Using white liquor as the alkali source in oxygen delignification

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ABSTRACT: This paper considers the potential impact on oxygen delignification stage performance when unoxidized white liquor and partially oxidized white liquor containing thiosulfate, or (OWL[T]), are used as the alkali source. A literature review was conducted to estimate the oxygen consumption of the pulp, the raw black liquor carryover, and the sulfur compounds in the charged white liquor and in the postoxygen washer filtrate recirculated to the oxygen stage. These values were used to calculate the total oxygen consumption (kg O_2/bone dry ton [BDT]) as a function of oxygen stage Δ kappa. The maximum oxygen charge was estimated using the generally accepted void volume (X_g) limit of 20%.

A delignification model was developed using an empirical equation for the rate of change of lignin in the pulp as a function of operating parameters. The initial (OH^-) concentration was adjusted to achieve 40% delignification at 0.70 MPa (100 psig) and 50% delignification at a pressure of 1.03 MPa (150 psig) for a 30 kappa pulp. The model predicted oxygen exhaustion and hence a reduction in achievable Δ kappa at operating pressures of less than 150 psig when OWL(T) was used as the alkali sources and the raw black liquor carryover was 30 kg/BDT

Application: Mills can reduce the oxygen stage demand and lower the potential for oxygen exhaustion by using white liquor that has had its sulfide oxidized to sulfate.

Oxygen delignification is a well-established technology used to lower bleaching chemical consumption and reduce a mill's impact on the aquatic environment. The process mixes oxygen, steam, and sodium hydroxide (NaOH) with washed pulp from the digester (i.e., brownstock) and sends the mixture to a pressure vessel or two pressure vessels in series.

Typical operating conditions for a medium consistency softwood pulp are:

- Consistency (10%–14%)
- Pressure (100–200 psig)
- Temperature (90°C–105°C)
- Inlet kappa no. (24–32)
- Percent delignification (30%–60%)
- Oxygen charge (1.2–1.8 kg/kappa unit drop)
- Alkali charge (1.3–2.0 kg/kappa unit drop)

The oxygen reacts with and modifies the lignin structure, making some of it alkali soluble. The solubilized lignin is washed from the pulp in a postoxygen washer system, and the pulp is sent to the bleach plant. The washer filtrate is used as the wash water for the last preoxygen washer.

Oxidized white liquor is often used as the alkali source for an oxygen delignification stage. The average amount used in the oxygen stage is dependent upon the amount and addition point of the mill's NaOH makeup requirement. Some mills use 100% white liquor in the oxygen stage and add makeup caustic elsewhere, while others vary the amount of NaOH and white liquor charged to the oxygen stage on the basis of liquor inventory.

The temperature and alkali charge are generally optimized to maximize delignification while maintaining acceptable cellulose fiber strength. Oxygen availability is not typically viewed as a constraint on the achievable delignification. Oxygen is consumed by the lignin and carbohydrates in the pulp, the raw black liquor (RBL) carryover from the digester, the sulfur compounds entering the stage with the white liquor charge, and the sulfur compounds entering the stage with the postoxygen washer filtrate recycled back to the stage.

The amount of oxygen charged to the stage is typically a ratio of the target kappa unit drop; however, there is a constraint on the total oxygen charge. In general, the volume of gas per volume of gas and liquid, X_g, should be limited to about 20% to avoid channeling in the reactor. As a result, operating conditions might exist where the availability of oxygen limits the achievable kappa reduction, particularly when white liquor is used as the alkali source.

Equations have been developed to predict the delignification rate as a function of pulp lignin content, alkali concentration, temperature, and oxygen partial pressure. An empirical equation was employed to estimate the reduction in pulp kappa and the consumption of alkali and oxygen as a function of time and pressure. Operating conditions were identified that resulted in the exhaustion of the available oxygen and consequently the achievable degree of delignification.

RECOVERY CYCLE

WHITE LIQUOR OXIDATION

White liquor used in the oxygen stage can be unoxidized, partially oxidized where the sulfide is primarily converted to thiosulfate (OWL[T]), or fully oxidized where the sulfide is oxidized to sulfate (OWL[S]).

The sodium sulfide (Na_2S) in white liquor dissociates via Eq. (1):

$$Na_2S + H_2O \rightarrow NaSH + NaOH \tag{1}$$

The basic oxidation equation is Eq. (2):

$$2NaSH + 2O_2 \rightarrow Na_2S_2O_3 + H_2O + heat \tag{2}$$

The thiosulfate ($Na_2S_2O_3$) can be further oxidized to sodium sulfate (Na_2SO_4) via Eq. (3):

$$Na_2S_2O_3 + 2O_2 + 2NaOH \rightarrow 2Na_2SO_4 + H_2O + heat \tag{3}$$

The overall reaction is Eq. (4) or Eq. (5):

$$NaSH + 2O_2 + NaOH \rightarrow Na_2SO_4 + H_2O + heat \tag{4}$$

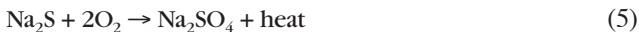$$Na_2S + 2O_2 \rightarrow Na_2SO_4 + heat \tag{5}$$

Table I documents the compositional changes when the sulfide in typical white liquor is oxidized to thiosulfate and sulfate.

Equal amounts of caustic are consumed in the conversion reactions of sulfide to sulfate and of thiosulfate to sulfate. The final NaOH (and active alkali and effective alkali) concentration of OWL(S) is equal to the NaOH concentration of the unoxidized white liquor. The sulfide and thiosulfate in the white liquor are essentially oxidized to sulfate in the oxygen reactor.

