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 an 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 results about the effect of gas bubble size dispersion on the performance of oxygen delignification. The results are based mainly on the detailed studies made in a Finnish hardwood mill where the oxygen bubble size distribution could be altered in the feed of the reactor. An essential part of these studies was the use of a new continuous in-line gas bubble size measurement systems to simultaneously determine the bubble size distribution in the feed and top of the reactor. Information in regard to oxygen consumption in the reactor could be obtained. Accordingly, these studies quantified the effect of oxygen bubble size on the kappa reduction. The effect of different operational factors on the oxygen bubble size will also be reviewed.

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

The new bubble size measurement, information which has and will be obtained from the processes, and a presented modelling approach give a very new base to understand, monitor, adjust and design oxygen delignification processes.

INTRODUCTION

The kinetics of oxygen delignification has been modelled as (van Heiningen et al. 2003):

$$-(dK/dt) = Ae^{-51000/(8,314T)}([OH^-])^{0.7}(C_{O2})^{0.7}(K)^2 \quad (1)$$

where K is the kappa number, A is the constant, T is the temperature (K), [OH-] is the hydroxide concentration (mol/l) and C_{o2} is the concentration of dissolved oxygen(mol/l).

This equation shows that there must be a high enough temperature, a sufficient amount of hydroxide anions [OH-], and dissolved oxygen present in a pulp suspension for delignification to occur. The temperature and the hydroxide concentration can be controlled by the addition of steam and alkali. The dissolved oxygen concentration is determined by the oxygen charge and 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 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 dispersion of oxygen in a finely distributed bubble suspension is required to ensure an efficient and stable delignification result. Due to the weak solubility of oxygen, the mass transfer surface of the bubbles has to be large enough, i.e. the average bubble size has to be small enough, to keep the dissolved oxygen concentration at the highest level.

Up to this point, there has been little or no knowledge on the state of oxygen gas dispersion in the reactor, even though this can have a dramatic impact on the operational performance of the oxygen delignification process. In earlier papers (Käyhkö et al. 2019 2018, Mutikainen et al. 2017 2015 2014, Liukkonen et al. 2015, Ilonen et al. 2014), a new imaging-based method for the characterization of the bubble sizes and dispersion in the oxygen delignification tower was described as well as its effect on the kappa reduction in the process.

This paper will present more results, a summary of the earlier studies, and make conclusions related to the state and role of gas dispersion in the oxygen delignification process.

MATERIALS AND METHODS

An in-line bubble size measurement was conducted by using a continuous Pixact Bubble Monitoring (PBM) system, Figure 1 and Figure 2. The measurement is based on the imaging of pulp flow and detecting the bubbles using a machine vision system, see Figure 3. This measurement system is described more precisely in our earlier publication (Mutikainen et al. 2017). Gas dispersion measurements in the oxygen reactor were made in three fiber lines in Finland. One measurement period was performed in a line producing hardwood pulp (birch) and the other two in lines producing softwood pulp.

