CAUSTICIZING REACTION KINETICS

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ABSTRACT

Variation in the conversion efficiency of sodium carbonate to sodium hydroxide during cauticizing of green liquor can be due to insufficient supply of lime or change in green liquor composition and overall concentration. Reduction in the causticizing efficiency due to shortage of lime can be corrected by adjusting lime addition to the slaker. However, if the drop in efficiency is due to increased green liquor concentration, excess lime addition would serve no purpose. A laboratory study was carried out and a model has been developed to predict the causticizing efficiency as a function of initial green liquor composition. Control application based on the model will prevent overliming or underliming and result in uniform quality white liquor.

KEYWORDS

Causticizing Efficiency, Kinetic Model, Green Liquor, Lime Charge

INTRODUCTION

In the causticizing process, inorganic chemicals are recovered from the spent cooking liquor (black liquor) and fresh white liquor is produced. Concentrated black liquor is burned in the recovery furnace and molten smelt containing mostly sodium carbonate and sodium sulfide flows from the furnace bottom. In the dissolving tank, the molten smelt is dissolved in weak liquor to produce green liquor. Lime is added to the green liquor in the slaker and slaking begins along with some causticizing. In the causticizers, slurry overflowing from the slaker continues to react for about 90 minutes. In the white liquor clarifier, solids are removed from the causticized slurry and the resulting clear white liquor is used as needed for cooking liquor in the digesters. Underflow from the white liquor clarifier is washed to recover chemicals and the resulting lime mud is dewatered and sent to the kiln where it is calcined to produce reburnt lime.

The goal of causticizing is to produce a uniform quality white liquor with a minimum of suspended solids. This aim is to be achieved while maintaining a high causticizing efficiency. The causticizing efficiency (ξ) is an expression for actual conversion of sodium carbonate to sodium hydroxide and it is defined as follows (1).

$$\xi = \frac{[NaOH]_{WL} - [NaOH]_{GL}}{[NaOH]_{WL} + [Na_2CO_3]_{WL} - [NaOH]_{GL}} \quad [1]$$

A low causticizing efficiency implies that the causticizing operation is not performing adequately and there is unconverted sodium carbonate circulating in the pulping and recovery systems.

The green liquor concentration greatly affects the equilibrium carbonate conversion and also determines the amount of lime which is added in the slaker. The equilibrium causticizing efficiency decreases as the concentration of green liquor increases (2,3). However, if the concentration of the green liquor is too low, more water must be removed in the black liquor evaporators which results in higher energy requirements. The lime charge must be sufficient to allow for maximum conversion of the carbonate present in the green liquor. Economic evaluations have shown that the green liquor should be as concentrated as possible and the causticizing efficiency should be at the lowest limit with respect to the carbonate dead load which can be tolerated in terms of scaling problems (4).

The causticizing reaction is reversible, thus the causticizing efficiency is generally in the range of 80 to 90% (5). The composition of the green liquor which enters the slaker varies with time, and as a result the causticizing efficiency also fluctuates. The lime requirement for the reaction is a function of the carbonate conversion. Hence, the lime dosage is indirectly related to the green liquor composition. A deviation in causticizing efficiency can result from underliming or variable composition and overall concentration of green liquor. If a decline in causticizing efficiency is due to insufficient lime dosage, then more lime can be added in the slaker. However, if the green liquor concentration increases, the carbonate conversion will not be affected by increasing the lime feed rate. Inefficient control of the causticizing process leads to low causticizing efficiency and improper lime feed rate to the slaker.
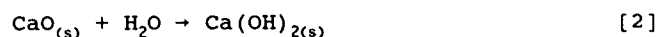
A few kinetic models have been developed that predict conversion with time (6,7). Rydin (6) developed a five parameter kinetic model as well as a three parameter model. Another kinetic model was later developed by Turc et al. (7). Both of these models included the concentrations of lime and calcium hydroxide in the rate expressions and therefore, the percent conversion depends on the initial concentrations of lime. Other studies (3,4) have shown that excess lime does not affect equilibrium causticizing efficiency. Therefore, these models may not accurately predict equilibrium causticizing conversion for a known composition of green liquor. Furthermore, these kinetic models were based on the assumption that the order of the reaction was the same as the reaction's molecularity, but this assumption was not validated.