White Liquor Composition	Original	Thiosulfate	Sulfate
NaOH	85.0	107.5	85.0
Na_2S	45.0	0.0	0.0
Na_2CO_3	20.3	20.3	20.3
Na_2SO_4	2.0	2.0	47.0
AA	130.0	107.5	85.0
EA	107.5	107.5	85.0
TTA	150.3	127.8	105.3
Causticity, %	80.7		
Sulfidity, % on AA	35		
Oxygen consumption, g O_2/L		18.0	36.0

NaOH = sodium hydroxide; Na_2S = sodium sulfide; Na_2CO_3 = sodium carbonate; Na_2SO_4 = sodium sulfate; AA = active alkali; EA = effective alkali; TTA = total titratable alkali; AA = active alkali.

I. White liquor composition when the sulfide is oxidized to thiosulfate and sulfate. Values are g/L expressed as NaOH unless otherwise noted.

Therefore, the unoxidized NaOH concentration (i.e., 85 g/L in Table I) should be used when calculating the contribution of caustic in the white liquor. When unoxidized or OWL(T) is charged to the oxygen stage the initial NaOH concentration is substantially higher as compared with the concentration when caustic is the alkali source. The increase is equal to the unoxidized white liquor effective alkali/NaOH ratio. At the concentration in Table I, the initial concentration would be 26% higher. This additional alkali will be consumed in the oxygen reactor to produce sulfate.

OXYGEN STAGE OXYGEN CONSUMPTION

The oxygen charged to the oxygen stage reacts with sulfur compounds, lignin and carbohydrate in the pulp (delignification), and raw black liquor (RBL) solids carryover from the brownstock washers.

Oxidized black liquor solids

Significant amounts of oxidized organic and inorganic materials are recycled to the oxygen reactor via the postoxygen washer filtrate, often referred to as OBL. This material consumes very little oxygen. However, the filtrate does consume alkali [1,2]. Vuorenvirta et al. [1] showed that the addition of approximately 100 kg OBL/BDT to a clean pulp required an additional charge of 7.5 kg NaOH/BDT to achieve the same outlet kappa as the clean pulp. The consumption in an oxygen stage will be dependent on the filtrate residual alkali content.

Sulfur compounds

There are three oxidizable sulfur inputs to an oxygen delignification stage: (1) the sulfur in the white liquor charge, (2) the sulfur in the postoxygen stage filtrate that is recirculated to the oxygen stage with the pulp, and (3) and the sulfur in the RBL. The literature [3–5] suggests that the majority of the input sulfur is converted to sulfate in the oxygen reactor. Tigerström and Sandström [3] showed that 30% of the thiosulfate input to the reactor came from the postoxygen washer filtrate and 70% was from the white liquor charge; 60% of the total input thiosulfate was oxidized in the reactor, which is equivalent to 86% of the input from the white liquor. Tomoda and coworkers [4] also measured the thiosulfate concentration in the pulp slurry before and after a commercial oxygen delignification reactor; all input thiosulfate was oxidized. Salmela et al. [5] reported that 45% of the thiosulfate input came from the pulp and 55% came from the white liquor. The data indicated that 66% of the total input thiosulfate was oxidized, which is more than 100% of the input from the white liquor. On the basis of this literature data, the oxygen consumption by sulfur compounds is approximately equal to the amount of oxygen needed to oxidize the sulfur entering the reactor with the white liquor charge.

Lignin/carbohydrate

In early work, Thompson and Corbett [6] measured a pulp oxygen consumption of about 0.6 kg O_2/Δ kappa unit. Salmela et al. [5] conducted a mass balance across a commercial

	COD Range, kg COD/ton	O$_2$ Consumption, kg O$_2$/kg COD	RBL Range, kg RBL/ton	O$_2$ Consumption, kg O$_2$/kg DS
Parthasarathy			0–85	0.18
Magnotta and Courchene				0.11–0.18
Iijima and Taneda	104	0.10		
Sankari and Ala-Kaila	0–300	0.30	0–300*	0.30
Vuorenvirta et. al.	0–200	0.08–0.09		
* Estimated from the data. COD = chemical oxygen demand; RBL = raw black liquor; DS = dry solids.				

II. Literature estimates of raw black liquor solids oxygen consumption.

	% of RBL	O$_2$ Consumption, kg O$_2$/kg	O$_2$ Consumption, kg O$_2$/kg DS
Lignin	37.4	0.34	0.13
Formic acid	4.0	0.83	0.03
Lactic acid	4.7	0.17	0.01
Tall oil	1.2	0.37	0.0
Thiosulfate, S$_2$O$_3$$^{2-}$	4.8	0.57	0.03
Hydrogen sulfide, HS$^-$	4.3	1.94	0.08
Total	**56.4**		**0.28**
RBL = raw black liquor; DS = dry solids.			

III. Calculated RBL oxygen consumption.

oxygen delignification stage. The estimated molecular oxygen consumption (from run 2) was between 0.4 and 0.74 kg O$_2$/Δ kappa unit, excluding sulfur compounds. The range is due to the presumed source of oxygen in the reactions to carbonate.

In the low oxygen consumption estimate, the authors assumed that the source of oxygen in carbonate production was split equally between molecular oxygen, alkali, and pulp. In the higher oxygen consumption estimate, they assumed that both of the oxygen atoms in carbon dioxide (CO$_2$), and ultimately carbonate, originated from molecular oxygen.