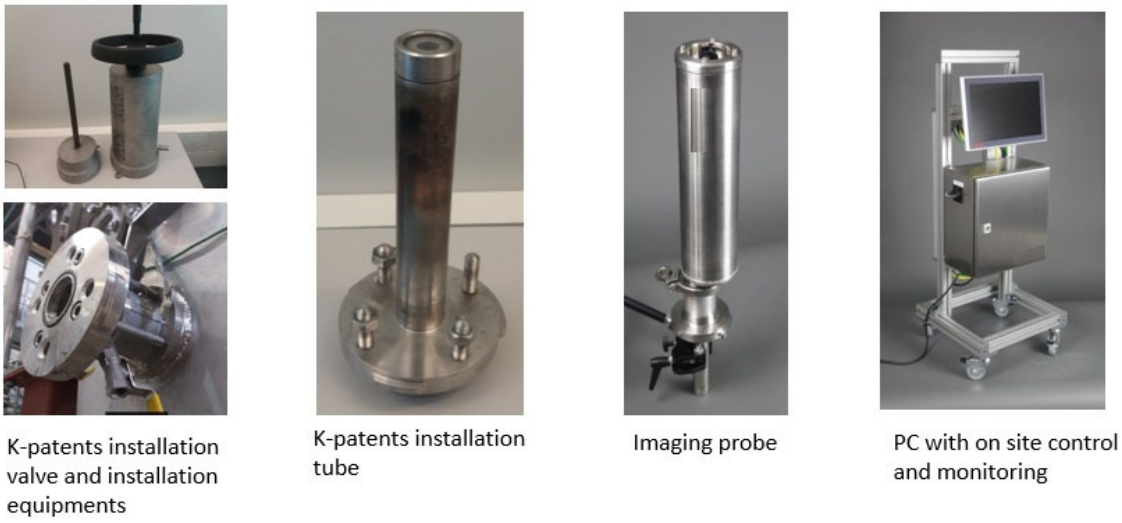


Figure 1: Essential parts of the bubble monitoring system

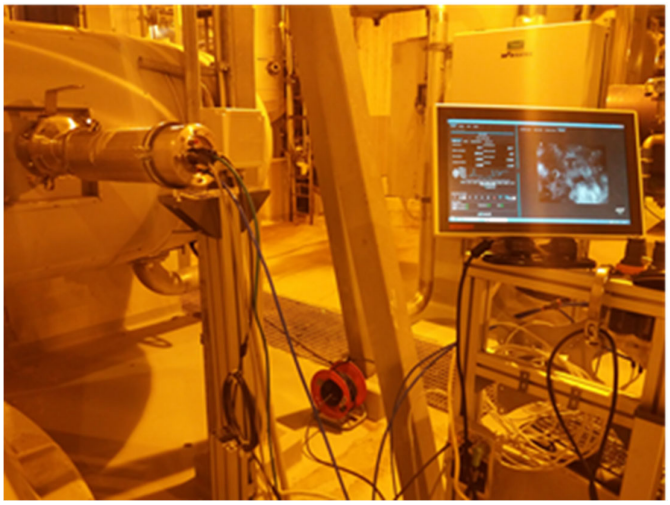
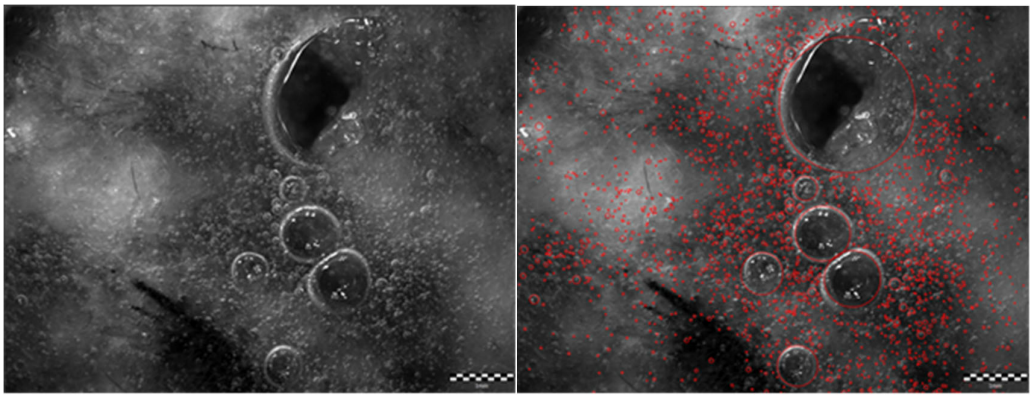


Figure 2: Bubble size measurement system installed in the process, including on-site control and monitoring capabilities



a) b)

Figure 3: a) The original image of bubble flow in the hardwood line after the oxygen mixer. b) The detected bubbles are circled with red outlines on top of the image (Mutikainen et al. 2017)

Laboratory measurements were conducted in a modified high-shear Mark reactor connected with a compact bubble size measurement system, Figure 4. This measurement system is built so that it is easy to transport and use in different mills. The laboratory measurements used bleached softwood pulp, brownstock softwood pulp collected after the digester, and hardwood pulp obtained after a diffuser washer and at the entrance of the oxygen delignification reactor.

