Experimental and Modeling of Carbonate Formation in the Effluent of Oxygen Delignification

D. C. Zhang, and J. Hsieh
The School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332

X.-S. Chai
Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta, GA 30332

A. J. Ragauskas
The School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332

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A quantitative model of carbonate formation in the effluent of one-stage oxygen delignification for a softwood kraft pulp was developed and experimentally validated. This model quantitatively described carbonate formation in the effluent of oxygen delignified SW kraft pulps and its kinetic characteristics. It could be used as an approach to predict pulp kappa numbers in the solid phase (fiber) from carbonate content in the liquid phase (filtrate). From the kinetic behavior of carbonate formation and its relationship to pulp kappa number, a control strategy was suggested. Constant kappa number curves used for parameter selection were developed to achieve target pulp kappa number while retaining pulp viscosity and total fiber charge properties. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 669–677, 2007

Keywords: carbon dioxide, carbonate, effluent, kappa number, kraft pulp, kinetics, oxygen delignification, viscosity

Introduction

The pulp and paper industry is a global industry that converts low-cost wood lignocelluloses into high-value fiber-based products in a sustainable manner. Energy efficiency, environment compatibility, and enhanced process efficiency have been the main research drives for the pulp and paper industry over the past three decades. Molecular oxygen—as the most abundant, inexpensive, energy-efficient, and environment-friendly oxidant—is a particularly attractive choice for many large-scale oxidative processes.[1] The industrial application of oxygen delignification (O) for pulp bleaching has expanded very rapidly since the first commercial system started in the 1970s. It has become the dominant operational technology to produce elemental chlorine free (ECF) and totally chlorine free (TCF) bleached pulps.[2–6] The main benefits for an oxygen delignification stage are its low process costs and environmental compatibility. The latter benefits are derived from the fact that both the chemicals applied in an O-stage and the materials removed from the pulp can be incinerated in the kraft chemical recovery system. Furthermore, the lignin removed in the O-stage reduces the levels of chlorinated organic by-products formed in subsequent chlorine dioxide bleaching operations.[2] In light of these benefits, extensive research efforts have been conducted to enhance the efficiency and selectivity of oxygen delignification.

Correspondence concerning this article should be addressed to A. J. Ragauskas at arthur.ragauskas@chemistry.gatech.edu.

Several aspects of this process have been examined including lignin/carbohydrate chemistry, process selectivity improvements, pulp yield retention, extended delignification, the efficiency of oxygen mass transfer, and pulp fiber modification.[7–15] Additionally, the large amount of dissolved lignin fragments and carbohydrate degradation products formed during oxygen bleaching has directed attention to their contribution to recovery boiler loads.[16–18] To date, however, the carbonate formed in the effluent during oxygen delignification has received little attention.

It is known that acidic groups and other oxidative structures are formed in residual lignin and pulp carbohydrates during oxygen delignification.[2,19] The fragmentation of these acidic groups and the decarboxylation of some of these carboxylic acids when exposed to heat and alkaline environments inevitably lead to the formation of carbonate in aqueous alkali solutions. This filtrate is used for brown stock washing and then mixed with black liquor. Thus, the carbonate formed during oxygen delignification will contribute to the carbonate content in black liquor.

It is well understood that carbonate in black liquor is one of the major species responsible for fouling and scaling in kraft mill evaporators during chemical recovery.[20] The solubility of sodium carbonate is strongly dependent on the total solid content in the black liquor. It has been acknowledged that two types of carbonate salt precipitates are formed during black liquor evaporation. Burkeite, a double salt ($2Na_2SO_4 \cdot Na_2CO_3$), is precipitated first, and then burkeite plus sodium carbonate is precipitated.[20] Therefore, the quantification of carbonate, its sources, and its solubility in black liquor is very important in controlling evaporator fouling and, thus, reducing mill downtime.

Chai et al.[21] reported that the concentration of carbonate in the spent liquor of kraft pulping softwood (SW) was in a range of 1.6–1.8 g/L for production of a bleachable-grade kraft pulp, corresponding to roughly 18% of the total carbonate in black liquor. Murphy et al.[22] studied the CO_2 evolution during H_2O_2 bleaching of lignin-containing pulps using dissolved pulps and milled wood lignin as models. The results indicated that the amount of carbon dioxide evolved was proportional to the lignin content of the pulp. The source of carbon dioxide was attributed to the decarboxylation of carboxylic groups formed in lignin fragments during alkaline hydrogen peroxide bleaching. Yuan et al.[23] studied the formation of gaseous products and its relation to pulp bleaching during the peracetic acid treatment of kraft pulp. Their results demonstrated that, although oxygen was the dominant product of the wasteful reactions, carbon dioxide was also formed under these conditions. Studies by Chai et al.[21] indicated that carbonate formation increased from 0.0 to 1.0 g/L during oxygen delignification of a loblolly pine kraft pulp with initial kappa number (K) of 20.9 for 0–120 min at 90°C with 2.5% NaOH and 0.689 MPa of molecular oxygen. To date, no detailed work has been reported to quantify carbonate formation and its kinetic behavior during oxygen delignification.