Berry et al. [7] calculated oxygen consumption in laboratory experiments by measuring the change in reactor pressure. The consumption at an operating temperature of 75°C was 0.87 kg O$_2$/Δ kappa unit and 0.55 kg O$_2$/Δ kappa unit at a temperature of 110°C. The authors assumed there was little evolution of gas into the headspace. Miller et al. [8] measured a CO$_2$ evolution of 0.462 kg CO$_2$/L of filtrate. Therefore, the lower value at 110°C found by Berry et. al. [7] might be, in part, due to CO$_2$ evolution. In other laboratory work, the measured oxygen demand per kappa unit reduction was 1.4 kg O$_2$/Δ kappa unit for a clean hardwood pulp [9] and 1.0 kg O$_2$/Δ kappa unit for loblolly pine [10]. The length of time that the lignin/carbohydrate reaction products experience the oxygen reactor conditions should be considered when assessing oxygen consumption. In a commercial system, the initial reaction products are on average recycled through the reactor at least three times.

Therefore, it would be expected that oxygen consumption will be higher in a commercial system than that measured in a laboratory experiment. On the basis of the literature data analysis, an oxygen consumption of 0.7 kg O$_2$/Δ kappa unit is a reasonable estimate.
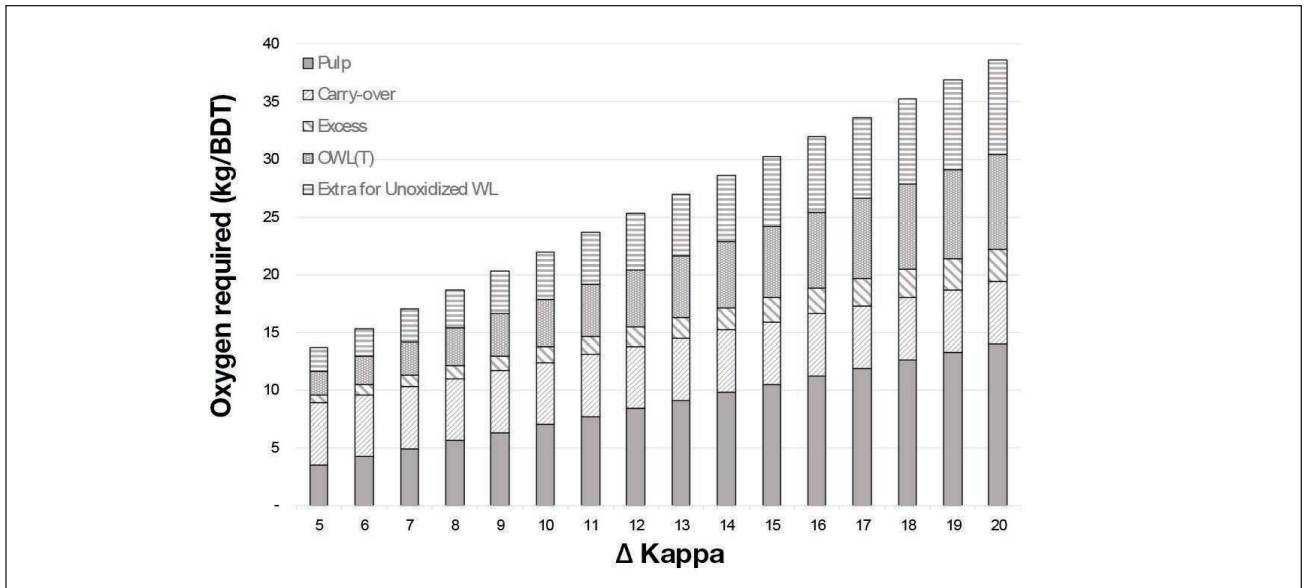
Raw black liquor
A number of authors have estimated the consumption of oxygen by RBL (**Table II**). The large range of values might be because of the composition of the RBL, handling methods, calculation method, and the evolution of carbon dioxide.

Sankari and Ala-Kaila [12] conducted the most extensive analysis. The average oxygen consumption over the 0–300 kg RBL range was 0.3 kg O$_2$/kg chemical oxygen demand (COD). The COD/dry solids (DS) ratio was approximately 1.0, which is typical. The authors also conducted factorial experiments to estimate the oxygen consumption of the primary chemical species in the raw black liquor. The lignin oxygen consumption was approximately 0.34 kg O$_2$/kg lignin, which is consistent with Ragnar and Ala-Kaila [13]. The main properties of the RBL were well documented. **Table III** calculates the oxygen consumption of the RBL according to its composition, the determined oxygen consumption of the organic compounds, and the oxygen consumption when Na$_2$S and Na$_2$S$_2$O$_3$ are oxidized to Na$_2$SO$_4$.

The calculated value is very close to the measured value of 0.34 kg O$_2$/kg RBL. The data also suggest that lower reported

1. Required oxygen charge as a function of Δ kappa.

values [1,9] in Table II literature might be because of low sulfide and thiosulfate content. Parthasarathy [10] also characterized the RBL composition. The measured consumption was 0.18 kg O_2/kg DS and the calculated consumption using the Sankari and Ala-Kaila [12] data was 0.20 kg O_2/kg DS. Parthasarathy [10] used liquor that had a much lower sulfide content, which accounts for the lower oxygen consumption. On the basis of the literature analysis, oxygen consumption of 0.18 kg O_2/kg RBL is a reasonable estimate.