Figure 4. Compact bubble size measurement system connected to the Mark reactor

RESULTS AND DISCUSSION

The effect of dissolved substances on the oxygen bubble size in the process

Figure 5 shows the volumetric bubble size distribution and an example of an image in the entrance of the reactor measured in the softwood and hardwood line. In the softwood line, the distribution is very narrow and represented by only one peak. In the hardwood line, the distribution is much wider and there are two peaks; a narrow distribution of very small sized bubbles of similar size as seen in the softwood line, plus a wide distribution of larger bubbles. The number and size of these larger bubbles is actually much higher, since the shape of the larger bubbles is more irregular and the machine vision system does not always recognize these as bubbles.

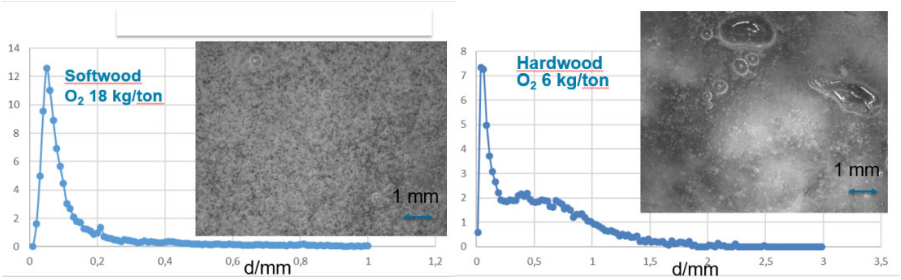


Figure 5: Typical volume weighted bubble size distribution and example of the image after the oxygen mixer in the softwood and hardwood fiber lines (Käyhkö et al. 2019)

Figure 6 shows the average volumetric bubble size measured in the other softwood line. It can be seen that the bubble size is at the same level as observed in the first softwood line.

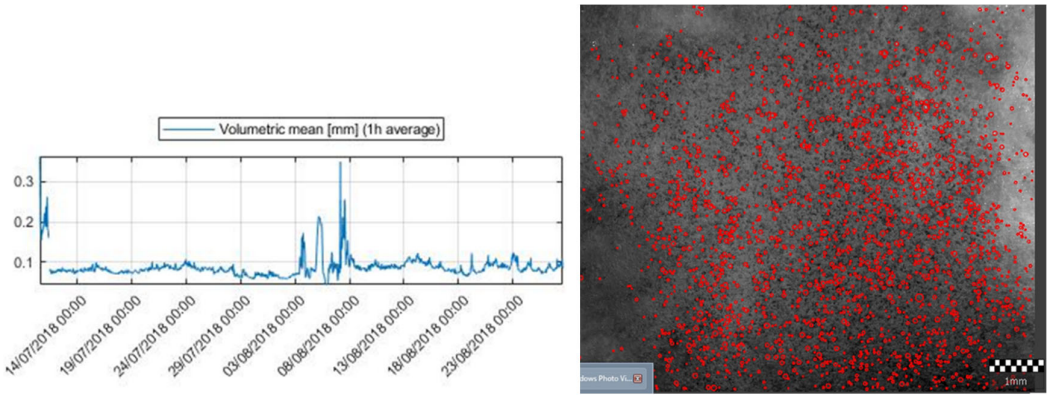


Figure 6. Average volumetric bubble size measured in the softwood line after the second stage oxygen mixer and the example of the bubble image.

