders must be considered as a parameter to be estimated, has used in Model 3.

Figures 6 and 7 show that Model 3, considering all proposed model, is the best Model in the validation test. This fact indicates that the estimation of the reaction orders do not make the over fit of the model. Moreover, these results show that, besides the estimation of the kinetics constants, the estimation of the reaction causticizing orders is an adequate methodology in modeling of the CENIBRA's causticizing system.

A. Application in industrial process

The proposed Model 3 has been used to propose changes in the real operational conditions. By using the obtained model, it was possible to get the following gains in 2008 compared to 2007 (Figueirêdo *et al.*, 2010):

1 - Decreasing of 4% in lime feeding (mass of lime / volume of liquor);
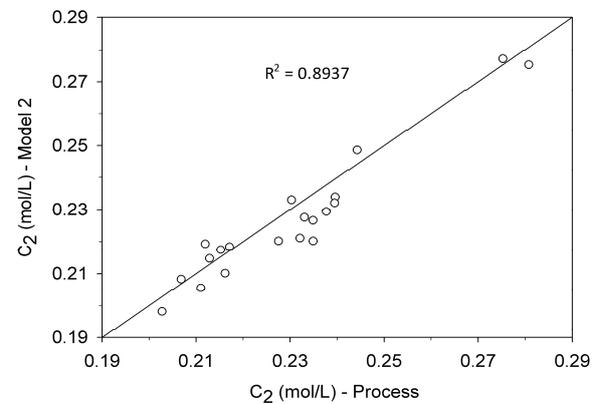
Figure 5: Model 2 validation results for Na_2CO_3 concentration in the outlet of the causticizing system.
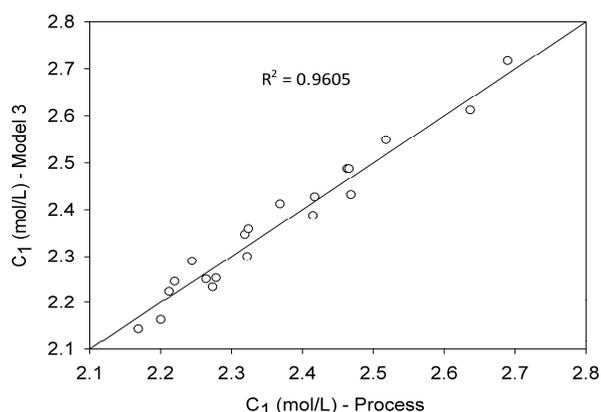
Figure 6: Model 3 validation results for NaOH concentration in the outlet of the causticizing system.
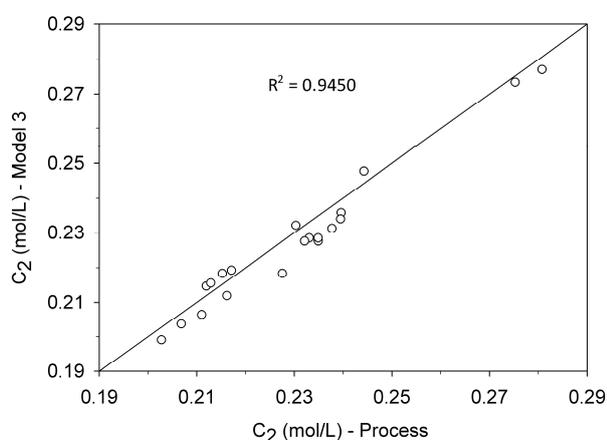

Figure 7: Model 1 validation results for Na_2CO_3 concentration in the outlet of the causticizing system.

2 - Reduction of 3% in specific consumption of produced lime per ton of cellulose generating around US$ 540,000 economy in the lime kilns;

3 - Reduction of 14% in acquisition of lime, thus generating around US$ 190,000 economy;

4 - Decreasing of 10% in the "dead load" (Na_2CO_3) of the recovery circuit;

5 - Elimination of overliming occurrence resulting in: a) more availability and efficiency of lime mud filters generating mud with more content of solids and a consequent improvement in the thermal efficiency of the lime kilns; b) less variation in white liquor effective alkali, resulting in less consumption in volume by digester; c) less content of suspended solids in white liquor, which improves its quality, reduces dead load in recovery cycle and decreases the degree of incrustation in the digesters, evaporators and recovery boilers.

These measured gains refer to around 6 months of operation, because the lime feed control was developed starting from the second semester of 2008.

IV. CONCLUSIONS

A real causticizing process is mathematically described in this study. Three semi empirical models are proposed and analyzed. All models are based on a steady state mass balance for the slaker and the causticizers of CENIBRA (plant 2), located in the State of Minas Gerais, in Brazil.

The difference between the models is due the used reaction orders. Model 1 uses the expected reactions orders, which are first order to the direct reaction and second order to the inverse reaction. Model 2 uses first orders the both reactions. Comparing the obtained results of these two models, Model 2 is better than Model 1 and this fact indicates that that factors not considered in the modeling process are presented in the estimated parameters. This fact stimulates the research of other reaction orders. This research is accomplished in the developing of Model 3.

Model 3 considers that the reaction orders are parameters whose values must be estimated. As expected, the value of the objective function (Sum of the Squared Errors) obtained in the estimation process is lower than the values for Model 1 and Model 2. Moreover, Model 3 has also the best performance in the validation process.

Model 3 has been used to analyze different real operational conditions. This strategy has allowed the industry to get important financial gains and improvements in the process. Finally, it is possible to affirm that the obtained model can be used as a soft sensor at the plant, which increases the related financial gains.

NOMENCLATURE

C = molar concentration (mol/L);

C_1 = Na_2CO_3 concentration inside the reactor (mol/L);

C_2 = NaOH concentration inside the reactor (mol/L);

$C_1^{(e)}$ = Na_2CO_3 concentration in the outlet of the reactor (mol/L);

$C_2^{(e)}$ = NaOH concentration in the outlet of the reactor (mol/L);

CE = causticizing efficiency (%);

F = is the liquor flow rate (L/s);

k_1 = kinetics constant of direct causticizing reaction $(mol^{(1-m_1)}L^{(m_1-1)}s^{-1})$;

k_2 = kinetics constant of inverse causticizing reaction $(mol^{(1-m_2)}L^{(m_2-1)}s^{-1})$;

K_e = equilibrium constant ($K_e = k_1/k_2$);

m_1 = causticizing direct reaction order (-);

m_2 = causticizing inverse reaction order (-);

r_1 = causticizing direct reaction rate (mol.$L^{-1}s^{-1}$);

r_2 = causticizing inverse reaction rate (mol.$L^{-1}s^{-1}$);

V = capacity of the reactor (m^3);

SSE = sum Squared Errors (mol^2/L^2);

X_i = calculated values for the concentration of Na_2CO_3 and NaOH (mol/L);

X = real values for the concentration of Na_2CO_3 and NaOH (mol/L);

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