The amount of RBL carried over to the oxygen stage is mill specific and depends upon the washer configuration and operating parameters (e.g., dilution factor). Miller and coworkers [14] calculated RBL carryover of 12 kg/BDT in a three-stage-O_2-two-stage washing system with a 3.0 dilution factor. Henderson and Hjört [15] calculated RBL carryover of 27 kg COD/BDT for a specified mill configuration running at its design capacity and carryover of 96 kg COD/BDT at a 50% production rate increase. A carryover of 30 kg RBL/BDT has been used in the following assessments, which reflects a mill that has a slightly overloaded brownstock washing system.

Compound	Value
Pulp (Lignin/Carbohydrate)	0.7 kg O_2/Δ kappa
Na_2S to Na_2SO_4	0.82 kg O_2/kg Na_2S
$Na_2S_2O_3$ to Na_2SO_4	0.41 kg O_2/kg
RBL	0.18 kg O_2/kg RBL
Excess	0.14 kg O_2/Δ kappa
Na_2S = sodium sulfide; $Na_2S_2O_3$ = thiosulfate; Na_2SO_4 = sodium sulfate; RBL = raw black liquor.	

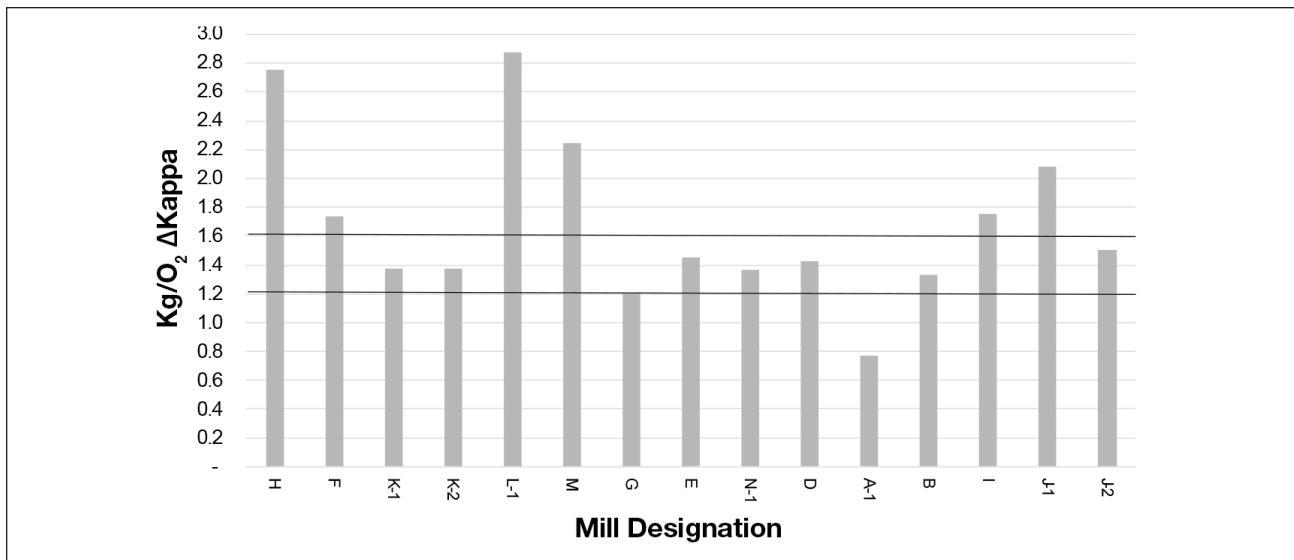*IV. Oxygen consumption rates.*

OXYGEN STAGE EXCESS OXYGEN

Salmela et. al. [5] estimated the amount of oxygen consumed with an industrial two-stage oxygen delignification system. In one of the experimental trials (run 2), the authors observed maximum oxygen consumption of 10.2 kg O_2/BDT when a total oxygen charge of 16 kg O_2/BDT was applied; this corresponded to minimum oxygen excess of 57%. Another experimental trial (run 1) was performed using a total oxygen charge of 8 kg O_2/BDT, which resulted in minimum oxygen excess of 20%. The only significant operating parameter difference between the two experimental runs was the oxygen charge applied and the resulting excess. The kappa unit reduction in run 1 was 7 and the reduction in run 2 was 10.5 for a Scandinavian softwood. This suggested that the run 1 kappa reduction was lower because of the lower oxygen excess level. From this literature analysis, oxygen excess of 20% is a reasonable estimate to calculate the oxygen need for delignification, as well as to calculate the oxygen demand.
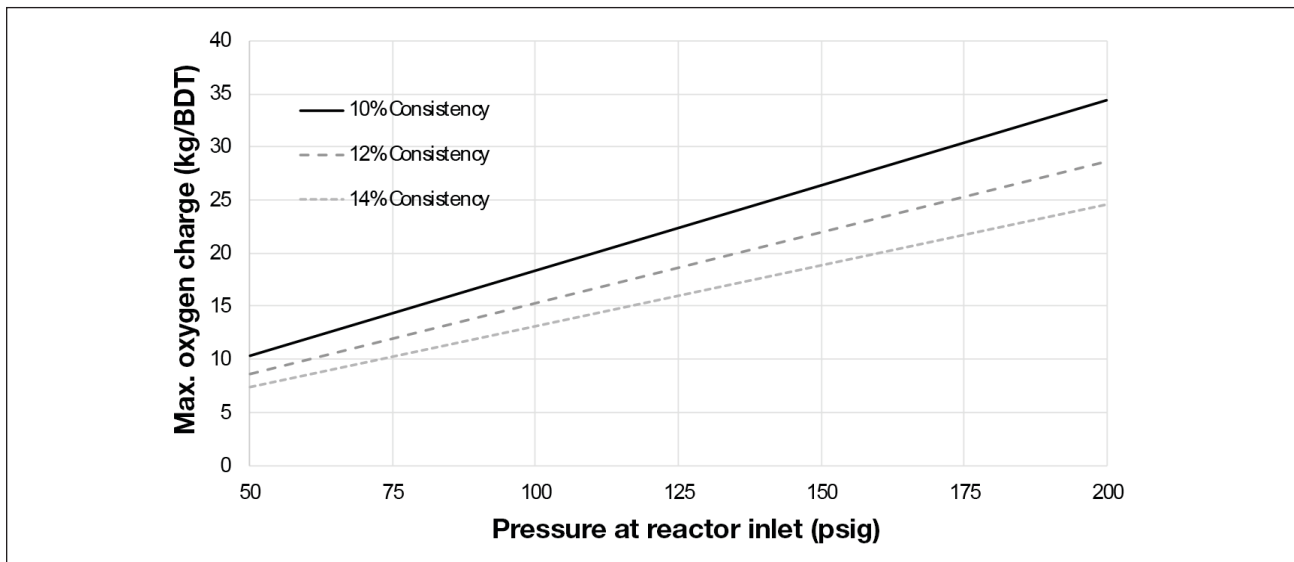
TOTAL OXYGEN DEMAND

