Kinetic model for the causticizing reaction

Jagadeesan Sethuraman, Jaya Krishnagopalan, and Gopal Krishnagopalan

ABSTRACT: Industrial causticizing systems are operated as open stirred tank reactors at temperatures near 100°C. Lower causticizing efficiency, ineffective liquor strength control, and higher energy consumption are some of the inherent problems associated with this system. Pressurized causticizing at elevated temperatures with appropriate sensors would lend itself to better control and minimize the above problems. This will result in uniform white liquor supply to the digester and, in turn, will yield improved pulp uniformity, productivity, and overall cost efficiency. A laboratory pressurized reactor was developed and analytical grade lime and synthetic green liquor were used to develop a kinetic model without mass transfer effects. A pseudo homogenous liquid phase kinetic model that can predict causticizing efficiency based on liquor properties has been developed. The model parameters were estimated with experimental data using standard optimization routines. The model predictions were found to be within 1% of the measured efficiency. Mass transfer effects encountered in an industrial system can be easily incorporated in this model, on the basis of data obtained for industrial lime and mixing conditions. The mill-specific model, supplemented with on-line liquor property measurements, will allow closure of the control loop to produce uniform white liquor with improved causticizing efficiency.

KEYWORDS: Causticizing, chemical reactions, cooking liquors, dynamics, kinetics, measurement, mechanics, models, on-line measurement, properties, white liquors.

Causticizing is a part of the kraft chemical recovery cycle and is the process that converts sodium carbonate in the green liquor to sodium hydroxide. The resulting white liquor is reused in the digester.

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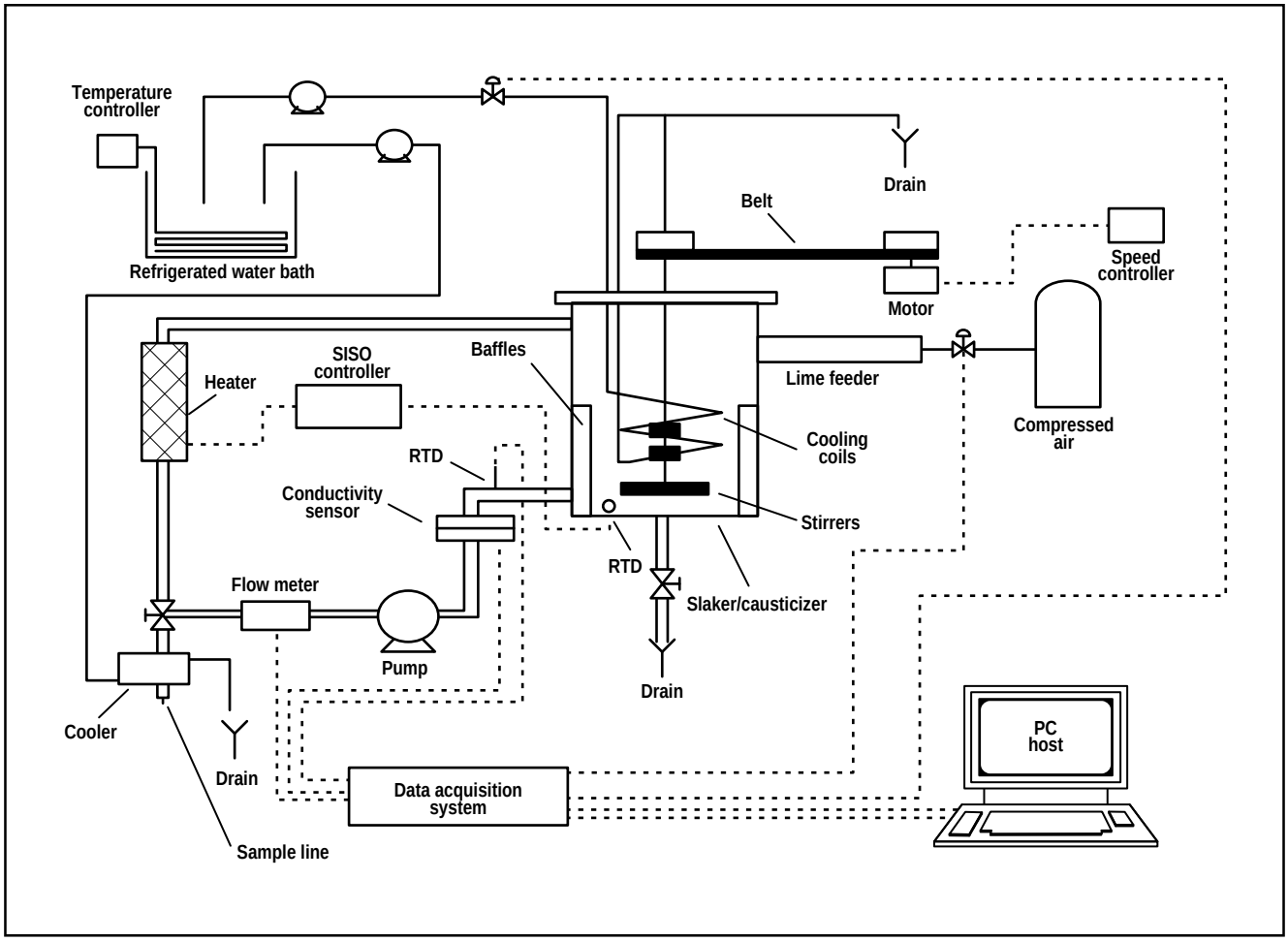
A typical causticizing system consists of a slaker and series of causticizers. The overall performance of a causticizing system is affected by various factors such as the quality and quantity of lime, concentrations of the components in the green liquor, temperature, and intensity of mixing. Control of the causticizing process is important to achieve maximum possible causticizing efficiency and produce white liquor of maximum concentration and clarity. It is important to avoid problems associated with overliming and underliming conditions. In order to achieve good control, it is necessary to have a reliable reaction model to predict the response of the system to process disturbances.

