# The role of gas dispersion in the oxygen delignification process

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**ABSTRACT:** Oxygen delignification is an essential part of the pulp production process. Delignification occurs with the aid of alkali and dissolved oxygen. Dissolved oxygen is obtained by dispersing oxygen gas into the pulp suspension by using efficient mixers. Little is known about the state of oxygen gas dispersion and its effect on oxygen delignification kinetics and efficiency.

This paper will present the results for the effect of gas bubble size on the performance of oxygen delignification. The results are mainly based on detailed studies made in a Finnish hardwood mill where the oxygen bubble size distribution could be altered at the feed of the reactor. An essential aspect of these studies was the use of a new continuous inline gas bubble size measurement system to simultaneously determine the bubble size distribution at the feed and top of the reactor. Information about oxygen consumption in the reactor could also be obtained through the bubble size measurements. Accordingly, these studies quantify the effect of oxygen bubble size on the kappa reduction of the pulp. The effect of different chemical factors on the oxygen bubble size is also studied.

Finally, the relationship between the gas bubble size and the liquid phase oxygen mass transfer coefficient (kLa) is presented. This connects the bubble size to the kappa reduction rate. Based on the presented modeling approach and the evaluation of practical factors that are not taken into account in the modeling, it was concluded that the volumetric average oxygen bubble size should preferably be smaller than 0.2 mm in practice.

The information obtained with the new gas bubble size measurement system and the presented modeling approach give a very new basis for understanding, monitoring, adjusting, and designing oxygen delignification processes.

***Application:*** Information about gas dispersion, its connection to the mass transfer of oxygen, and meaning of this for delignification offer the possibility to develop and improve the performance of the oxygen delignification processes.

The kinetics of oxygen delignification has been modeled as [1]:

$$-\frac{dK}{dt} = Ae^{-51{,}000/(8.314T)}([OH^-])^{0.7}([C_{O2}])^{0.7}(K)^2 \quad (1)$$

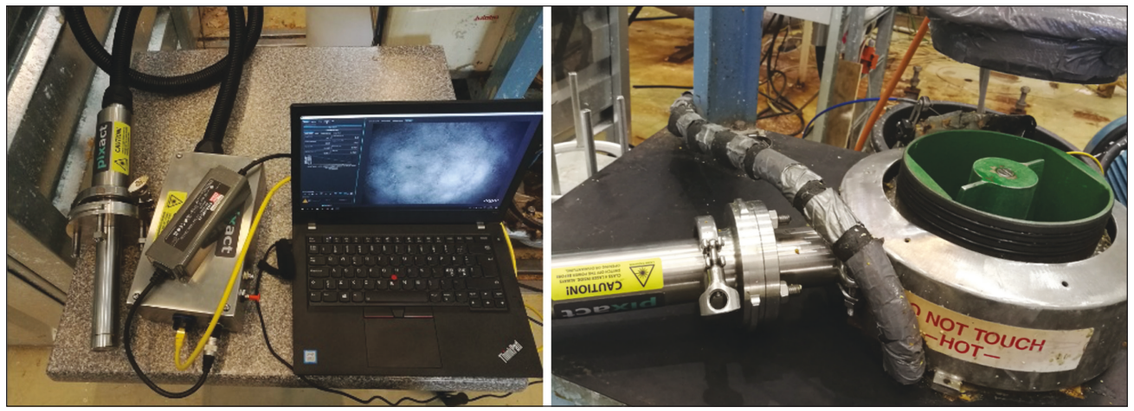
where $K$ is the kappa number, $A$ is the constant, $T$ is the temperature (K), $[OH^-]$ is the hydroxide concentration (mol/L), and $[CO_2]$ is the concentration of dissolved oxygen (mol/L).