Table IV summarizes the oxygen consumption rates and the excess oxygen used to determine the total oxygen demand of an oxygen delignification stage.

Figure 1 illustrates the required oxygen charge as a function of the kappa reduction across the oxygen delignification stage at an alkali consumption of 1.55 kg/Δ kappa unit, which includes the alkali consumption by the lignin and the OBL.

At a kappa reduction of 15, the O_2 kg/Δ kappa unit ratio is 1.6 when OWL(T) is the alkali source. This ratio is 1.2 O_2 kg/Δ kappa unit when NaOH is used as the alkali source. **Figure 2** illustrates a comparison of these values with the data from Bennington and Pineault [17].

2. Oxygen per Δ kappa unit ratios calculated from Bennington and Pineault [17] mill survey data.

3. Maximum oxygen charge versus pressure (bottom of reactor); 90% purity oxygen at 10%, 12%, and 14% consistency and 20% gas volume.

OXYGEN MIXING: THE CHARGE LIMIT

There is a limit to the amount of gas that can be effectively mixed in an oxygen stage mixer. The parameter used to define this limit is either phase ratio (volume gas/volume liquid) or volume fraction (gas volume/ (gas volume + pulp volume), X_g. The typically cited maximum acceptable volume fraction is 20% [16]. At higher fraction levels, the bubble size will increase and can result in reactor channeling. The maximum charge (kg O_2/BDT) is a function of the pressure at the bottom of the reactor and the pulp consistency. Most mills supply oxygen to the delignification stage from a vacuum swing adsorption oxygen plant, which produces 90% purity oxygen. **Figure 3** plots the maximum oxygen charge as a function of 10%, 12%, and 14% consistency; 20% gas volume fraction; and 90% oxygen purity.

Purity and consistency have a significant impact on the maximum oxygen charge. However, the propensity for channeling decreases at higher consistencies, so it can be argued that the maximum value of X_g may be higher at 14% consistency.
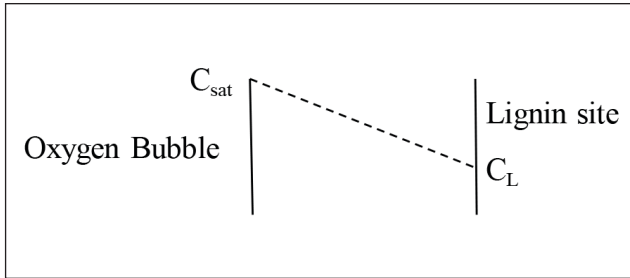
OXYGEN STAGE MODEL

To determine under what conditions the use of unoxidized or OWL(T) affects the kappa reduction of an oxygen stage, a spreadsheet was constructed to calculate the kappa reduction across an oxygen reactor using the reasonable estimates of parameter values given in the previous section.

Delignification reaction rate

The empirical delignification rate equation developed by Ji

4. Schematic of oxygen concentration gradient.

5. Oxygen concentration gradient with sulfur compounds in bulk fluid.

and coworkers [18] was used to calculate the Δ kappa across the oxygen reactor. The rate expression at 90°C is given by Eq. (6):
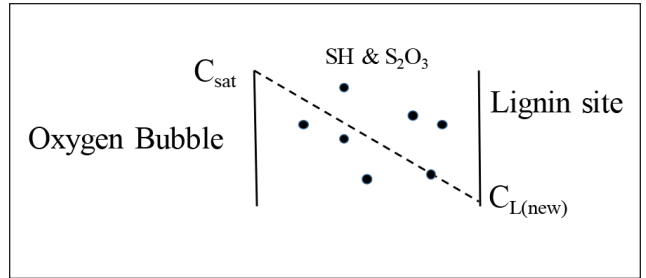
$$-\frac{dL_c}{dt} = 0.175 * \frac{[OH]}{0.111+[OH]} * \frac{P_{O2}}{1+3.39*P_{O2}} * L_c \qquad (6)$$

where L_c is mg lignin/g pulp (HexA free), [OH] is mol/L of NaOH, and PO_2 is MPa of O_2.