Figure 7 presents the bubble size development measured in the Mark reactor for different pulps. The biggest bubbles are formed with the softwood bleached pulp and clearly the smallest with the softwood pulp obtained after the digester. Hardwood pulp obtained from the feed of the oxygen reactor yields much bigger bubbles, compared to the pulp obtained after the diffuser from the same pulping line. All of these results indicate that the amount and nature of the dissolved substances has a great impact on the dispersion of oxygen in the pulp. Similar differences related to softwood and hardwood pulp have been also observed earlier (Rantala 2010, Mutikainen 2011). According to these results, it was assumed that dissolved substances in softwood pulp promote the dispersion of oxygen better, 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 compared to softwood, that it is more difficult to obtain a kappa reduction with hardwood pulps 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 using birch, which states a question that how well this represents the situation in other hardwood pulp lines.

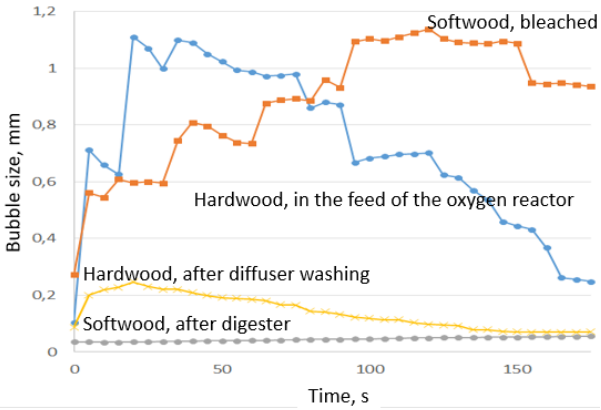


Figure 7. Bubble size measured in the Mark reactor with different pulps. The pulp was first mixed 800 rpm for five seconds and then with 100 rpm.

The effect of the dissolved substances on the dispersion of oxygen has also been seen in the process, see Figure 8. When the amount of dissolved substances decreases, the oxygen bubble size increases.

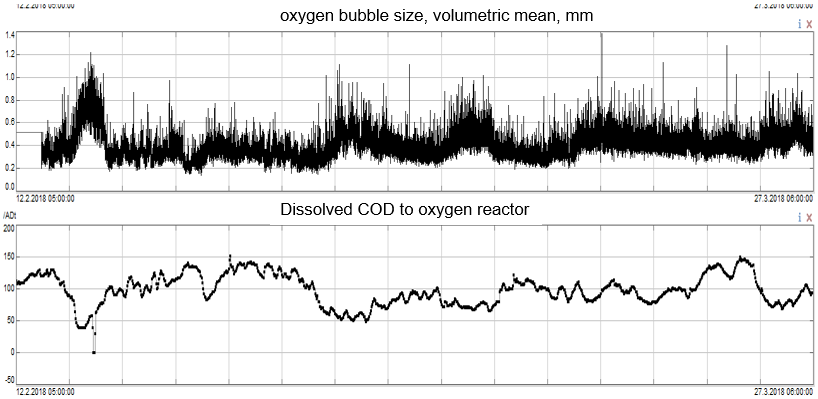


Figure 8. The correlation between oxygen bubble size and COD. COD was measured with a refractometer in the feed of the oxygen reactor in the hardwood line.

The effect of different process parameters on the oxygen bubble size

Besides dissolved substances originating from the wood, the usage of defoamers might have a great effect on oxygen dispersion. Defoamers are used in the fiber line in order to control content of air bubbles in the pulp suspension, which would otherwise decrease pulp washing efficiency. The defoamers promote the coalescence of the gas bubbles and when the bubbles are larger they can be separated from the pulp and the wash liquor displaces the black liquor more uniformly. A test was conducted in the hardwood line to examine whether the usage of defoamer had an effect on the oxygen bubble size by shutting off the feed of the defoamer to the washing stage before the oxygen delignification. Figure 9 shows that this had a clear decreasing effect on the oxygen bubble size. This indicates that the defoaming chemistry and the performance of the washing stages and oxygen delignification should be optimized together.