Equation 1 shows that there must be a high enough temperature and a sufficient amount of hydroxide anions $[OH^-]$ and dissolved oxygen $[CO_2]$ present in a pulp suspension for delignification to occur. The temperature and hydroxide concentration can be controlled by the addition of steam and alkali. The dissolved oxygen concentration is determined by the oxygen charge, the reactor pressure, and the mass transfer rate of the oxygen from the gas phase to the fiber suspension. The latter is mainly determined by the pressure, as well as the amount and size of the oxygen bubbles in the reactor. This is why the effective mixing of oxygen in the high-shear mixer is important for the proper functioning of the delignification process. The pulp suspension passes in a plug-flow state through the reactor tower, and the dispersion of oxygen in a finely distributed bubble suspension is required to ensure an efficient and stable delignification result. Due to the low aqueous solubility of oxygen, the mass transfer surfaces of the bubbles have to be large enough (i.e., the average bubble size has to be small) to keep the dissolved oxygen concentration at the highest level.

In our previous paper, we summarized the knowledge related to oxygen bubble size and how different process parameters may affect it [1]. This knowledge is based on our earlier studies that were performed by utilizing a new continuous inline bubble size measurement system [2-13]. This paper presents some new results for the state of oxygen dispersion in the process, but the main aim is to show the effect of bubble size on kappa reduction during the oxygen delignification process.

## MATERIALS AND METHODS

An inline bubble size measurement was conducted using a continuous Pixact Bubble Monitoring (PBM) system (Pixact Ltd.; Tampere, Finland) [7]. Gas dispersion measurements in the oxygen reactor were made at three different fiber




*1. Compact bubble size measurement system connected to the Mark IV Quantum mixer/reactor [2].*

lines in Finland. One measurement period was performed in a line producing hardwood pulp (birch) and the other two were in lines producing softwood pulp.

Laboratory measurements were conducted in a modified high-shear Mark IV Quantum mixer/reactor **(Quantum Technologies; Akron, OH, USA)** that is connected to a compact bubble size measurement system (**Fig. 1**). This measurement system is built so that it is easy to transport and use in different mills. The laboratory measurements used bleached softwood pulp and unbleached softwood pulp collected after the digester, as well as hardwood pulp obtained after a diffuser washer and at the entrance of the oxygen delignification reactor.

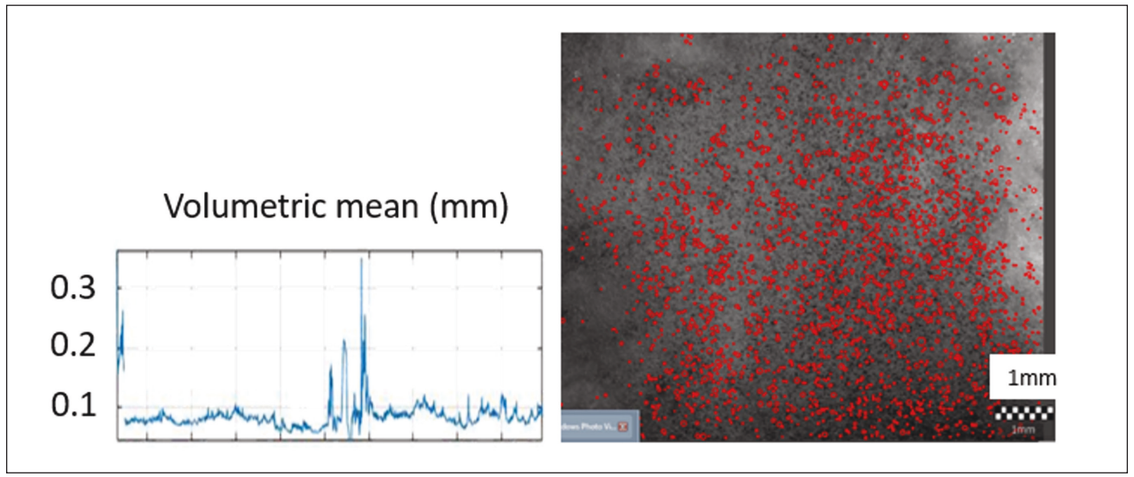
## RESULTS AND DISCUSSION

### *Effect of dissolved substances on the oxygen bubble size in the process*

Previous mill measurements have shown that the average volumetric bubble size of oxygen was about 0.1 mm at one softwood mill, whereas at a hardwood mill, this value was nearly ten times higher. These processes also exhibited a great deal of variation in the oxygen bubble size [5]. The question arose as to what the reason is for these observations, and a potential answer is related to the amount and nature of the dissolved substances.