This article examines the dynamic change of carbonate formation in the effluent of a series of laboratory one-stage oxygen delignification treatments of a SW kraft pulp and its dependency on process conditions. An empirical dynamic model was developed to predict the amount of carbonate in the effluent and its application for pulp kappa number prediction. Based on the carbonate formation characteristics, a control strategy was suggested to achieve a pulp kappa number with desirable pulp viscosity and total fiber charge.

Table 1. One-Stage Oxygen Delignification Conditions

Parameter	Unit	Symbol	Conditions
NaOH	wt % on pulp	*N*	1.5, 2.5, 3.5
Temperature	°C	*T*	85, 100, 115
Oxygen	MPa	*P*	0.64, 0.80, 0.96
Time	min	*t*	0, 10, 20, 30, 45, 60

Note: 10% pulp consistency and the molar ratio of Mg:Mn = (31–33): 1.[25]

Experimental

Materials

A thoroughly washed commercial southern U.S. pine kraft pulp with a kappa number of 32.5 [% of mass lignin content = 0.13 × pulp kappa number (K)[24]] and a viscosity of 24.6 mPa•s was used for the oxygen delignification study. The Ca, Mn, and Mg concentrations in the pulp were 1850, 44.7, and 473.9 ppm, respectively. The deionized water had a Ca content of 4.41 ppm. All other chemicals and solvents were commercial reagent grade and used as received.

Oxygen delignification

All one-stage oxygen delignification experiments were conducted in a 2-L inclined rotary stirred Parr reactor. Experimental conditions used are summarized in Table 1.

In a typical experiment, never dried (30.00 g o.d.) unbleached SW kraft pulp was mixed with 1.00 N NaOH solution and $MgSO_4$ (see Table 1 for details), and pulp consistency was adjusted to 10% with deionized water. The reaction mixture was then added to the preheated reactor (70–90°C), sealed, pressurized to the target pressure with molecular O_2, purged three times, sealed, and then rapidly (~5 min) heated to the target temperature (see Table 1). Upon completion of the reaction, the vessel pressure was cooled, vented, and the oxidized pulp was filtered, washed with deionized water, and then stored at 2°C for further analysis. The filtrate in post-O delignified pulp was pressed, immediately collected, and charged to a vial without headspace, for further sodium carbonate determination. Control reactions without pulp were also conducted to obtain the carbonate content in the solution attributed to the absorption of CO_2 from the air.

Pulp carboxylic acid and filtrate carbonate content determination

Pulp sample preparation and procedures to determine carboxylic acid followed the method developed by Chai et al.[26] Sodium carbonate content in filtrate was measured using Headspace Gas Chromatography (HSGC).[27]

Metal ion concentration

Metal ion concentrations in pulp samples were analyzed using inductively coupled plasma emission spectroscopy following a literature method.[28]

Table 2. Pulp Properties Measured with Three Replicates at Three Different Treatments under the Same Conditions

		Pulp Kappa Number		Fiber Carboxyl Groups (μmol/g)		Carbonate in Effluent (g/L, Na_2O)	
Run	Test Replicate	Average	SD	Average	SD	Average	SD
1	3	20.8	0.03	105.6	1.35	0.62	0.02
2	3	20.9	0.02	102.2	1.08	0.61	0.03
3	3	20.4	0.05	103.8	1.40	0.64	0.03

Note: SD, standard deviation.

Pulp analysis

Data from *TAPPI Testing Methods*[29] were used to measure pulp kappa number (T-236 om-99) and pulp viscosity (T-230 om-89).

Reproducibility and replicability analysis

Each data point was a composite of three treatments under the same conditions. The samples from each treatment were analyzed with three replicates for pulp kappa number, carboxyl group content, and carbonate content in the corresponding effluent. For example, after 30 min oxygen delignification typical values for each pulp with respect to kappa number, fiber carboxyl group content, and filtrate carbonate content are shown in Table 2. Their corresponding standard deviations for these measurements of three replicates under the same conditions are <0.05, 1.40, and 0.03, respectively.

Results

Carbonate formation kinetics in the effluent of one-stage oxygen delignification

To quantify the amount of carbonate formed in the effluent of oxygen delignification and investigate carbonate formation kinetics, a series of one-stage oxygen delignification experiments were conducted under the conditions described in Table 1. The experimental parameters examined included: reaction time, oxygen pressure, caustic charge, and temperature. The typical dynamic profiles for sodium carbonate formation in the filtrate of the oxygen delignified SW kraft pulps at different caustic charge are shown in Figure 1.