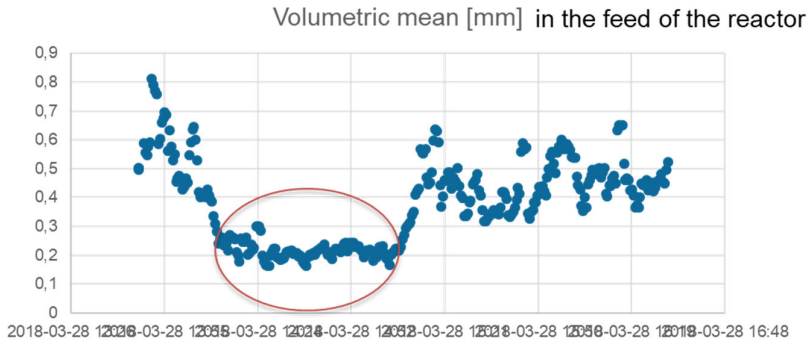


Figure 9: Volumetric average bubble diameter in the feed of the reactor, when the antifoaming agent feed to the washer before the oxygen reactor was shut off for the period of one hour.

Washing may also be connected to the oxygen delignification in two other ways. Firstly, the amount of dissolved substances may affect the oxygen bubble size as was seen in the Figure 8. Secondly, it is well known that dissolved substances consume oxygen in the reactor, which may lead to a 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 kappa reduction obtained, see Figure 10. This correlation could be much stronger if the dissolved substances were not promoting the dispersion of oxygen as seen in the Figure 8. Together these figures also indicate that in this fiber line the dissolution of oxygen restricts the obtainable kappa reduction.

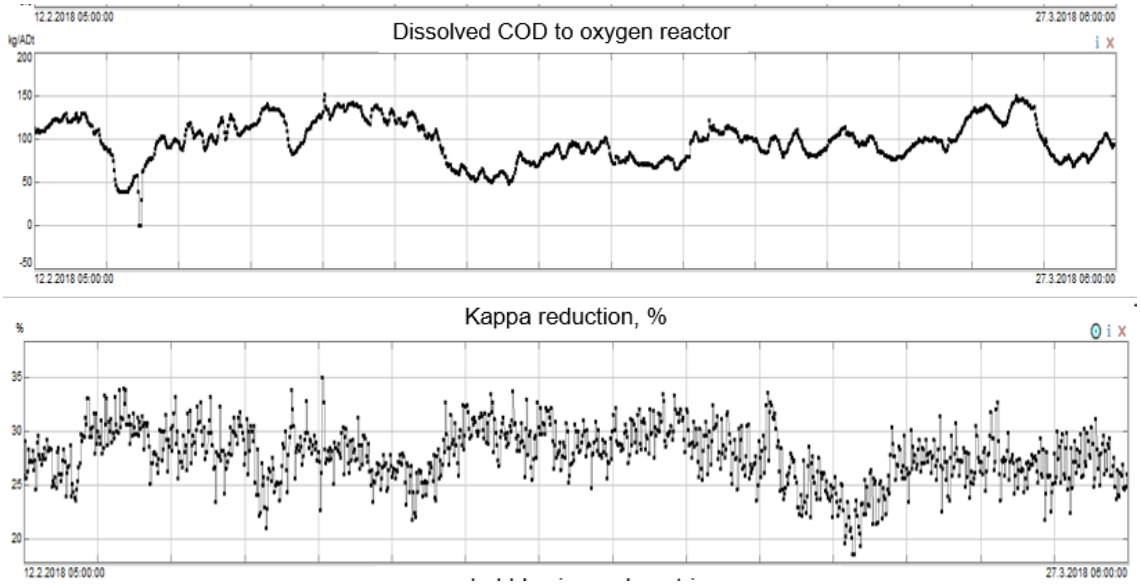


Figure 10. The correlation of the dissolved COD and kappa reduction measured in the hardwood line.