**Figure 2** shows the average volumetric bubble size measured at the other softwood line. It can be seen that the bubble size is at the same level as observed in the softwood line of the previous study [5].

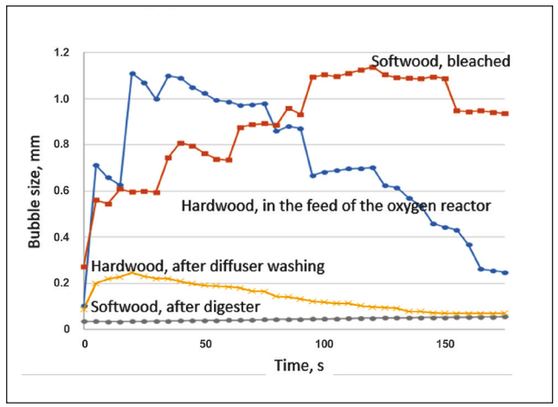
**Figure 3** presents the bubble size measured in the Mark IV Quantum mixer/reactor for different pulps. The biggest bubbles are formed with the softwood bleached pulp and the smallest with the softwood pulp obtained after the digester. Hardwood pulp obtained from the feed of the oxygen reactor yields much bigger bubbles when compared to the pulp obtained at an earlier process stage




*2. Average volumetric bubble size measured in the softwood line after the second stage oxygen mixer over a period of one month (left), and an example of the imaged bubble sizes highlighted in red (right).*








*3. Bubble size measured in the mixer/reactor with different pulps. The pulp was first mixed at 800 rpm for 5 s and then at 100 rpm.*

after the diffuser from the same pulping line. All of these results imply that the amount and the nature of the dissolved substances in pulp slurries have a great impact on the dispersion of oxygen in the pulp. Similar differences related to softwood and hardwood pulp have also been observed earlier [12,13]. According to these results, it was assumed that dissolved substances in softwood pulp better promote the dispersion of oxygen, as compared to the dissolved substances in the hardwood pulp. This could be one reason, in addition to the greater amount of hexenuronic acids in the hardwood pulps vs. softwoods, **that** it is more difficult to obtain kappa reduction with hardwood pulps when compared to softwood pulps in the oxygen delignification stage. All of these observations related to the dispersion of oxygen with hardwood pulp are based on the same hardwood pulping line that used birch, which raises the question of how well this example represents the situation at other hardwood pulp lines.

The effect of the dissolved substances on the dispersion of oxygen has also been seen in the process (**Fig. 4**). When the amount of dissolved substances decreased, the oxygen bubble size increased.

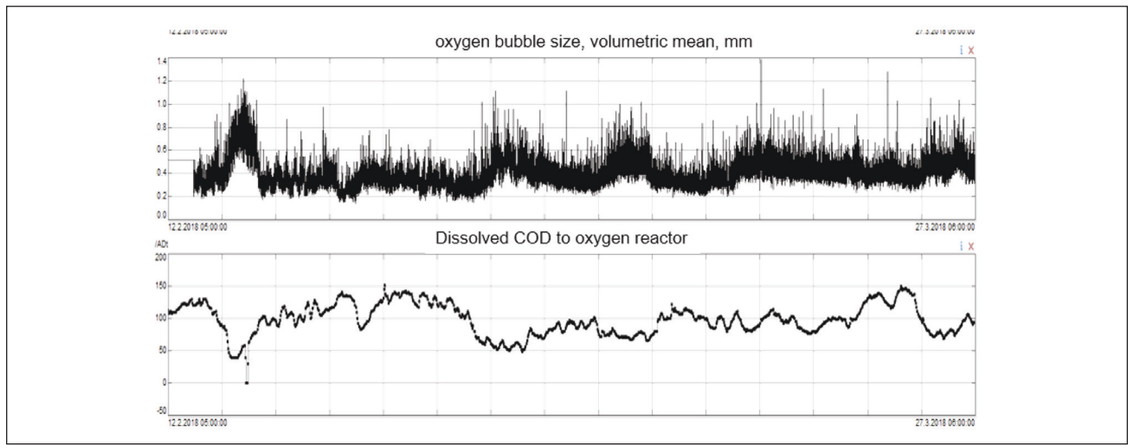
It is well known that washing loss (i.e., dissolved substances) consumes oxygen in the reactor, which may lead to decreased kappa reduction. In this hardwood line, there seems to be—at least to some extent—a negative correlation between dissolved COD entering the oxygen delignification stage and the kappa reduction obtained (**Fig. 5**).