Background

There are few studies on causticizing kinetics and on available kinetic models. Rydin *(1)* proposed two kinetic models, one with three parameters and the other with five parameters. Rydin observed that his five-parameter model, with the concentrations of all the solids (calcium oxide, calcium hydroxide and calcium carbonate) in the system, was more accurate than the other three parameter models. On the other hand, other investigators *(2, 3)* have reported the reaction rate to be independent of the concentrations of these solids. Rydin *(1, 4)* also studied the effect of internal structure of lime on the causticizing rate and found it to have no appreciable effect. Turc *et al. (5)* investigated the causticizing kinet-

1. Schematic diagram of experimental setup



ics, and their model included the calcium hydroxide term, but not calcium carbonate and calcium oxide.

Lindberg and Ulmgren *(3)* introduced a term *Q* defined as:

$$Q_t = [OH^-]_t^2/[CO_3^{--}]_t \qquad (1)$$

where $[OH^-]_t$ and $[CO_3^{--}]_t$ represent the concentrations of hydroxide and carbonate ions in the reacting mixture at any time *t*. Their model incorporated the rate of change of *Q* as a function of the difference between the observed equilibrium constant (K_c) and Q_t.

Mondal and Krishnagopalan *(6)* developed a preliminary model to predict the causticizing efficiency with time. This model assumed the reaction to be pseudo homogeneous and the model had orders 1 and 3 for the forward and reverse reactions, respectively. Dotson and Krishnagopalan *(7)* further validated this model with synthetic green liquor. This model predicted the causticizing efficiency accurately as the reaction approached equilibrium, but was inaccurate during the early stages of the reaction because of the inaccuracy in the estimation of forward rate constant.

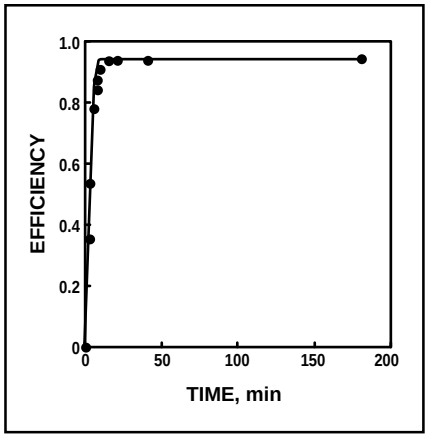
Holman *et al. (8)* used mill green liquor and lime to study the kinetics using the model developed by Dotson and Krishnagopalan and found that the predictions were good when the rate constants and the reaction orders were tuned.