The changes in kappa, alkali, and oxygen consumption were determined using the same approach used by other researchers [19,20], where the pulp suspension is assumed to pass through the retention tower by plug flow. The tower is dividing into a large number of layers of height (ΔH) and volume (ΔV). Each layer is represented as a continuous stirred tank reactor (CSTR), which is connected in series to one another. The incremental change of each parameter across the ΔV is calculated and the output values become the input values to the next ΔV.

Oxygen mass transfer

Incorporating mass transfer effects into the model is quite complex. Susilo [20] and van Heiningen et. al. [19] included oxygen mass transfer effects for each ΔV and used the k_La values calculated by Rewathar and Bennington [21]. In the simplest terms, the rate of oxygen mass transfer is equal to the rate of oxygen consumed, as in Eq. (7):

$$k_La*(C_{sat}-C_L)*\Delta V = R_{O2}(C_L)*\Delta V \qquad (7)$$

where k_La is the volumetric gas-liquid mass transfer coefficient, C_{sat} is the saturated dissolved oxygen concentration at the operating pressure, C_L is the oxygen concentration at the lignin site, and $R_{O2}(C_L)$ is the reaction rate at an oxygen concentration of C_L. **Figure 4** is a simple schematic showing this relationship.

For the purposes of this paper, a simple approach to oxygen mass transfer was taken. In the work of van Heiningen [19], an 11 kappa unit reduction in the nominal 60-min no. 2 reactor was achieved at a k_La of 0.01 s^{-1}. The average total pressure was 0.655 MPa (95 psig) and per the simulation, the fractional saturation was 77%. Therefore, the average value of C_L as an equivalent pressure at saturation would be 0.503 MPa (73 psig). At an oxygen consumption of 1.40 kg O_2/kappa unit used by van Heinengen, the oxygen consumption would be
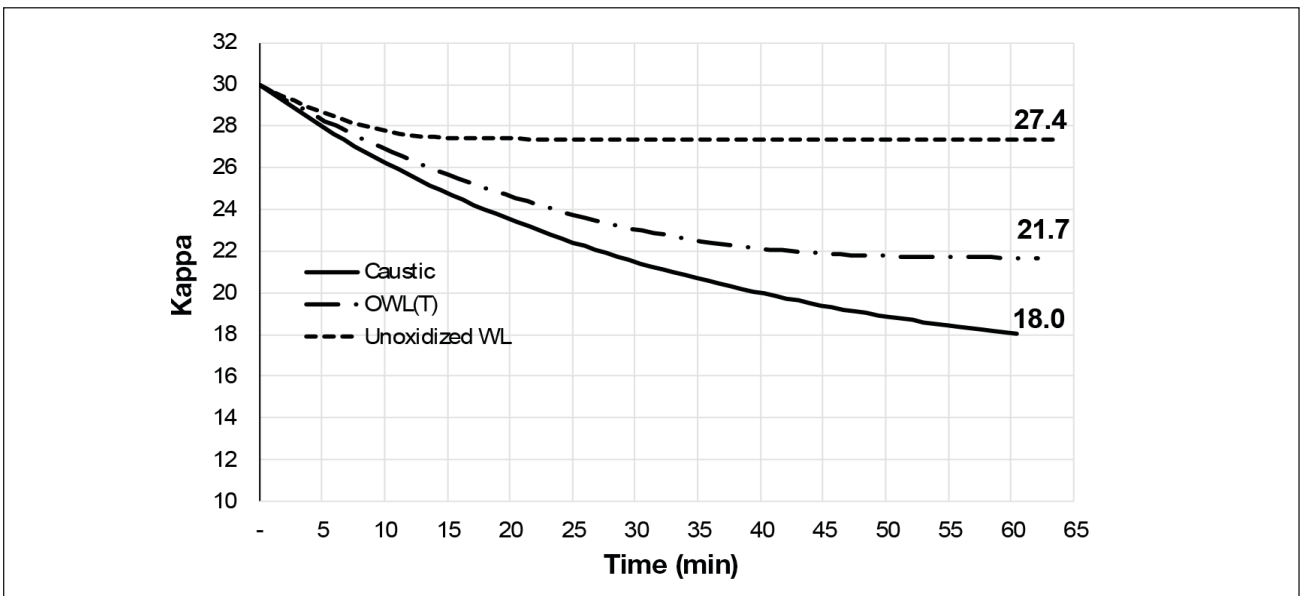
6. Model delignification prediction at 0.70 MPa (100 psig).
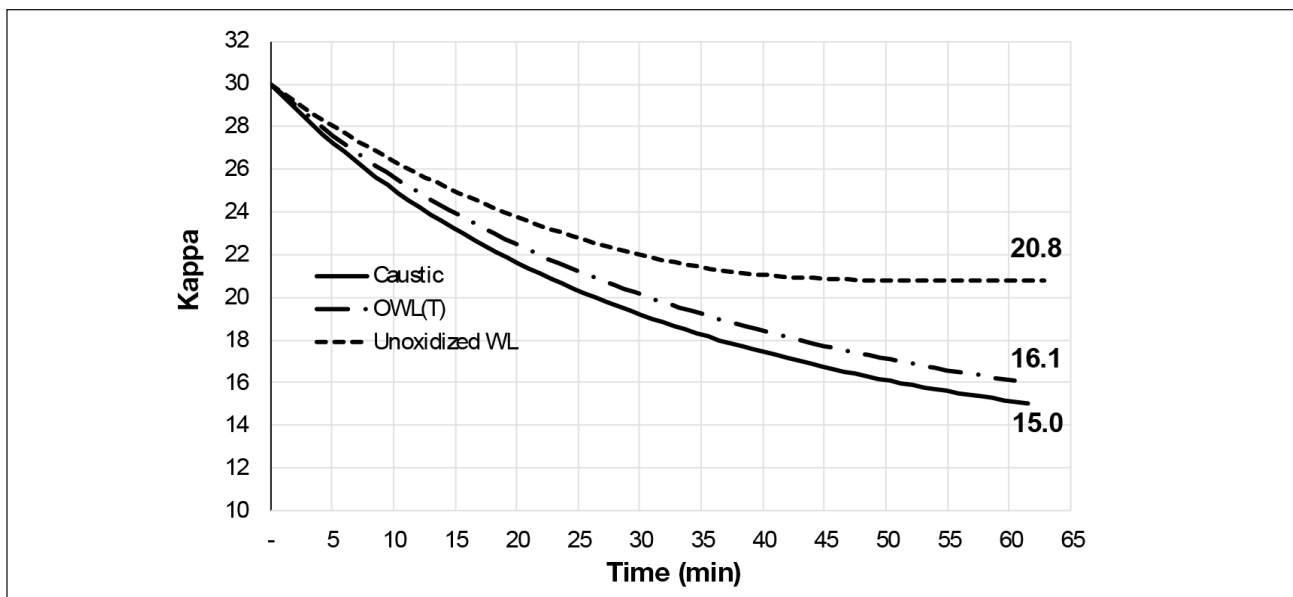
7. Model delignification prediction at 1.03 MPa (150 psig).