The Ca, Mn, and Mg concentrations in the initial pulp were 1850, 44.7, and 473.9 ppm respectively, as determined by ICP (inductively coupled plasma) testing. The deionized water had a Ca content of 4.41 ppm. After 30 min oxygen delignification at 100°C, 800 kPa O_2, and 1.5% NaOH, the concentrations of Ca, Mn, and Mg in the oxygen delignified pulps were 1780, 41.6, and 558 ppm, respectively, and 14.1, 0.27, and 13.7 ppm, respectively, in the corresponding filtrate. Thus, deionized water at most provides only a very small amount of calcium detected in the effluent (that is, $<1.34\%$), regardless of counter anions.

The results in Figure 1 indicate that filtrate carbonate formation increases steadily as oxygen delignification proceeds under the conditions studied. When applied sodium hydroxide increases from 1.5 to 3.5%, the carbonate content in the filtrate increases $>100\%$, suggesting that the process parameters, such as caustic charge, have a profound impact on the carbonate formation. At the end of oxygen delignification reactions, the carbonate concentration typically ranged from 0.60 to 1.40 g/L in the effluent, corresponding to 16–23% of total solid in the effluent (Figure 2). As reported by Chai et al.,[21] the typical carbonate content in the black liquor of SW kraft pulping is 1.6–1.8 g/L. Therefore, the amount of carbonate in the filtrate from oxygen delignification is an important contribution to the carbonate concentration of

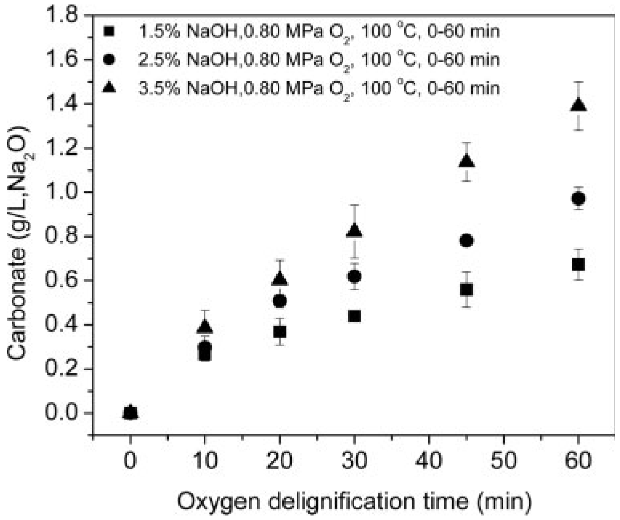

Figure 1. Dynamic change of carbonate content in the effluent of one-stage oxygen delignification of a softwood (SW) kraft pulp.

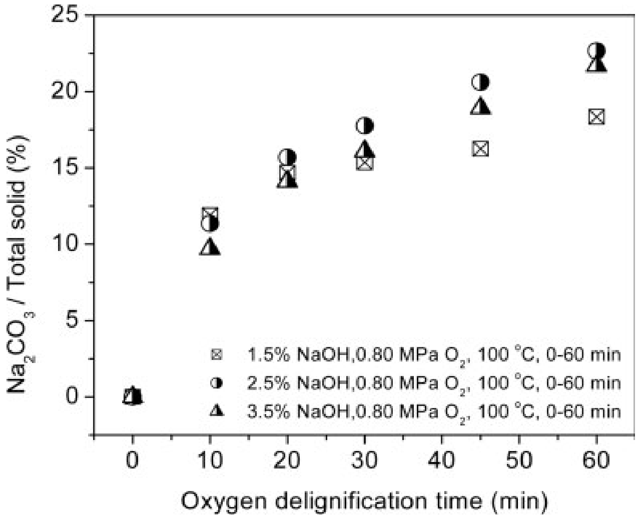

Figure 2. Percentage of carbonate on total solid basis in the effluent of oxygen delignified SW kraft pulps.

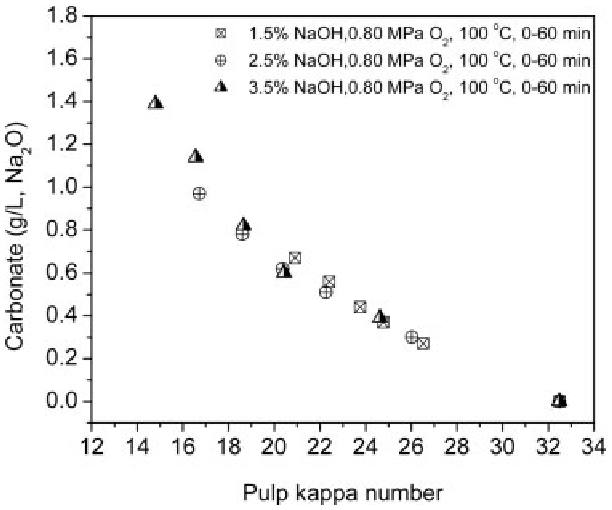

Figure 3. Carbonate formation with kappa number reduction during oxygen delignification of a SW kraft pulp.

weak black liquor and needs to be taken into account when addressing the source of carbonate in the black liquor for pulp bleaching mills with an oxygen delignification stage.