Theliander *(9)* proposed that the reaction occurred in the solid–liquid interphase and that the reaction is

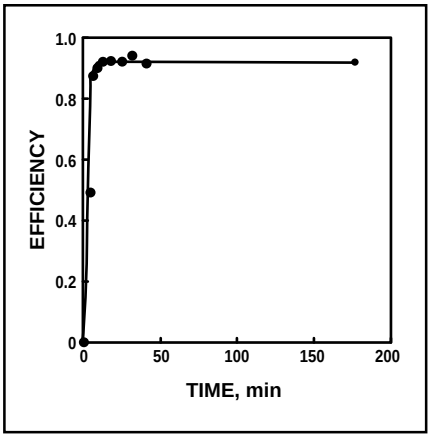
I: Reaction conditions used in the experimental study

Process variables	*Ranges*
Temperature	80 - 110°C
Green liquor concentration, g/L	
Sodium carbonate	75 - 125
Sodium sulfide	0 - 30
Sodium hydroxide	0 - 25

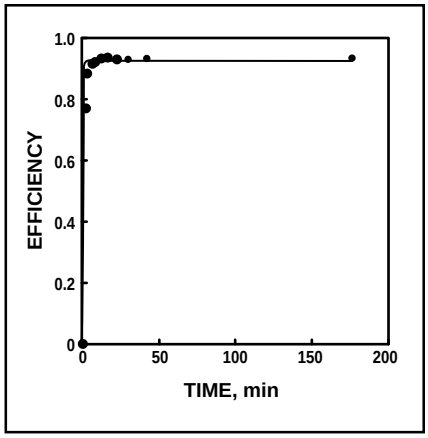
2. Best fit of experimental data with kinetic model predictions with 100 g/L Na_2CO_3 at 80°C.



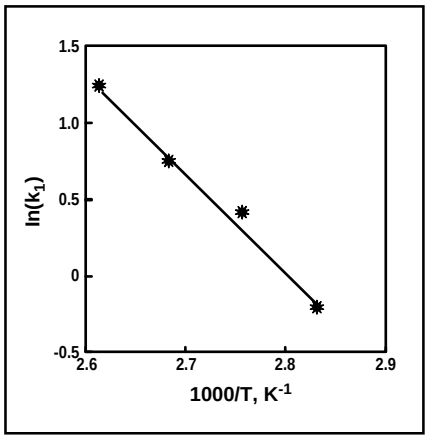
3. Best fit of experimental data with kinetic model predictions with 80 g/L Na_2CO_3 at 90°C



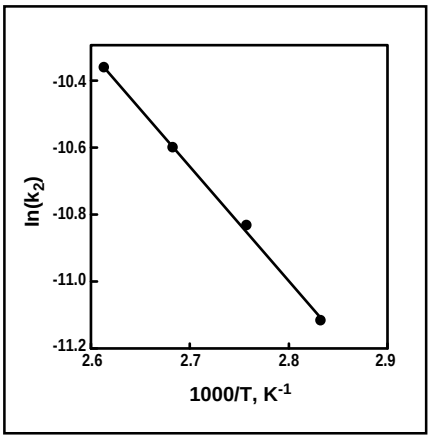
4. Best fit of experimental data with kinetic model predictions with 100 g/L Na_2CO_3 at 100°C