about 15.4 kg O_2/(BDT/h). Therefore, the required pressure drop per kg O_2(BDT/h) is about 0.010 MPa (i.e., (0.655–0.503)/15.4 = 0.00987). The value at a k_La of 0.004 s^{-1} is about 0.026 MPa/kg O_2(BDT/h) and the average is 0.018 MPa/kg O_2/(BDT/h).

Using this simplified approach, the oxygen partial pressure to be used in the previous kinetic equation can be estimated from the total pressure and the oxygen consumption. For example, (and from below), the oxygen consumption given 30 kg RBL/BDT and Δ kappa of 12, is 14 kg O_2/BDT when NaOH is the alkali source. Thus, the required Δ oxygen partial pressure would be about 0.250 MPa (i.e., 0.018*14 = 0.250 MPa).

Figure 5 illustrates a switch from NaOH to OWL(T). If it is assumed that the reaction kinetics are similar to lignin, and the SH and S_2O_3 ions are in solution and the consumption is 4 kg O_2/(BDT/h), then the additional Δ oxygen partial pressure would be 0.07 MPa (i.e., 4*0.018 = 0.07 MPa). This ap-

Parameter	Unit	Value
Initial pressure	MPa	0.7–1.03
Static head	MPa	0.4
Pulp residence	min	60

VI. Oxygen reactor parameters.

Parameter	Unit	Value
Volume fraction	%	20 (max.)
O_2 purity	%	90
Caustic consumption	kg/Δ kappa	1.55

VII. Other operating parameters.

proach was used to estimate the impact of using white liquor on delignification rate. Rewathar and Bennington [21] determined the gas holdup (X_g) of 9% consistency pulp was between 0.075 and 0.1 for superficial gas velocities (U_g) greater than 0.5 m/s. However, the authors observed that k_La dropped exponentially at superficial gas velocities below about 0.01 m/s. Therefore, it would be expected that k_La will be low and the rate of delignification would be insignificant for a low value of X_g. For the modeling results presented in this paper (**Fig. 6** and **Fig. 7**), the effect of a low X_g has been ignored (i.e., the oxygen is allowed to go to exhaustion). Therefore, the reported results will represent the best-case scenario.

Model parameters

The model parameters used are given in **Tables V–VII**. Caustic is consumed in the delignification reaction and by the organics in the postoxygen washer filtrate that is recirculated

Parameter	Unit	Value
Entering kappa		30
Target Δ kappa		12–15
Lignin/Kappa		1.5
HexA	mmol/kg	20
Kappa (HexA free)		28.0
Consistency		12%
RBL carryover	kg/BDT	30
BDT = bone dry ton; RBL = raw black liquor.		

V. Pulp characteristics.

Parameter	Unit	NaOH	OWL(T)	White Liquor
Gas volume	%	19.8	20	20%
Total gas charge	kg/BDT	17.2	17.0	17.4
O_2 charge	kg/BDT	14.6	15.2	15.2
O_2 consumed				
RBL	kg/BDT	5.4	5.4	5.4
White liquor	kg/BDT	0	4.0	8.0
Delignification	kg/BDT	8.4	5.8	0.1
Excess	kg/BDT	0.8	0.0	0.0
Total	kg/BDT	14.6	15.2	15.2
Δ Kappa		12.0	8.3	2.6
NaOH = sodium hydroxide; OWL(T) = oxidized white liquor with thiosulfate; BDT = bone dry ton; RBL = raw black liquor.				