The present work was aimed at developing a kinetic model from which causticizing efficiency could be predicted as a function of green liquor composition and time. This model, used in conjuction with on-line measuring techniques for causticized liquor, can be utilized to develop a feedforward and feedback control scheme for the causticizing process. Such a control strategy can be used to regulate the lime feed to the slaker.
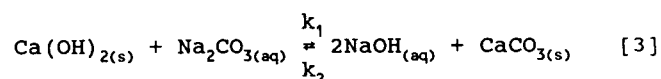
CHEMISTRY OF CAUSTICIZING

Causticizing proceeds via the following two reactions:

Slaking:

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

Causticizing:

$$Ca(OH)_{2(s)} + Na_2CO_{3(aq)} \overset{k_1}{\underset{k_2}{\rightleftharpoons}} 2NaOH_{(aq)} + CaCO_{3(s)} \qquad [3]$$

where k_1 and k_2 are the forward and reverse rate constants of the causticizing reaction. The slaking reaction, which takes place first, involves the hydrolysis of lime to form calcium hydroxide. This reaction is exothermic with a heat of reaction equal to -65 kJ/mol (8). The causticizing reaction begins as soon as some calcium hydroxide is produced from slaking. Sodium carbonate reacts with the calcium hydroxide to produce sodium hydroxide and calcium carbonate. At high concentrations of green liquor the causticizing reaction is slightly endothermic (ΔH=6-9 kJ/mol) (8). The slaking reaction is faster than the causticizing reaction; thus, the overall rate of the reaction is controlled by the causticizing reaction.

MODEL DEVELOPMENT

To develop a kinetic model, the following simplifying assumptions are made.

1. The overall reaction is considered to be zero order with respect to calcium oxide, calcium hydroxide, and calcium carbonate.
2. The reacting system is considered pseudo homogeneous and mass transfer effects are negligible.

Previous kinetic models (6,7) assumed the slaking reaction to be first order and these models also included calcium hydroxide in the rate equations. Thus, the causticizing efficiency would be a function of calcium oxide concentration. Calcium oxide, calcium hydroxide, and calcium carbonate have low solubilities and their concentrations can be expected to remain constant in the reaction mixture. The reaction rate constants, k_1 and k_2, can account for these terms, and the overall reaction can be considered zero order with

respect to calcium oxide, calcium hydroxide, and calcium carbonate.

Research done by Rydin et al. (6,9) to study the effect of lime quality on the rate of the causticizing reaction has shown that the characteristics of the lime used, i.e. the porosity and the available surface area, had little effect on the equilibrium causticizing efficiency (9). From the results of their studies, they concluded that the causticizing reaction is a heterogeneous reaction which occurs at the interface of the slaked lime and the bulk liquid. Therefore, Rydin concluded that the reacting system is pseudo homogeneous and the kinetics of the causticizing reaction are not affected by the type of lime used.

Thus, a simplified rate expression for the disappearance of sodium carbonate can be written as follows:

$$r_{Na2CO3} = -\frac{d[Na_2CO_3]}{dt} = k_1[Na_2CO_3]^a - k_2[NaOH]^b \qquad [4]$$

where the reaction is assumed to be of order $\underline{a}$ with respect to sodium carbonate and of order $\underline{b}$ with respect to sodium hydroxide. This rate expression is simplified because the reaction is considered to be zero order with respect to calcium oxide and calcium hydroxide.

The amount of sodium sulfide present in the liquor remains unchanged throughout the causticizing process. Hence, an overall sodium oxide balance on the system can be represented as follows:

$$[NaOH]_{GL}+[Na_2CO_3]_{GL} = [NaOH]_{WL}+[Na_2CO_3]_{WL} \qquad [5]$$

$[i]_{GL}$ = concentration of species i in green liquor
$[i]_{WL}$ = concentration of species i in white liquor

All concentrations are expressed as g/l Na_2O equivalents. The water consumed during the slaking reaction and the water lost due to evaporation is neglected in Equation [5].

Equation [5] can be substituted in Equation [1] and the causticizing efficiency may now be expressed in terms of carbonate conversion by the following equation:

$$\xi = \frac{[Na_2CO_3]_{GL} - [Na_2CO_3]_{WL}}{[Na_2CO_3]_{GL}} \qquad [6]$$

At any given time during the reaction, the causticizing efficiency may be represented as follows:

$$\xi = \frac{([Na_2CO_3]_0 - [Na_2CO_3])}{[Na_2CO_3]_0} \qquad [7]$$

$[i]_0$ = initial concentration of species i
$[i]$ = concentration of species i at any given time

For concentration ranges where commercial causticizing takes place, the hydrolysis of sodium sulfide is assumed to proceed completely to the right as follows:

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH \qquad [8]$$
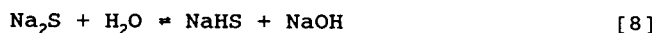
Thus, the initial hydroxide ion concentration of the green liquor is equal to the initial effective alkali concentration, $[EA]_0$, of the liquor and is defined as follows:

$$[EA]_0 = [NaOH]_0 + 1/2[Na_2S]_0 \qquad [9]$$

At any given time, the concentrations of sodium hydroxide and sodium carbonate can be expressed in terms of causticizing efficiency and green liquor concentration in the following manner:

$$[NaOH] = [Na_2CO_3] \cdot \xi + [EA]_0 \qquad [10]$$

$$[Na_2CO_3] = [Na_2CO_3] \cdot (1-\xi) \qquad [11]$$

By substituting Equations [10] and [11] into Equation [4] the following rate expression in terms of causticizing efficiency, initial sodium carbonate concentration, and initial effective alkali concentration can be derived.

$$\frac{d\xi}{dt} = k_1 \cdot \{[Na_2CO_3]_0 \cdot (1-\xi)\}^a -$$
$$k_2 \cdot \{[Na_2CO_3]_0 \cdot (\xi) + [EA]_0\}^b \qquad [12]$$

where all concentrations are expressed as g/l Na_2O. The units of k_1 are $(1/g\ Na_2O)^a/min$, and k_2 is expressed as $(1/g\ Na_2O)^b/min$.

At equilibrium the causticizing efficiency no longer changes with time, so Equation [12] can be equated to zero. Thus, the equilibrium constant (K_c) can be expressed as follows:

$$K_c = \frac{k_1}{k_2} = \frac{[NaOH]_e^b}{[Na_2CO_3]_e^a} \qquad [13]$$

The following linear equation is obtained by rearranging Equation [13]:

$$\ln[Na_2CO_3]_e = (b/a) \cdot \ln[NaOH]_e - (\ln K_c/a) \qquad [14]$$

In Equation [14] the magnitude of (b/a) can be estimated from a plot of $\ln[Na_2CO_3]_e$ versus $\ln[NaOH]_e$. For any given a, the magnitude of b is fixed and values for these constants can be estimated.

If the green liquor sodium carbonate concentration $([Na_2CO_3]_0)$, effective alkali concentration $([EA]_0)$, and values for a and b are known, then values may be obtained for k_1 and k_2 by fitting Equation [12] to the experimental data.

EXPERIMENTAL

The semi-batch experimental reactor system shown in Figure 1 was used to carry out the causticizing experiments. The system consists of two 3-liter stainless steel vessels one of which is a heating vessel, and the other being the causticizing vessel. Two 3-way valves and a pump allow the liquor to circulate in one of the vessels or to be transferred between the two vessels. The liquor was heated to the reaction temperature by an electrical heater located in the recirculation line, and the temperature of the liquor was measured by a Rosemount temperature transmitter.

Reagent grade lime was added to the wire-mesh basket attached to the agitator shaft. The lime dosage was fixed at 10% excess based on the reaction stoichiometry. After reaching the reaction temperature, a preset volume of green liquor was then transferred to the reactor vessel. When the temperature of the reactor contents began rising during slaking, cooling water was circulated through the cooling coil to remove excess heat produced by the exothermic slaking reaction. Samples of the reacting mixture were taken at preset times and immediately cooled in an ice water bath. The samples were then centrifuged, and the clear white liquor was decanted and analyzed by ABC titration (10). The reactions were allowed to continue for 3 hours so equilibrium causticizing efficiency data could be collected.

The green liquors used in these experiments were made with reagent grade chemicals. Most of the experiments were carried out with green liquors composed of sodium carbonate only. The lime dosage was based on the amount of sodium carbonate present in the greeen liquor. In the case of industrial green liquors the sodium carbonate concentration varies from about 80 g/l to 105 g/l as Na_2O. Therefore, the green liquors used for the experimental runs had sodium carbonate concentrations in this range. Few experiments were conducted with green liquors containing sodium hydroxide and sodium sulfide. For green liquors containing sodium hydroxide and sodium sulfide in

addition to sodium carbonate, the TTA did not exceed 120 g/1 as Na_2O. The experiments were carried out at temperatures of 80°C, 90°C, 100°C, 110°C, and 120°C.

RESULTS AND DISCUSSION

Batch experiments were conducted to study the order of the causticizing reaction with respect to sodium carbonate and sodium hydroxide. To determine the magnitude of (b/a), the natural logarithm of the equilibrium concentrations of sodium carbonate and sodium hydroxide were plotted. Based on the experimental equilibrium data the magnitude of (b/a) was estimated to be 3.00.