Kinetic Model Development

General analysis

As shown in Figure 3, the initial increase of carbonate content in the filtrate correlated very well with the pulp kappa number, suggesting that carbonation formation in the initial oxygen delignification phase originates primarily from lignin degradation. However, when the rate of delignification decreases in the late stage of oxygen delignification (Figure 3), the carbonate formation accelerated, especially at higher alkali charge (3.5% NaOH). These results suggest that the degradation of carbohydrate and/or further oxidation of degraded organic products lead to additional carbonate formation.

It is known that 40–50% of residual lignin in kraft pulp can be readily removed by one-stage oxygen delignification processes.[2] The typical oxygen delignification process indicated by kappa number reduction with time is characterized by an initial fast phase followed by a slow second phase of delignification.[30] Study by Genco et al.[31] on the kinetics of oxygen delignification of southern hardwoods demonstrated an apparent high rate order with respect to the kappa number was obtained in medium-consistency oxygen delignification experiments. The observed high rate order is actually a mathematical representation of the slow second phase of the delignification reaction, which is not the result of lignin recondensation reactions or mass-transfer limitations in the system studied but of a large number of parallel first-order reactions taking place simultaneously during the delignification process arising from the presence of different lignin moieties. In addition, some carbohydrates are attacked by active oxygen species, under alkaline conditions ($pH > 13.0$) at elevated temperature (75–115°C), leading to degraded water-soluble products. The oxidative components include: aliphatic acids (mono- and dicarboxylic acids, formic acid, acetic acid, etc.), carbohydrate, methanol, and carbon dioxide.[32,33] However, the mechanism for carbon dioxide formation as a product from an O-stage have not been studied in detail during oxygen delignification. Possibly sources of CO_2 generation during oxygen delignification include oxidative degradation or decarboxylation of residual lignin and carbohydrate, or their oxidative products. The conditions affecting the rate of lignin removal during oxygen delignification are primarily caustic charge, temperature, oxygen pressure, and reaction time. The effect of caustic charge on carbonate formation in the oxygen delignification effluent is shown in Figure 1. Subsequently, it is reasonable to assume that carbonate formation should depend on the total carbon (lignin and carbohydrate fraction), oxygen pressure, hydroxide charge, reaction temperature, and reaction time.

Although carbon dioxide can be produced from pulp chemical components, mainly lignin and carbohydrate in the unbleached kraft pulps, considering the complexity and these reaction conditions, the following apparent kinetic mechanism for CO_2 and carbonate formations was proposed.

Carbon dioxide formation from alkaline oxidation of macromolecules of residual lignin and carbohydrate (designated "C")

$$a\mathrm{C} + b\mathrm{O}_2 + c\mathrm{NaOH} \xrightarrow{k_1} \mathrm{C}^* + \mathrm{CO}_2 \tag{1}$$

where C represents total carbon from residual lignin and carbohydrate, C* represents oxidatively degraded products, and k_1 is the rate constant.

During alkaline oxygen delignification, the final pH of the effluent is typically >11. Therefore, any carbon dioxide produced from the oxidative reactions will instantly react with alkali in the liquid phase to form sodium carbonate as shown in Eq. 2, that is, the rate of CO_2 consumption = the rate of CO_3^{2-} formation, $k_2 > k_1$:

$$\mathrm{CO}_2 + \mathrm{NaOH} \xrightarrow{k_2} \mathrm{Na}_2\mathrm{CO}_3 + \mathrm{H}_2\mathrm{O} \tag{2}$$

Chemical kinetics

From Eqs. 1 and 2, the kinetic equation of carbonate formation can be derived as follows:

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = k_1[\mathrm{C}]^a P^b N^c \tag{3}$$

where k_1 is rate constant [$k_1 = f(1/T)$, g L^{-1} min^{-1} MPa^{-b}]; P is oxygen pressure (MPa); N is caustic charge (% on pulp); and a, b, and c are the powers of each parameter.

During typical oxygen delignification, oxygen pressure and reaction temperature are kept constant. Therefore, Eq. 3 can be simplified as Eq. 3a with Eq. 4:

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = k_2'[\mathrm{C}]^a \tag{3a}$$

$$k_2' = k^0 \cdot P^b \cdot N^c \exp\left(-\frac{E}{RT}\right) \tag{4}$$

where k^0 is constant and E is the activation energy (J/mol).