VIII. Summary of model results at 0.70 MPa (100 psig).

Parameter	Unit	NaOH	OWL(T)	White Liquor
Gas volume	%	16.4	20	20
Total gas	kg/BDT	19	23.2	24.3
O_2 charge	kg/BDT	17	20.9	21.8
O_2 consumed				
RBL	kg/BDT	5.4	5.4	5.4
White liquor	kg/BDT	0	5.0	10.0
Delignification	kg/BDT	10.5	10.5	6.4
Excess	kg/BDT	1.1	0.0	0.0
Total	kg/BDT	17.0	20.9	21.8
Δ Kappa		15.0	13.9	8.2

IX. Summary of model results at 1.03 MPa (150 psig).

to the oxygen stage. The value of 1.55 kg NaOH/Δ kappa is based on data from Vuorenvirta et al. [1] and Susilo [20]. The residual caustic in the RBL is assumed to be equal to the caustic consumption demands of the organic and sulfur compounds in the RBL. The hydroxide ion concentration was manipulated to achieve the desired delignification.

Model results

Figure 6 plots the results at a pressure of 0.70 MPa (100 psig), and **Table VIII** summarizes the results. The target delignification was 40% (i.e., 12 kappa units).

The model predicts that delignification would be limited to 8.3 kappa units when OWL(T) is the alkali source. The use of unoxidized white liquor would have a very significant im-

pact on delignification. It is interesting to note that in the NaOH case, the excess oxygen is less than 20% (X_g <0.1). This would suggest that the oxygen availability could limit the percent of delignification with a reactor operating at 100 psig, even in the case where NaOH is used as the alkali source.

Figure 7 plots the results at a pressure of 1.03 MPa (150 psig), and **Table IX** summarizes the results. The target delignification was 50% (i.e., 15 kappa units).

Although not as substantial, the use of OWL(T) as the alkali source does result in oxygen exhaustion and limits delignification versus NaOH. Unoxidized white liquor, on the other hand, continues to have a significant impact on delignification and oxygen consumption.

CONCLUSIONS

The temperature and initial hydroxyl ion concentration [OH⁻] of an oxygen stage are typically optimized to maximize the kappa unit reduction of the inlet pulp at an acceptable loss of pulp strength. Oxygen exhaustion within the reactor is not generally thought to be a limiting factor. As clearly demonstrated in this paper, when OWL(T), and in particular unoxidized white liquor, is the alkali source for oxygen stage, the amount of available oxygen can limit the delignification that can be achieved. Oxygen stages operating in the 0.70 MPa (100 psig) range are more susceptible to oxygen exhaustion than higher pressure systems due to the pressure dependence of the volume fraction.

A mill should use makeup caustic in the oxygen stage and supplement this with white liquor or OWL(T) if the makeup requirement is less than the NaOH requirement of the oxygen stage.

A mill using white liquor in the oxygen stage should consider using a white liquor oxidizer unit to produce either OWL(T) or OWL(S) to minimize oxygen consumed by the sulfide. If OWL(T) is being used, then the mill should consider modifying their oxidized white liquor system to produce OWL(S), or in the case of an air-based oxidizer unit, adding a polishing unit to oxidize the thiosulfate to sulfate. These modifications will minimize the potential for oxygen exhaustion caused by unproductive oxidation of inorganic sulfur species and possibly increase delignification.

The oxygen charge is often adjusted on the basis of a fixed ratio to the desired Δ kappa (e.g., 1.5 kg O_2/Δ kappa). A better way to adjust the oxygen charge might be to base it on the estimated RBL carryover, at 0.18 kg O_2/kg RBL; the oxygen demand of white liquor, about 0.20 kg O_2/kg white liquor-NaOH for OWL(T), which will vary with the state of oxidation; the oxygen required for delignification at about 0.7 kg O_2/Δ kappa; and an excess of at least 10%.

Adjustment to the white liquor ratio could be made on the basis of an ABC test of the white liquor. This would minimize the oxygen consumption and maximize residence time and delignification. It would also allow a mill to identify a situation where oxygen exhaustion is possible, (e.g., high inlet kappa and high white liquor usage). **TJ**

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ABOUT THE AUTHORS

The research was conducted to develop a method of determining the total oxygen consumption in an oxygen delignification stage. Another objective was to estimate the impact of using caustic, white liquor, and partially oxidized white liquor where the liquor sulfide is oxidized to thiosulfate on oxygen stage performance.

Others have estimated the consumption of oxygen in lignin/carbohydrate reactions, by raw black liquor carryover, and by white liquor/oxidized white liquor. This work is complementary as it establishes a means of estimating the total oxygen consumption in an oxygen stage. It also considers the amount of oxygen that can reasonably be charged to an oxygen stage and determines the impact of the raw black liquor carryover and alkali source on performance.

The most difficult aspect of this work was to arrive at estimates for the consumption of oxygen in the lignin/carbohydrate reaction and consumption by raw black liquor. For both instances, there was a large range in the literature data. The lignin/carbohydrate estimate was based on evaluating the method of measurement and preponderance of values.

An analysis of the range in raw black liquor data suggested that composition of the raw black liquor and, in particular, the state of the sulfur compound strongly influenced the data. It was discovered that oxygen availability can limit the degree of achievable delignification across an oxygen stage.

The information can be used at all mills with an oxygen delignification stage (>50). The next step is to validate the impact of raw black liquor and white liquor/oxidized white liquor on oxygen stage performance. A particular focus will be to measure the oxygen consumption and document a reduction in delignification because of the use of white liquor/oxidized white liquor.

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