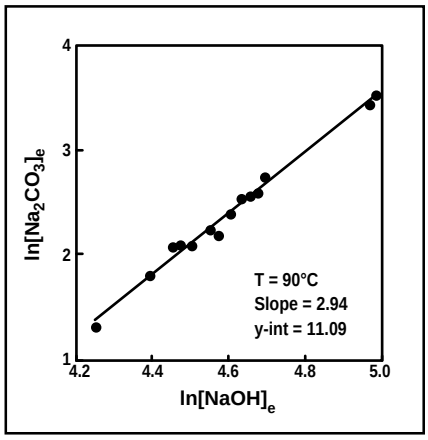
5. Arrhenius plot for forward reaction



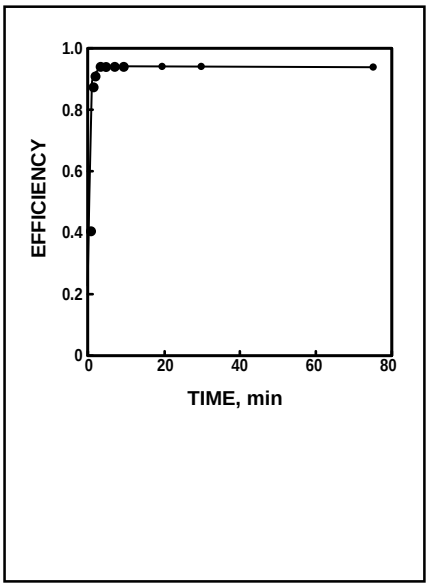
6. Arrhenius plot for reverse reaction



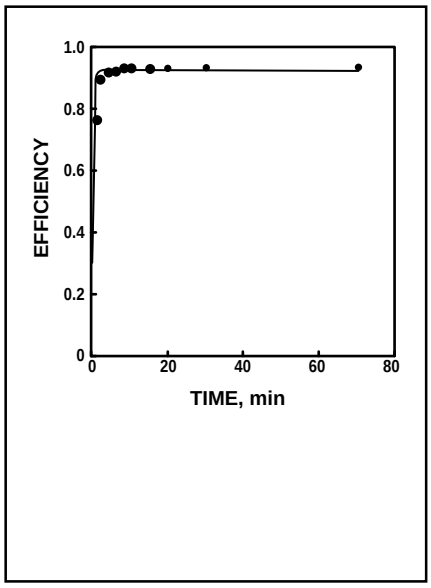
7. Equilibrium concentration plot



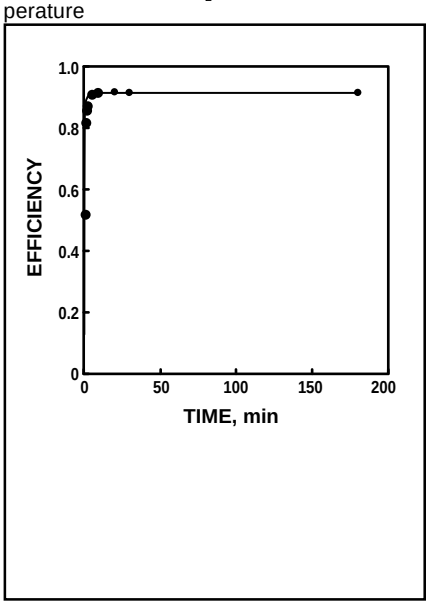
8. Comparison of actual efficiency with predicted efficiency with 80 g/L Na_2CO_3 at 100°C initial temperature



9. Comparison of actual efficiency with predicted efficiency with 100 g/L Na_2CO_3 at 110°C initial temperature



10. Comparison of experimental data with model predictions with 65 g/L Na_2CO_3, 14 g/L NaOH, 14 g/L Na_2S at 100°C initial temperature



diffusion controlled. This is in contradiction to what others had observed*(1–4)*, and his model is complex and requires rigorous computation of the model equation.

Most of the models now available in literature do not isolate the effects of mass transfer on the reaction rate. Mass transfer effects can vary from one mill to another and within a mill, can vary from time to time, based on the operating conditions. The models which partially account for the mass transfer effects are complicated and cannot be used with the on-line measurement devices that are currently available.

The purpose of this study is to develop a model to represent the kinetics of causticizing reaction when the mass transfer effects are negligible. Once the mass transfer effects are accounted for in the model, the model should be simple to use in an industrial system. This model when combined with on-line liquor measurements of causticized liquor would allow the closing of the control loop.