To integrate Eq. 3a, one must define a relationship between carbonate concentration and initial total carbon concentration,

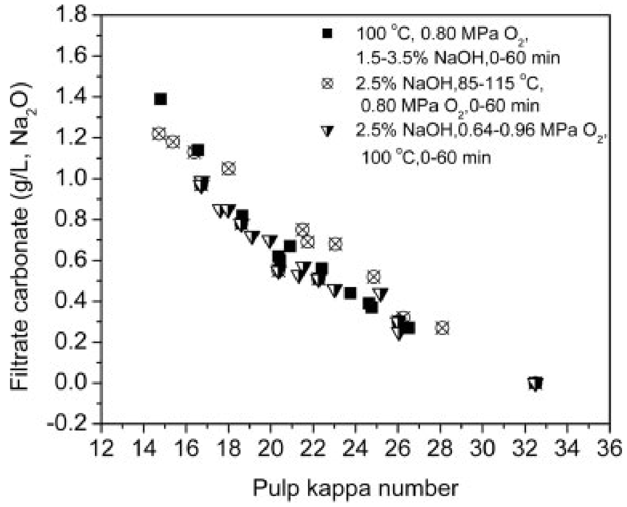

Figure 4. Relationship between filtrate carbonate content and pulp kappa number during oxygen delignification of a SW kraft pulp.

which is not available. However, the experimental data in Figure 4 demonstrate that there is a relationship between filtrate carbonate concentration and pulp kappa number (K) in the form

$$[\mathrm{CO}_3^{2-}] = -\mathrm{A}\ \ln(K) + \mathrm{B} \tag{5}$$

where A and B are constants.

The estimates for A and B in Eq. 5 were estimated using a SAS linearized (LIN) procedure (SAS Institute, Cary, NC) as shown in Table 3.

Because both carbonate formation and pulp kappa number reduction are the function of delignification time, for derivatives of both sides of Eq. 5 over time t, we obtained the following expression:

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = -\frac{\mathrm{A}}{K}\frac{dK}{dt} \tag{6}$$

Using the relationship of lignin content (L) and pulp kappa number, that is, [L] = 0.13K,[24] a derivative equation was obtained:

$$\frac{dK}{dt} = \frac{1}{0.13}\frac{d[\mathrm{L}]}{dt} \tag{7}$$

Therefore

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = -\frac{\mathrm{A}}{\kappa}\frac{dK}{dt} = -\frac{\mathrm{A}}{0.13K}\frac{d[\mathrm{L}]}{dt} = -\frac{\mathrm{A}}{[\mathrm{L}]}\frac{d[\mathrm{L}]}{dt} \tag{8}$$

Typically, the rate of oxygen delignification can be expressed as follows with $k_\mathrm{L} = k_0\exp[-(E_\mathrm{L}/RT)]$[34]:

$$\frac{d[\mathrm{L}]}{dt} = -k_\mathrm{L}\cdot P^m \cdot N^n \cdot [\mathrm{L}]^q \tag{9}$$

Simplify Eq. 9 to obtain Eq. 10 with $k'_\mathrm{L} = k^0_\mathrm{L} \cdot P^m \cdot N^n \cdot \exp[-(E_\mathrm{L}/RT)]$

Table 3. Estimate, Standard Error, and *p*-Value of the Parameters in Eq. 5 (R^2 = 0.9586)

Parameter	Estimate	Standard Error	*p*-Value
A	−1.5201	0.04268	<0.0001
B	5.2890	0.1323	<0.0001

$$\frac{d[\mathrm{L}]}{dt} = -k'_\mathrm{L}[\mathrm{L}]^q \tag{10}$$

Because oxygen delignification is not a first-order reaction to lignin,[31,34] therefore $q \neq 1$ in Eq. 10. At $t = 0$ min, $[\mathrm{L}] = [\mathrm{L}]_0$, integrate Eq. 10 and apply the initial condition to arrive at the following equation:

$$[\mathrm{L}]^{q-1} = \frac{[\mathrm{L}]_0^{q-1}}{[1 + (q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}t]} \tag{11}$$

Combine Eqs. 8 and 10 to obtain

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = \frac{Ak'_\mathrm{L}}{[\mathrm{L}]}[\mathrm{L}]^q = Ak'_\mathrm{L}[\mathrm{L}]^{q-1} \tag{12}$$

A comparison of Eq. 12 with Eq. 3a shows that both equations have the same format. Therefore, it is safe to define $[\mathrm{C}]^a = f([\mathrm{L}]^{q-1})$. Moreover, we can use Eq. 12 to develop the kinetic model for filtrate carbonate formation.