Experiments were performed to collect causticizing efficiency data for the purpose of determining the final form of the kinetic model given in Equation [12]. The causticizing efficiency data were used to determine the forward and reverse rate constants, k_1 and k_2. In order to obtain this information, Equation [12] was solved numerically with a Runga-Kutta 4-point method. Equation [12] was fitted to the data from each experimental run. For any given value of a the value of b is fixed and the best data fit was for a and b equal to 1 and 3.00, respectively. Thus, the final form of the kinetic model given in Equation [12] is represented below:

$$\frac{d\xi}{dt} = k_1 \cdot \{[Na_2CO_3]_o \cdot (1-\xi)\}^1 - k_2 \cdot \{[Na_2CO_3]_o \cdot (\xi) + [EA]_o\}^3 \qquad [15]$$

To determine the rate constants for each experimental run, different values for k_1 and k_2 were substituted in Equation [15] until an optimum error difference was found between experimental data points and the corresponding points predicted by Equation [15]. For a typical experimental run, Figure 2 shows the best fit of Equation [15] with the data.

The rate expression given in Equation [15] is a function of composition and temperature; the rate constants, k_1 and k_2, account for the temperature dependence. The temperature dependence of the rate constants is well represented by Arrhenius' law. Figures 3 and 4 show the Arrhenius plots for experimental runs containing sodium carbonate solution initially. The rate constants are also shown

in Table 1. From these plots, the temperature dependency of the rate constants can be represented as follows:

$$\ln k_1 = \frac{-29.0}{RT} + 4.25 \qquad [16]$$

$$\ln k_2 = \frac{-25.6}{RT} - 8.30 \qquad [17]$$

where:
    R = ideal gas law constant
    T = reaction temperature

The energies of activation in the two above equations have the units of kJ/gmol. The coefficients of variation for Equations [16] and [17] are 2.81% and 1.00%, respectively.

Experiments were also done with synthetic green liquors containing a mixture of sodium carbonate, sodium hydroxide, and sodium sulfide. The experimentally determined rate constants for these experiments are listed in Table 2. The temperature dependency for these rate constants can be expressed as follows:

$$\ln k_1 = \frac{-37.0}{RT} + 6.66 \qquad [18]$$

$$\ln k_2 = \frac{-28.0}{RT} - 7.25 \qquad [19]$$

where the energies of activation have the units kJ/gmol. The coefficients of variation for Equations [18] and [19] are 3.08% and 0.799%, respectively.

Experiments were carried out to test the prediction accuracies of the model. Experimental runs were performed with green liquor which contained only sodium carbonate and with green liquors containing sodium carbonate, sodium hydroxide, and sodium sulfide. The green liquor concentrations and the reaction temperatures were also varied in these experiments. Figures 5 and 6 show the predicted causticizing efficiency profile and the experimental values. The model closely predicts the causticizing efficiency after the initial unsteady period. The results from two of these experiments along with the causticizing efficiencies predicted by the kinetic model are given in Tables 3 and 4.

The model for green liquors containing only sodium carbonate has better prediction capabilities than the model for green liquors containing sodium carbonate, sodium hydroxide, and sodium sulfide, and this is primarily due to the fact that this correlation is based on several experiments. Only a few experiments were performed for green liquors containing sodium carbonate, sodium hydroxide, and sodium

sulfide.

It is observed during the first 15 to 20 minutes of the reaction, that the predicted efficiencies are slightly greater than the experimental causticizing efficiencies. This is a result of poor estimations for the forward rate constant, k_1. Evidently, the values of the forward rate constants predicted by Equations [16] and [18] are slightly greater than the actual rate constants. This was expected for Equation [18], since the energy of activation was less than the value reported in the literature. After the initial unsteady period, the model predicts the causticizing efficiency within one percent for green liquors containing only sodium carbonate. But for green liquors containing sodium carbonate, sodium hydroxide, and sodium sulfide, the kinetic model continues to predict efficiencies which are greater than experimental causticizing efficiencies. This reinforces the opinion that more data should be taken for these green liquors.

The error in the estimated values for the forward rate constants is due to the unsteady nature of the overall reaction during its initial stages. Since the slaking reaction is exothermic, heat is generated and it was difficult to maintain a constant reaction temperature in the experimental set-up. As the rate constants are strong functions of temperature, the forward rate constant, k_1, is affected by temperature fluctuations during the first few minutes of the reaction. As a result, a high value for k_1 is predicted and the predicted causticizing efficiency is greater than the actual causticizing efficiency.

CONCLUSIONS

The prediction capability of the kinetic model proved to be good for green liquors containing only sodium carbonate. During the first 15 to 20 minutes of the reaction, the predicted causticizing efficiencies were 2 to 4 percent greater than the actual efficiencies. But after the initial unstable period, the efficiencies predicted by the model were within 1 percent of the measured causticizing efficiencies. Therefore, the kinetic model could be useful in a feedforward control loop to determine lime dosage to the slaker.