Chemistry of causticizing

The following reactions occur in the process of conversion of green liquor to white liquor:

Slaking reaction:

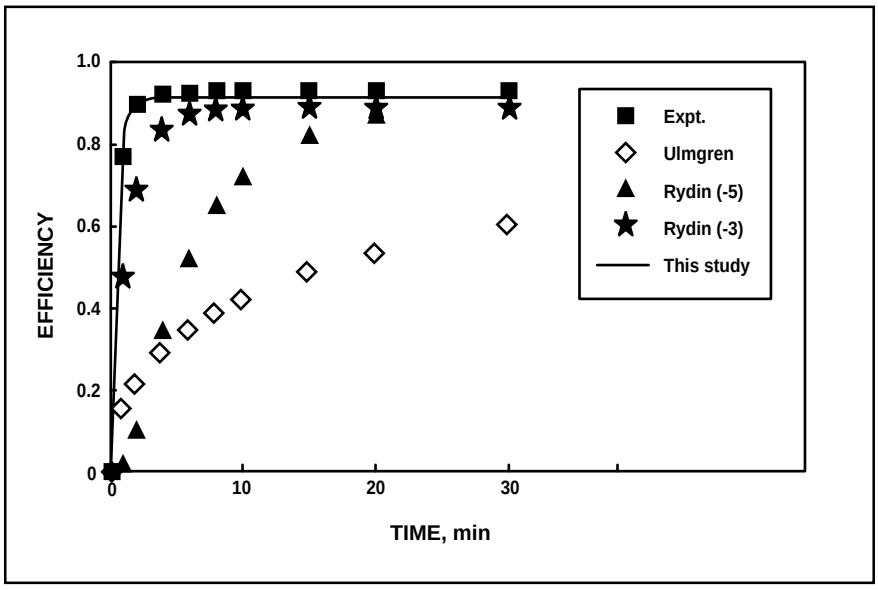
$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(s)} \qquad (2)$$

Causticizing reaction:

$$Ca(OH)_{2(s)} + Na^2CO_{3(l)} \underset{k^1_2}{\overset{k^1}{\rightleftharpoons}} 2\,NaOH_{(l)} + CaCO_{3(3)} \qquad (3)$$

Slaking is an exothermic reaction and the causticizing reaction is slightly endothermic. The slaking reaction is much faster than the causticizing reaction and, in a well mixed system, the overall reaction rate is controlled by the causticizing reaction.

11. Comparison of experimental data with predictions obtained from various models



Model development

In the present work, it is assumed that the reaction is pseudo homogenous and takes place in the liquid phase, and that the reaction rate does not depend on the concentrations of calcium hydroxide and calcium carbonate in solution. The concentration of the solids are very high in the reacting mixture in comparison to their solubility at the temperatures considered. The slaking reaction is assumed to be instantaneous and to have no effect on the overall reaction rate. The reaction rate for the caustizing reaction can be written as:

$$-d[Na_2CO_3]/dt = k_1' \cdot [Na_2CO_3]^a \cdot [Ca(OH)_2]^c - k_2' \cdot [NaOH]^b \cdot [CaCO_3]^d \qquad (4)$$

where

k_1 = forward reaction rate constant

k_2 = reverse reaction rate constant

[i] = concentration of the chemical species i in the liquid phase

a,b,c,d = the orders of the reaction with respect to the respective chemical species.

The concentrations of sodium carbonate and sodium hydroxide in the above equation are expressed in terms of grams per liter (g/L) as Na_2O equivalents. As the concentrations of calcium carbonate and calcium hydroxide are constant:

$$k_1 = k_1'[Ca(OH)_2]^c_{(l)} \qquad (5)$$

$$k_2 = k_2'[CaCO_3]^d_{(l)} \qquad (6)$$

Causticizing efficiency, η, is defined as:

$$\eta = \{[NaOH]_{WL} - [NaOH]_{GL}\}/\{[NaOH]_{WL} + [Na_2CO_3]_{WL} - [NaOH]_{GL}\} \qquad (7)$$

Material balance for the chemicals in the liquor gives:

$$[NaOH]_{GL} + [Na_2CO_3]_{GL} + [Na_2S]_{GL} = [NaOH]_{WL} + [Na_2CO_3]_{WL} + [Na_2S]_{WL} \qquad (8)$$

The concentration of sulfide can be assumed to be constant throughout the reaction and can be removed from Eq. 8.