Substitute Eq. 11 into Eq. 12 to obtain the following expression:

$$\frac{d[\mathrm{CO}_3^{2-}]}{dt} = \frac{Ak'_\mathrm{L}[\mathrm{L}]_0^{q-1}}{1 + (q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}t} \tag{13}$$

Integrate Eq. 13 as

$$[\mathrm{CO}_3^{2-}] = \frac{Ak'_\mathrm{L}[\mathrm{L}]_0^{q-1}}{(q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}}\ln[1 + (q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}t] + c1$$

and simplify

$$[\mathrm{CO}_3^{2-}] = \frac{A}{(q-1)}\ln[1 + (q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}t] + c1 \tag{14}$$

Apply the initial condition ($t = 0$ min, $[\mathrm{CO_3}^{2-}] = 0$) to Eq. 14, $c1 = 0$. Therefore, Eq. 14 is now expressed as Eq. 15 with Eq. 16:

$$[\mathrm{CO}_3^{2-}] = \frac{\mathrm{A}}{(q-1)}\ln[1 + (q-1)[\mathrm{L}]_0^{q-1}k'_\mathrm{L}t] \tag{15}$$

Table 4. Estimate, Standard Error, and *p*-Value of the Parameters in Eq. 17 (R^2 = 0.9785)

Parameter	Estimate	Standard Error	*p*-Value
α	0.7977	0.0807	<0.0001
β	4411.3	5596.2	0.4341
m	0.7986	0.2216	0.0007
n	1.4259	0.1260	<0.0001
E_L/R	4736.908	443.8	<0.0001

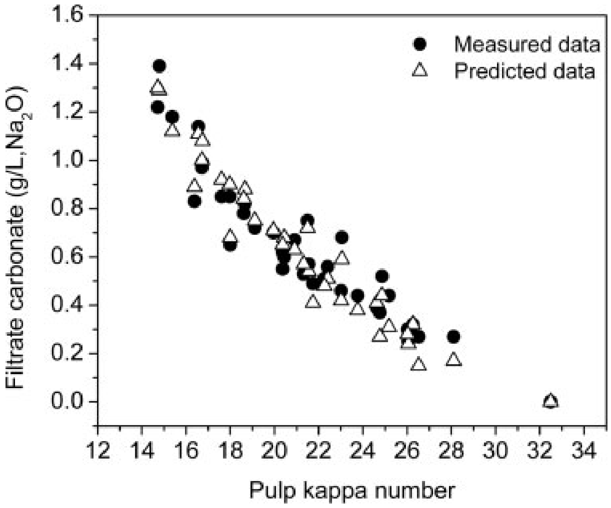

Figure 5. Measured and model predicted carbonate content in the effluent of one-stage oxygen delignified SW kraft pulps.

$$k'_{\mathrm{L}} = k^0_{\mathrm{L}} \cdot P^m \cdot N^n \exp\left(-\frac{E_{\mathrm{L}}}{RT}\right) \qquad (16)$$

Therefore, Eq. 15 with Eq. 16 constitutes a general kinetic model developed for carbonate formation in the effluent of one-stage oxygen delignification of a SW kraft pulp.

To use this model for filtrate carbonate prediction, the variables in Eqs. 15 and 16 need to be estimated. For a fixed $[\mathrm{L}]_0$, $(q - 1)[\mathrm{L}]_0^{q-1}k^0_{\mathrm{L}}$ is constant. Let us denote it as parameter β and denote $A/(q - 1)$ as α, then Eq. 15 is simplified as

$$[\mathrm{CO}_3^{2-}] = \alpha \ln\left[1 + \beta \cdot P^m \cdot N^n \cdot \exp\left(-\frac{E_{\mathrm{L}}}{RT}\right)t\right]. \qquad (17)$$

Using the experimental data and $[\mathrm{L}]_0 = 0.13 \times 32.5$,[24] the least-square estimates of the parameters in Eq. 17 were estimated using SAS nonlinearized (NLIN) procedure as shown in Table 4.

From p-values in Table 4, the estimates for α, m, n, and E_{L}/R are all significant. The estimate for constant β is not significant which may be caused by the fact that β in this equation, as an empirical constant, contains only lignin related carbon source effect. Figure 5 shows the plots of both model predicted carbonate content upon Eq. 17 and measured carbonate content in the effluent of one-stage oxygen delignified SW kraft pulps under the same reaction conditions studied. The predicted data fit the measured data very well (Figure 5).

To test whether there is systematic error between the measured carbonate (y) and predicted carbonate ($\hat{y}$) from Eq. 17, we can assume $\hat{y} = a + by$ and test the hypothesis that $a = 0$ and $b = 1$ using Statistic F. When $n = 54$, $\hat{y} = -0.0079 + 1.00219y$ with $R^2 = 0.9793$. $F = 0.3654$, its p-value $= 0.6956$, which is >0.05, implying we accept the hypothesis and the predicted carbonate agrees closely with measured carbonate. Therefore, the developed model is valid and can be used for the prediction of carbonate concentration in the effluent of one-stage oxygen delignification of a SW kraft pulp under the experimental conditions studied.

It must be pointed out that the coefficients and constants obtained in Table 4 were obtained from the experimental data for one-stage oxygen delignification of a U.S. southern pine kraft pulp (kappa number of 32.5) at 10% pulp consistency. However, the model in Eq. 17 was derived in terms of the fundamental concepts with necessary assumptions, which can be used for other SW species. When it applies to a different species or different pulp consistency, the coefficients and constants in Eq. 17 will change and need to be adjusted according to experimental data.