For green liquors composed of sodium carbonate, sodium hydroxide, and sodium sulfide, the causticizing efficiencies predicted by the model are lower than the actual efficiencies. This implies that the experimentally determined energies of activation are low. More data are being collected for these green liquors to better determine the temperature dependency of the rate constants.

Table 1 Experimental Rate Constants for Green Liquors Containing Only Sodium Carbonate

$[Na_2CO_3]_0$ g/l as Na_2O	Temperature °C	k_1*	$k_2 \times 10^{-6}$**
80	80	0.29	3.04
90	80	0.32	4.00
100	80	0.39	4.40
80	90	0.47	5.02
90	90	0.59	6.66
100	90	0.53	6.28
80	100	0.54	6.08
90	100	0.50	5.27
100	100	0.78	7.49
80	110	0.76	8.52
90	110	0.75	7.67
100	110	0.71	6.89
90	120	0.98	8.87
100	120	0.98	11.6

* k_1 [=] 1/g $Na_2O \cdot min$
** k_2 [=] $(1/g\ Na_2O)^3/min$

Table 2 Experimental Rate Constants for Synthetic Green Liquors

Temperature °C	k_1 1/g $Na_2O \cdot min$	$k_2 \times 10^{-6}$ $(1/g\ Na_2O)^3/min$
80	0.24	5.04
90	0.38	6.37
100	0.61	9.99
110	0.61	9.91

Table 3 Comparison of Experimental Causticizing Efficiency with Kinetic Model Predictions for Green Liquors Containing Only Sodium Carbonate (Run1)

$[Na_2CO_3]_0$ = 85 g/l as Na_2O
Temperature = 95°C

Time (minutes)	Actual Causticizing Efficiency (%)	Predicted Causticizing Efficiency (%)
12	89.6	93.5
22	92.2	93.6
45	93.7	93.7
60	93.8	93.7

Table 4 Comparison of Experimental
Causticizing Efficiency with
Kinetic Model Predictions for
Synthetic Green Liquors (Run 4)

$[Na_2CO_3]_0 = 85$ g/l as Na_2O
$[EA]_0 = 30$ g/l as Na_2O
Temperature = 105°C

Time (minutes)	Actual Causticizing Efficiency (%)	Predicted Causticizing Efficiency (%)
5	79.8	82.1
18	83.4	84.8
25	83.6	84.8
60	84.6	84.8