Equation 8 can be substituted in Eq. 7 to give:

$$\eta = \{[Na_2CO_3]_{GL} - [Na_2CO_3]_{WL}\}/[Na_2CO_3]_{GL} \qquad (9)$$

Equation 9 can then be written in terms of the initial and instantaneous concentrations as:

$$\eta = \{[Na_2CO_3]_0 - [Na_2CO_3]\}/[Na_2CO_3]_0 \qquad (10)$$

where

$[Na_2CO_3]_0$ = initial concentration of the sodium carbonate

$[Na_2CO_3]$ = instantaneous concentration of sodium carbonate.

In the liquor, sulfide is assumed to be completely hydrolyzed and hence the hydroxide ion concentration in the liquor is expressed as effective alkali concentration, which is given as:

$$[EA] = [NaOH] + 1/2\ [Na_2S] \quad (11)$$

At any time the concentration of sodium hydroxide and sodium carbonate can be written as

$$[NaOH] = [Na_2CO_3]_0 \cdot \eta + [EA]_0 \quad (12)$$

$$[Na_2CO_3] = [Na_2CO_3]_0 \cdot (1 - \eta) \quad (13)$$

where

$[EA]_0$ = initial effective alkali concentration in the green liquor.

Substituting Eqs. 5, 6, 12, and 13 in Eq. 4 yields a differential equation expressing rate of change of causticizing efficiency as a function of instantaneous causticizing efficiency and the initial concentration of the liquor:

$$d\eta/dt = k_1[Na_2CO_3]_0^{(a-1)}(1-\eta)^a - (k_2/[Na_2CO_3]_0)\,([Na_2CO_3]_0\,\eta + [EA]_0)^b \quad (14)$$

At equilibrium, the causticizing efficiency does not change with time, and the equilibrium constant can be expressed as:

$$K_c = k_1/k_2 = [NaOH]_e^b/[Na_2CO_3]_e^a \quad (15)$$

where

$[i]_c$ = equilibrium concentration of the species i.

Rearranging the equation and expressing in logarithmic form:

$$\ln [Na_2CO_3]_e = (b/a) \cdot \ln [NaOH]_e - (1/a) \cdot \ln K_c \quad (16)$$

Values of parameters a, b, k_1 and k_2 are to be estimated from kinetic data.

Experimental

The experimental setup used is shown in **Fig. 1**. It consists of a well insulated, 3 L stainless steel vessel provided with a recirculation line. An electrical heater located in the recirculation line heats the liquid to the reaction temperature and maintains the temperature thereafter. The lime feeding system consists of a cylinder welded horizontally to the side of the vessel. The cylinder has an airtight flap with a locking arrangement to prevent steam from entering the lime feeder. The locking arrangement can be released at desired times so that lime can be discharged, using a pneumatic mechanism, into the reactor. A Rosemount temperature sensor fitted into the vessel monitors the process temperature and, in turn, is used to control the temperature of the liquor. A computer controlled cooling system allows the removal of the exothermic heat during the slaking reaction. The temperature of the reaction system is maintained within ± 0.5°C from the setpoint. Control and data acquisition are achieved using a Keithley data acquisition system in conjunction with a microcomputer using Quick500 software and user written control program. Synthetic green liquor prepared using reagent grade chemicals was used for the experiments. Causticized liquor samples were extracted from the recirculation line through a sampling valve with a built-in cooling system. Samples were immediately filtered and analyzed.

Parameter estimation

The model developed to determine the causticizing efficiency as a function of time had four parameters to be determined. These parameters were the forward and reverse rate constants and their orders. The range for the process variables used in the experiments are given in **Table I**.