Model Applications

Pulp kappa number prediction

During oxygen delignification, exposure of kraft pulp to caustic and oxygen at elevated temperature results in an oxidative depolymerization of lignin and the solubilization of oxidized lignin fragments. The rate of lignin removal varies as a function of process conditions, including temperature, caustic charge, oxygen pressure, and reaction time. Meanwhile, the oxygen radical by-products, such as hydroxyl radical, cause random cleavages of the cellulose chain, resulting in the degraded carbohydrate products as side reactions, which are also affected by the process conditions. The resultant effect of these process conditions can be represented by a lignin measurement parameter: pulp kappa number (K). Because hexenuronic acid in the pulp does not change during oxygen delignification[35,36] and carbonate formation is a function of reaction parameters as shown in the developed model, a correlation between pulp kappa number and carbonate formation was anticipated. A relationship between pulp kappa number and filtrate carbonate concentration was readily developed from experimental data, as shown in Figure 4 and Eq. 5. Therefore, pulp kappa numbers, under different oxygen delignification conditions, can be predicted by the models described in Eqs. 5 and 17. Table 5 presents the predicted kappa numbers for oxygen delignified pulps at 45 and 60 min as 12.7 and 11.2, respectively, when oxygen delignifies the kraft SW pulp under the conditions of 3.5% NaOH and 115°C with 0.80 MPa oxygen applied. The predicted pulp kappa

Table 5. Pulp Kappa Number Prediction for Oxygen Delignified SW Kraft Pulps

Time (min)	NaOH (%)	Oxygen (MPa)	Temperature (°C)	Filtrate Carbonate (g/L, Na_2O)		Pulp Kappa Number	
				Measured	Predicted	Measured	Predicted
45	3.5	0.80	115	1.56	1.42	12.6	12.7
60	3.5	0.80	115	1.68	1.62	11.5	11.2

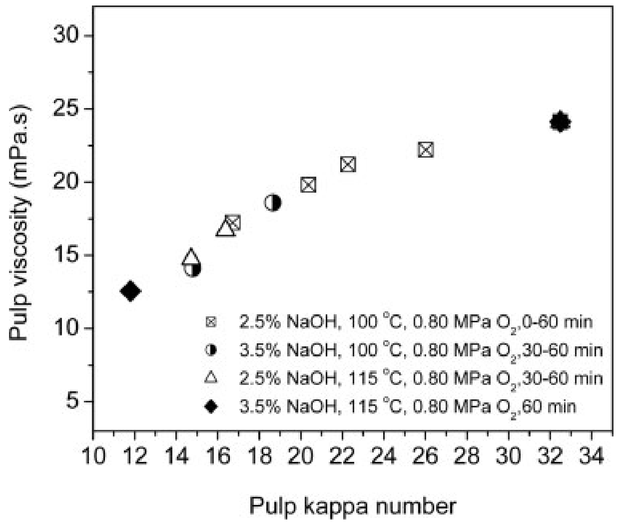

Figure 6. Relationship between pulp viscosity and pulp kappa number for one-stage oxygen delignified SW kraft pulps.

numbers are roughly equal to 12.6 and 11.5, respectively, from experimental measurement.

Process control strategy

From Figures 4 and 5, one can observe a transition region at kappa numbers ranging from 18.0 to 20.0, corresponding to a carbonate content of 0.6–0.85 g/L in the effluent of one-stage oxygen delignification. Beyond this region, lignin removal leads to enhanced carbonate formation, which significantly increases the inorganic compound load in the effluent. A similar transition region was also found for pulp viscosity and total fiber charge as a function of pulp kappa number (Figures 6 and 7). After the transition region, both pulp viscosity and fiber charge dramatically decreased.

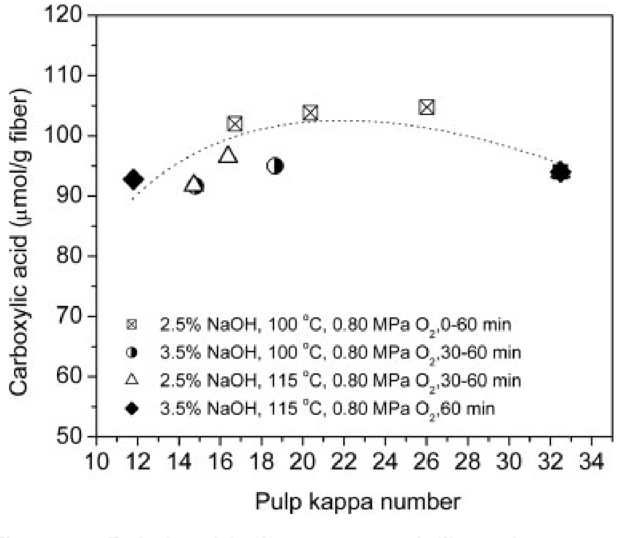

Figure 7. Relationship between total fiber charge and pulp kappa number for one-stage oxygen delignified SW kraft pulps.