This correlation could be much stronger if the dissolved substances were not promoting the dispersion of oxygen as seen in Fig. 4. Together, these figures also indicate that in this fiber line, the dissolution of oxygen restricts the obtainable kappa reduction.

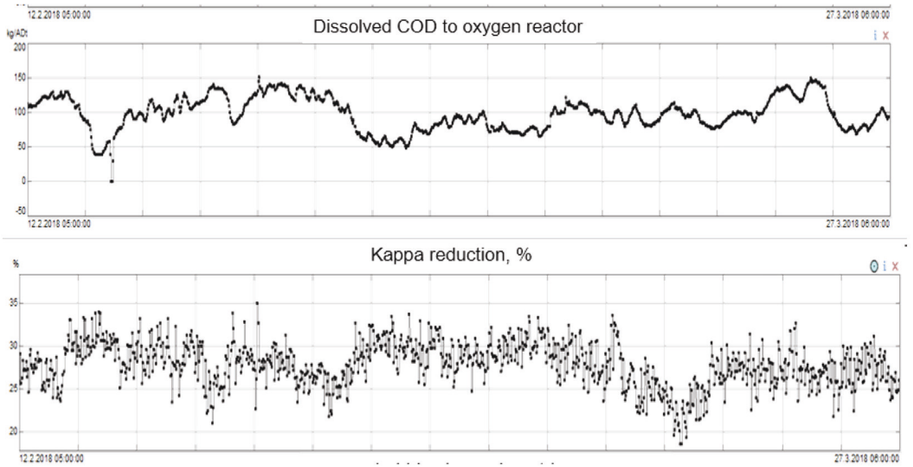
### *Effect of bubble size on delignification*

The important question here is what is the quantitative effect of the oxygen bubble size on the kappa reduction in oxygen delignification. Long-term mill experiments where oxygen bubble size is changed are difficult to implement in the production line and have not been done yet. In the short-term tests performed in the hardwood line, the oxygen bubble size was decreased by lowering the defoamer dosage in the process before the oxygen delignification stage; the amount of residual oxygen was decreased (i.e., the consumption of the applied oxygen increased) [2]. In the long-term tests conducted in the same line, an increase in pressure increased the amount of delignification [2].

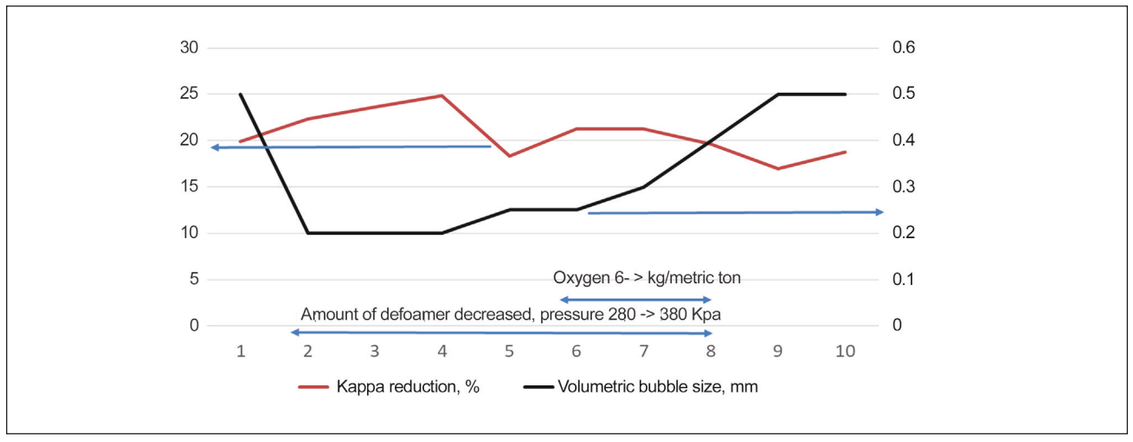
**Error! Reference source not found.** presents the effect of bubble size on kappa reduction in the test conducted at the hardwood line. When the defoamer dosage at the washer before oxygen delignification was eliminated and the pressure at the top of the reactor was increased, the bubble size decreased and the kappa reduction increased