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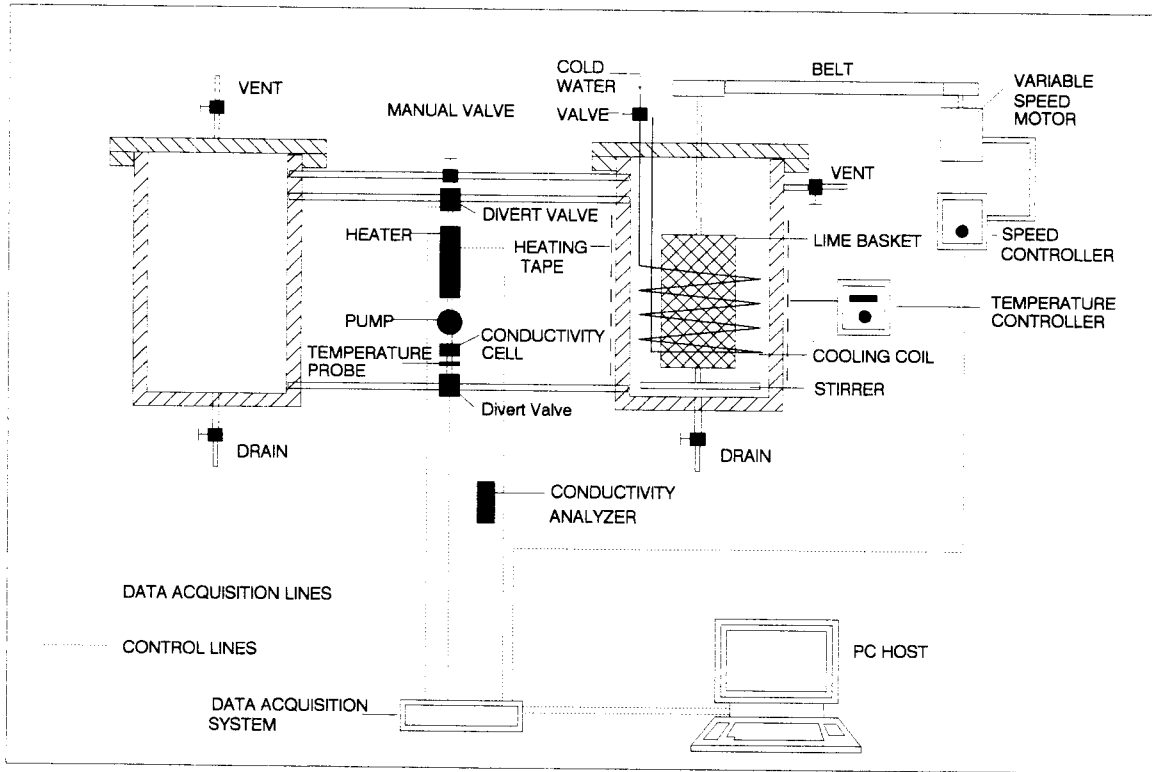
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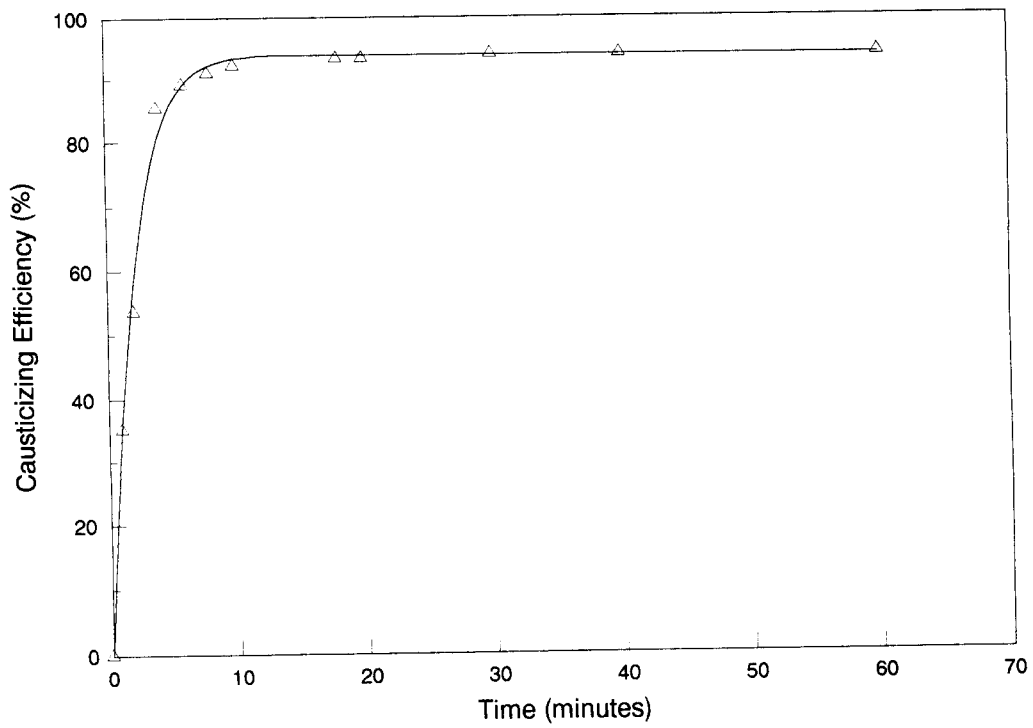
Figure 1. Experimental Set-Up and Data Acquisition System

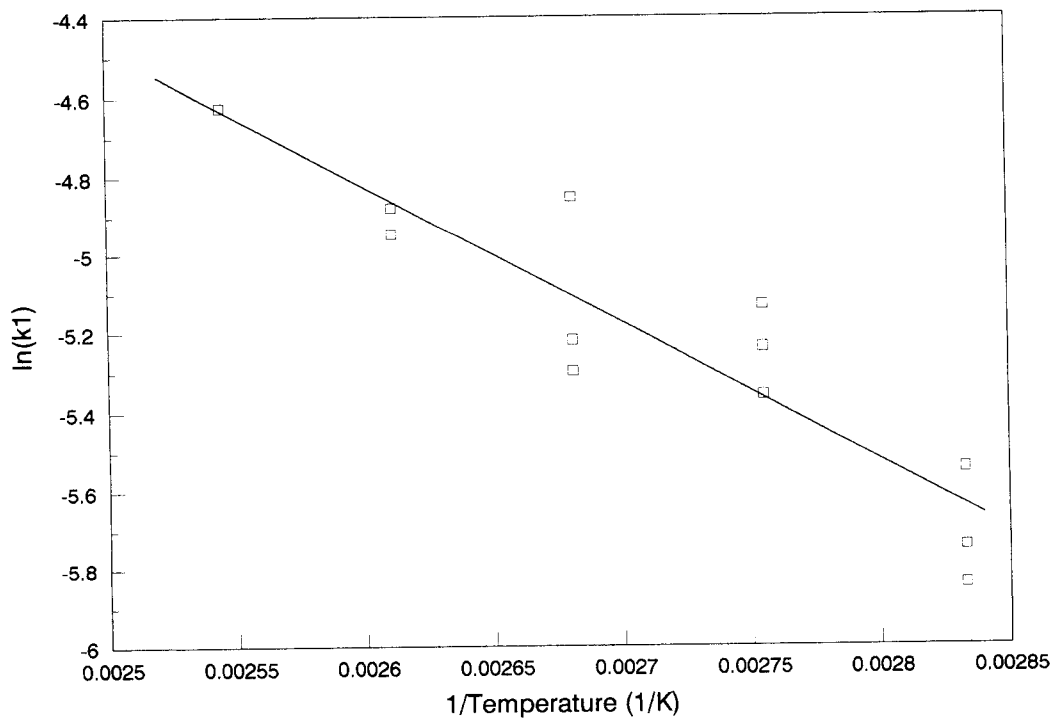Figure 2.   Best Fit of Experimental Data with
Kinetic Model Predictions