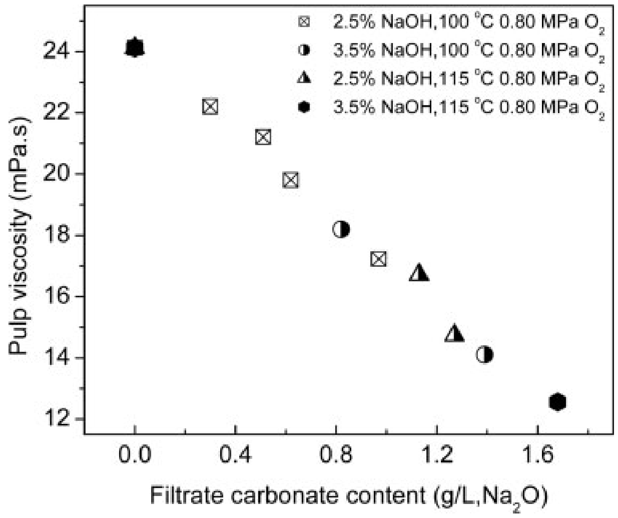

Figure 8. Relationship between pulp viscosity and carbonate content in the effluent of one-stage oxygen delignified SW kraft pulps.

10% pulp consistency.

When plotting pulp viscosity vs. filtrate carbonate content, an inversely linear relationship was obtained for these two parameters (Figure 8), suggesting that products of depolymerization likely lead to the formation of carbonate.

Based on these results, to retain better pulp viscosity and total fiber charge with less carbonate formation, one-stage oxygen deignification treatment for a SW kraft pulp should not be delignified to a point of a pulp kappa number <17.0 (48.0% delignification) for the pulp studied.

For control purposes, process parameters should be adjusted to achieve this target kappa number. Among oxygen delignification conditions, 60 min is usually chosen to allow enough time for better mixing and reaction. Medium pulp consistency (8.0–15.0%) is used for economic and operating consideration. For oxygen delignification reactions at 10% pulp consistency for 60 min, constant kappa number (18.5) at three different oxygen pressure levels (0.72, 0.80, and 0.90 MPa) were obtained from Eqs. 5 and 17 by changing reaction temperature and caustic charge. These results are presented in Figure 9. Any point on the curves represents a set of process parameter combinations to achieve the same targeting pulp kappa number (18.5) at 10% pulp consistency for a 60-min reaction.

Therefore, to select appropriate oxygen delignification conditions, the reaction temperature, oxygen pressure, and caustic charge can be adjusted to address specific operation requirements.

Conclusions and Significance

A new approach to quantitative modeling of carbonate formation in the effluent of one-stage oxygen delignification for a SW kraft pulp was developed and tested. The model was developed by assuming that the oxidation of carbon in the residual lignin and carbohydrate constituted the major pathway for carbon dioxide/carbonate formation.

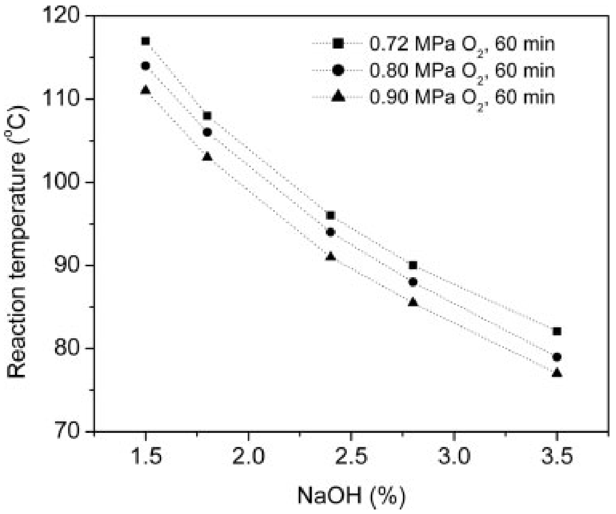

Figure 9. Constant kappa number (18.5) curves at different combinations of reaction temperature, caustic charge, and oxygen pressure.

10% pulp consistency and 60-min delignification time.

This model predicts the dynamic change of carbonate content in the effluent of one-stage oxygen delignification from a SW kraft pulp and describes the kinetic characteristics of delignification when correlating with pulp kappa number, a parameter that represents pulp lignin content. The good linear correlation between the model predictions and 54 independent experimental results from statistic testing supports the essential validity of the modeling concepts, providing strong incentives for application. With this model, pulp kappa number in the solid phase (fiber) can be predicted from the behavior of the liquid phase (carbonate formation in the effluent).

Furthermore, this model could be used to develop a process control parameter program to achieve the target delignification for a SW kraft pulp with desirable pulp viscosity and total fiber charge property.

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