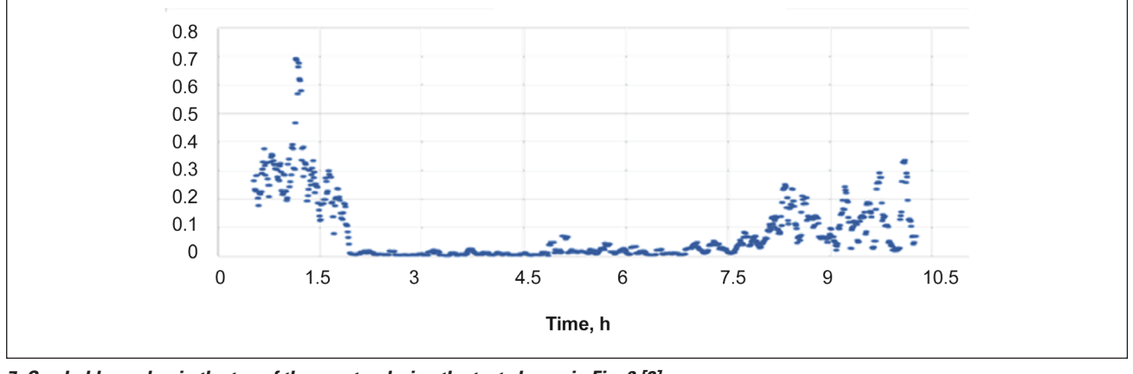

*4. Correlation between oxygen bubble size and chemical oxygen demand (COD) over a period of 1.5 months. The COD was measured with a refractometer in the feed of the oxygen reactor in the hardwood line.*




*5. Correlation of dissolved COD and kappa reduction for the period of 1.5 months measured in the hardwood line.*



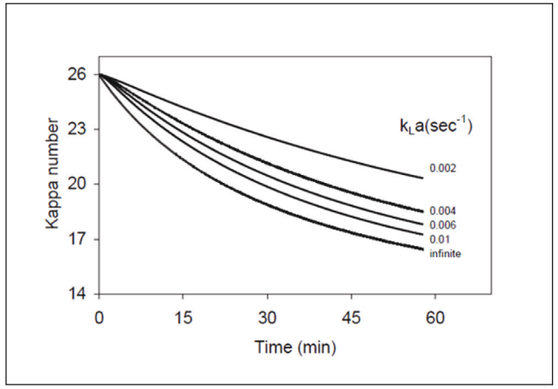

*6. Effect of bubble size on kappa reduction in the test conducted in the hardwood line [2].*




*7. Gas holdup value in the top of the reactor during the test shown in Fig. 6 [2].*








*8. Kappa number reduction in the oxygen reactor tower as a function of the mass transfer rate (kLa). Softwood pulp, sodium hydroxide (NaOH) charge 2.0%, oxygen charge 2.0%, pulp consistency 10%, oxygen pressure at reactor inlet 8.3 bar, height of the reactor 38 m, and temperature 95°C [1]*

from 20% to 25%. Without the defoamer addition, the pulp washing efficiency decreased; the operator then had to apply the washer defoamer again. Because of that, the bubble size increased concomitantly with decreased kappa number reductions (**Fig. 6**, at point 5). Increasing the oxygen charge slightly improved the kappa reduction. When the bubble size decreased, the amount of residual oxygen at the top of the reactor decreases to an immeasurable value (**Fig. 7**). These results indicate that, at this mill, the kappa reduction could be increased if the oxygen bubble size was smaller.