Figure 3.   In(k1) versus 1/Temperature for Green Liquors
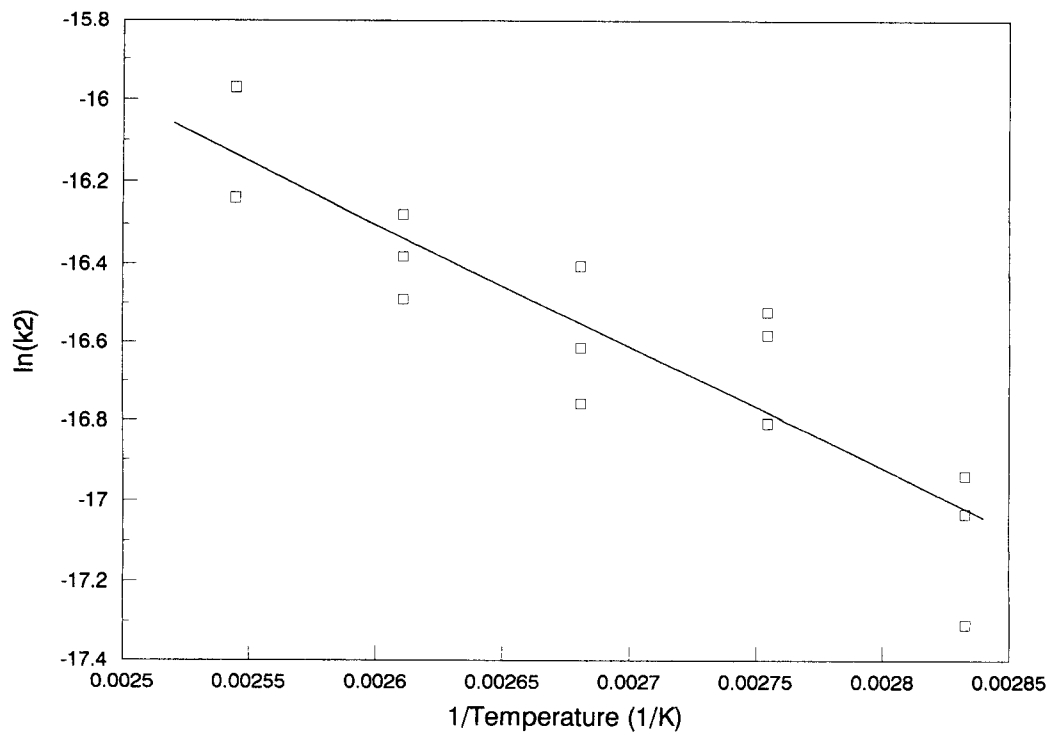Containing Only Sodium Carbonate