Data from each experimental run was used to optimize the parameters using standard International Mathematical and Statistical Library (IMSL) subroutine. It should be noted that the initial concentration of the sodium carbonate in the liquor before the causticizing reaction was determined using the measured concentration of green liquor and correcting the measured concentration for the water loss due to slaking reaction. The reaction orders a and b were found to be 1 and 3 respectively, and these findings were found to be in agreement with the previous studies *(6, 7)*. With the estimation of these parameters, the final form of the model was found to be:

$$d\eta/dt = k_1[1-\eta)^1 - (k_2/[Na_2CO_3]_0)\,([Na_2CO_3]_0\,\eta \bullet [EA]_0)^3 \quad (17)$$

For a typical experimental run, **Figs. 2 through 4** show the best fit for Eq. 17 with the data. Analytical grade lime has been used for all the experiments. This, in combination with proper mixing, resulted in higher reaction rates than that observed in industrial systems. The forward and reverse reaction rate constants were estimated and plotted against $1/T$. **Figures 5 and 6** show the best fit for the Arrhenius plot at a r^2 of 0.99. The activation energies and the frequency factors for the reactions are given below:

E_1 = Forward reaction activation energy = 12608 cal/g·mol

E_2 = Reverse reaction activation energy = 6646 cal/g·mol

A_1 = Forward reaction frequency factor = 5.32E7 min^{-1}

A_2 = Reverse reaction frequency factor = 0.1964 $(g/L)^{-2}$ min^{-1}.

The final equation for the reaction rate constants can be expressed as:

$$k_1 = 5.32 \times 10^7 \exp - (12608/RT) \quad (18)$$

$$k_2 = 0.1964 \exp - (6646/RT) \quad (19)$$

where

R = 1.987 cal/g·mol °K

A logarithmic plot of equilibrium concentrations of Na_2CO_3 against NaOHconcentration, according to Eq. 16 , will give a straight line with a slope equal to (b/a) and intercept

equal to ln K_c/a. Data obtained from the equilibrium runs at 90°C are shown in **Fig. 7**, and the slope and intercept determined are given below:

$$\text{Slope} = b/a = 2.94 \quad (20)$$

$$K_c = \exp(\text{Intercept} \cdot a) = 65512 \quad (21)$$

These are close to values of b/a = 3 and K_c = 69939 found using the model.

Model validation

Additional experiments were conducted to test the final form of the model. For these experiments, cooling water was not used to quench the exothermic heat evolved during the slaking reaction but the temperature of the reaction mixture was monitored continuously. **Figures 8 through 10** show the predicted causticizing efficiency profile and the experimental values. The model predictions were found to be good and were within 1% of the experimental efficiency values.

The activation energy for the forward reaction was found to be higher than that reported by Dotson and Krishnagopalan *(7)*, while that for the reverse reaction was comparable to the reported values *(7)*. The activation energy for the forward reaction also agreed with the value reported by Rydin *(1)*. It can be seen from Figs. 8–10 that the present model predicts causticizing efficiencies accurately during the initial stages which is essential for good control of the process.

In order to compare the predictions from the developed model with that available in the literature, data were simulated with Rydin's three and five parameter models and Lindberg and Ulmgren's model for the experimental conditions and compared with the experimental measurements. **Figure 11** shows experimental data with various model predictions. The simulated data indicate lower reaction rates, due to the presence of mass-transfer effects in their systems. It should be noted that the purpose of this study is to develop a model without the effects due to mass transfer and hence it is not possible to compare these models.

Application

The developed model can be used (as an empirical model) to predict the causticizing efficiency of an industrial system provided the initial concentration of the green liquor is accurately known *(10)*. The model parameters obtained in this study have been estimated for conditions where the mass transfer effects are negligible and will be significantly different for each installation. However, these parameters can be tuned, and one set of parameters can be arrived at, for each causticizing system. Holman *et al. (8)* used industrial lime to find the model parameters and reported that the model predictions closely represented observed efficiency. The effects due to variability in lime and mixing conditions can be accounted for by incorporating mass-transfer terms in the developed model.

Conclusion

The predictive capability of the model developed from pressurized batch reactor data was found to be within 1% of the experimental values of efficiency. The synthetic green liquor used for these experiments did not contain sulfate, thiosulfate, and sulfite. Fine tuning of model parameters for industrial applications will involve the inclusion of these components in the green liquor and industrial lime. An additional mass transfer term can be incorporated in the model, to account for the variations in lime quality and mixing conditions. The model, along with the on-line green liquor analysis and the causticized liquor conductivity–concentration relationship, can be used for control purposes. ■

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