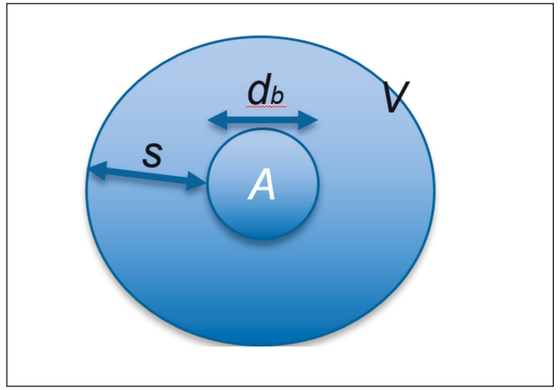
Another and more fundamental way to quantify the effect of bubble size on kappa reduction is through physical modeling of the delignification process. In earlier modeling studies [1], there was no direct physical basis to model the mass transfer of oxygen. However, this is now possible based on measured data of the oxygen bubble size in the reactor. Moreover, based on the mill measurements, it can be assumed that excessive coalescence of the bubbles in the reactor does not occur and that the oxygen passes through the reactor at the same speed as pulp [5]; these assumptions help to simplify the modeling efforts.

**Figure 8** displays an example of the effect of the oxygen mass transfer rate, $k_La$, on the kappa reduction rate.

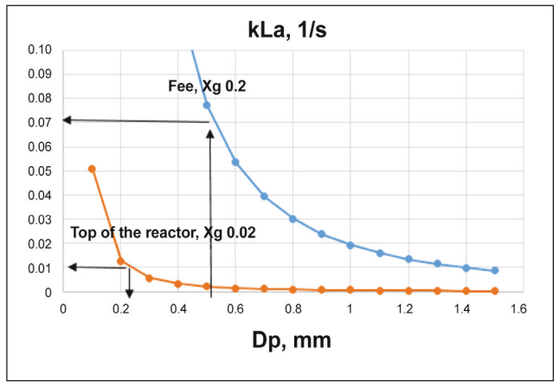
Now, the question is what is the relationship between the $k_La$ and the oxygen bubble size, db? The $k_La$ term can be defined as:

$$k_La = \frac{D_{O2}A}{sV} \quad (2)$$

where;
$DO_2$ = diffusion coefficient of oxygen (= 5.7*10-9 m²/s)
$A$ = surface area of the gas
$S$ = average thickness of the liquid film surrounding the bubble




*9. Definition of liquid film thickness s.*




*10. Mass transfer coefficient (kLa) as a function of the bubble diameter at typical mill oxygen delignification conditions shown in Table I (Xg = gas void fraction).*

$V$ = volume of the whole system

The liquid film thickness (**Fig. 9**), $s$, can be calculated according to Eq. 3:

$$s = \frac{d_b}{2}((1/X_g)^{1/3} - 1) \quad (3)$$

where:
$X_g$ = Gas void fraction, dimensionless
$d_b$ = bubble diameter, m

Then, Eq. 2 can be written to the following form, which defines relationship between $k_La$ and oxygen bubble size, $d_b$:

$$k_La = \frac{12D_{O2}X_g}{((1/X_g)^{1/3} - 1)d_b^2} \quad (4)$$

**Figure 10** presents the $k_La$ values at the inlet and discharge of the oxygen reactor tower, which are based on the values listed in **Table I**.

To obtain maximal kappa reduction at the top of the

| | Inlet of Reactor | Top of Reactor |
|---|---|---|
| $O_2$, kg/ metric ton | 20 | 1 |
| *P*, bar | 7 | 3.5 |
| $X_g$ | 0.2 | 0.02 |
| *P* = reactor pressure; $X_g$ = gas void fraction. | | |

***I. Values used in the* $k_La$ *calculation.***

reactor, the $k_La$ value should be larger than 0.01 1/s (see Fig. 8). This is achieved when the bubble size at the top of the reactor is smaller than 0.23 mm, which means that it will then be 0.5 mm in the feed of the reactor.