Figure 4.   ln(k2) versus 1/Temperature for Green Liquors
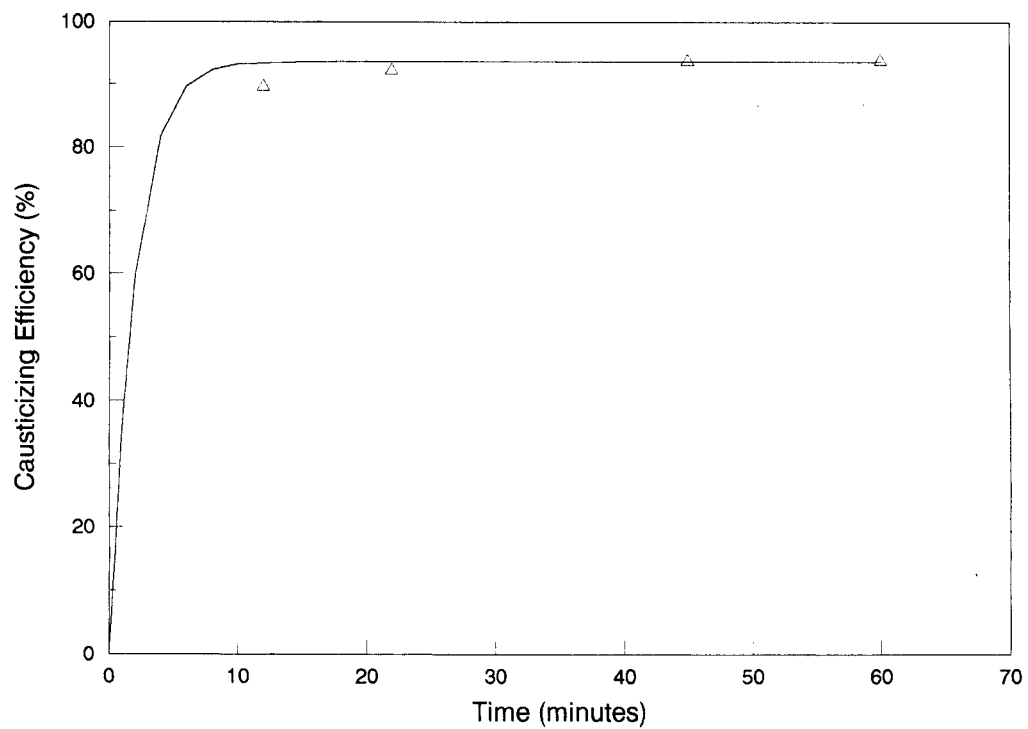Containing Only Sodium Carbonate

Figure 5.   Comparison of Actual Efficiency with
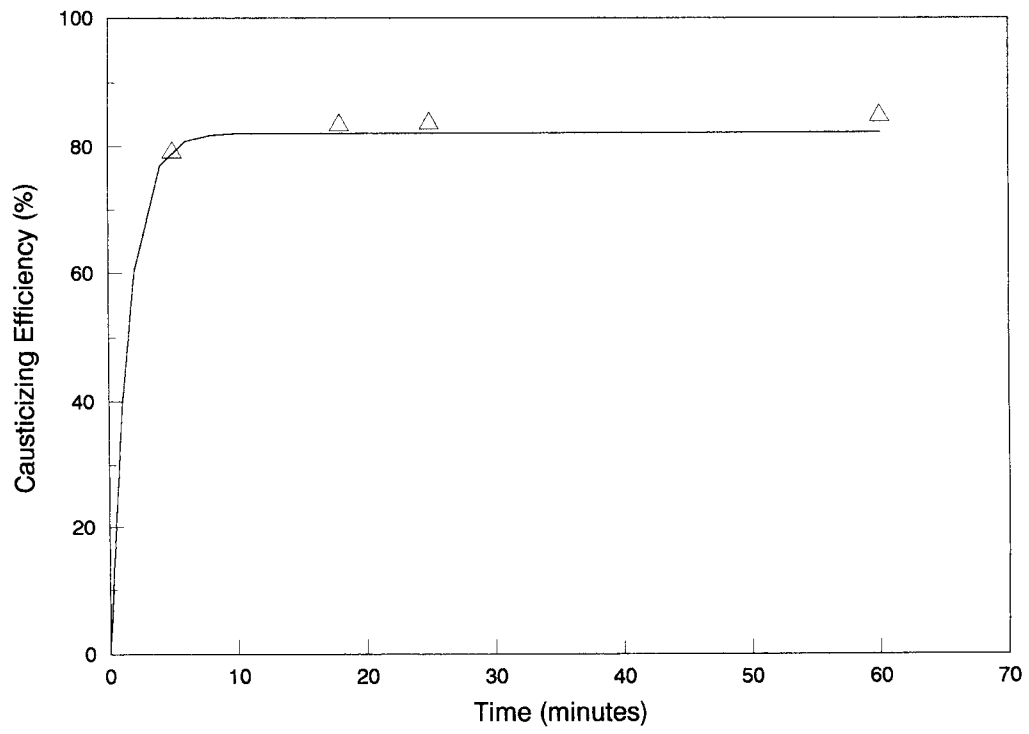Predicted Efficiency (Run 1)

Figure 6.   Comparison of Actual Efficiency with
             Predicted Efficiency (Run 4)