However, the present analysis does not account for several phenomena that can result in requiring an even smaller bubble size, such as:

- Fibers exist in the reactor in the form of flocs, which require more intense oxygen mass transfer.
- Instead of using the average volumetric bubble size, the bubble size distribution should be used in the numerical modeling, which would yield lower $k_La$ values in the top of the reactor when smaller bubbles are dissolved.
- Bubbles may not be evenly distributed in the reactor, meaning they may form aggregates that would then decrease the mass transfer (aside from smaller bubble coalescences to larger ones).
- Substances adsorbed on the surface of the bubble may inhibit the dissolution of oxygen.
- The consumption of oxygen in the mill may be greater due to oxygen reaction with dissolved organics in the pulp slurry, which would decrease the required oxygen bubble size. Additional oxygen consumption could also be caused by partially oxidized white liquor used for alkali [14].

As a result of all these issues, the preferable average bubble size in the feed of the reactor may be smaller than the 0.5 mm estimated using Eq. 4. Thus, the previously described fundamental modeling of the mass transfer rate shows that the average bubble size should be below a certain level to achieve maximum oxygen delignification. However, there are still several unanswered questions and the presented modeling approach must be incorporated into the overall model of an oxygen delignification tower [1]. This comprehensive model, which uses the measured bubble size distribution and other operating data as input, could be an important tool for control, troubleshooting, and further improvement of industrial oxygen delignification reactors. Additional modeling work is being done, and these modified models will be verified by experiments at the mill and laboratory using the developed online bubble size measurement technique.

## CONCLUSION

In the present article, it was shown that:

- An online analytical technique for continuous bubble size measurement has been developed, and it is working well at the mill.
- In the softwood lines, the average volumetric bubble size was about 0.1 mm; in the hardwood line, the bubble size was almost ten times larger. The mixing of oxygen in these lines was very similar, so the delignification difference must likely result from different surface chemistry phenomena with these two lines.
- For both fiber lines, there was a considerable long-term variation in the measured bubble size.
- In both lines, the increase in the rotation speed of the mixer decreased the bubble size, whereas the increase of oxygen charge increased the bubble size.
- Coalescence of bubbles in the reactor was not observed in the softwood line; however, in the hardwood line, some coalescence into larger bubbles certainly occurred in the reactor.
- In the test with the hardwood line, the use of a defoamer increased the oxygen bubble size.
- Increasing the reactor pressure and decreasing the oxygen bubble size improved the kappa reduction in the hardwood line.
- Based on the presented modeling approach, it was concluded that in industrial practice, the volumetric average oxygen bubble size should be around 0.2 mm or smaller.

With the newly developed online bubble size measurement system and the new modeling approach, it may be possible to better understand, monitor, control, and design oxygen delignification processes. The integration of the present modeling approach with the overall model of an oxygen delignification tower [1] may provide a new route to improving the oxygen delignification process. Our research is continuing through modeling and mill studies (e.g., studying how the use of defoamers should be optimized from the perspective of the performance of the oxygen and washing stages). Information related to bubble size in oxygen reactors at different production lines will also be collected. **TJ**

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*About this journal*

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In previous studies, we discovered new information about gas dispersion in the oxygen delignification process that created a need for information about the effect of bubble size on oxygen mass transfer and delignification. Earlier studies related to modeling of delignification and oxygen mass transfer found they could not be modeled properly. Based on the information **here** about gas dispersion and its behavior in the reactor, this **modeling** is now possible.

The most difficult aspect of this research was obtaining information about the effect of bubble size on mass transfer of oxygen and delignification. Some mill results were obtained, but more are certainly needed.

Our most interesting discovery in this study was that mechanistic modeling of mass transfer seemed to provide at least reasonable results. If oxygen mass transfer and delignification can be modeled well enough in the mill scale reactor, this offers interesting possibilities for further developing oxygen delignification processes.

Another interesting finding was the strong and clear effect of dissolved substances on bubble formation and delignification. Basically, this means that the effect of dissolved substances (i.e., washing loss) on the delignification chemistry have to be studied and better understood.

From this study, mills may get new ideas on how to improve the performance of the oxygen stage. Longer term, modeling studies will bring new information related to the function of this process and may even form a new basis for developing, running, and adjusting oxygen delignification stages.

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