The rotation speed of the mixer and oxygen charge have a clear effect on the bubble size, both in the hardwood and softwood line, see Figure 11 and Figure 12 respectively. It is interesting that in the hardwood line, a doubling of the oxygen charge also doubles the bubble size. This means that when the oxygen charge is doubled, the mass transfer and hence dissolution of the gas does not, perhaps, increase at all. So, the oxygen charge can be quite an inefficient way to adjust the amount of dissolved oxygen and other measures, e.g. mixer rotation speed or oxygen pressure in the reactor, could be beneficially included in the kappa control loop.

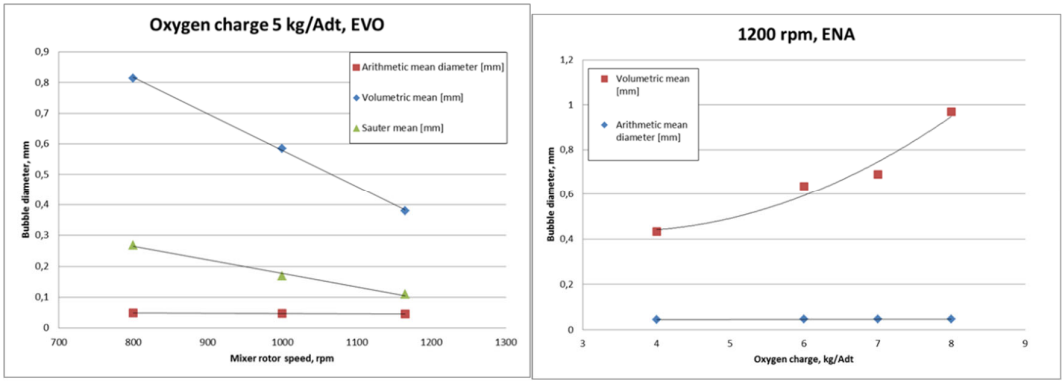


Figure 11: Effect of mixer rotation speed and oxygen charge on the average bubble size in the hardwood line (Käyhkö et al. 2019)

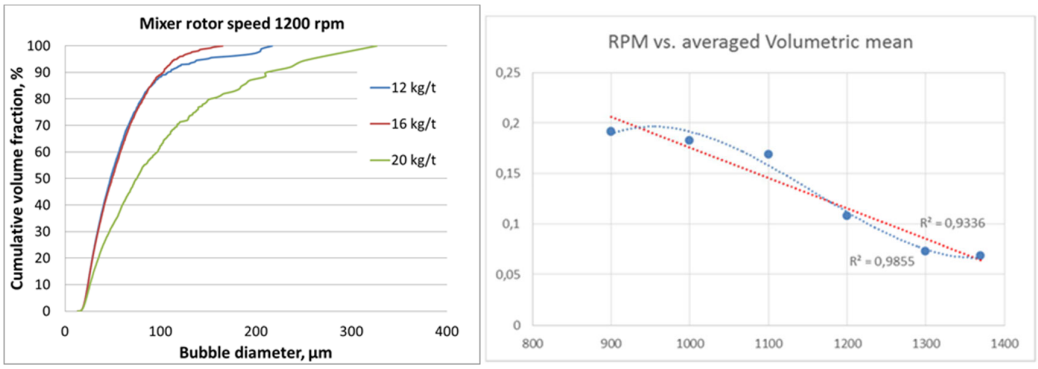


Figure 12: Effect of mixer rotation speed and oxygen charge on the bubble size in the softwood line (Mutikainen et al. 2014)

The effect of bubble size on the kappa reduction in the oxygen delignification

The important question here is what is the quantitative effect of the oxygen bubble size on the kappa reduction in the 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, but there are also other ways to obtain this information. Figure 11 shows the effect of reactor pressure on delignification. In this case, according to Figure 13 and the factorial analyses made in that study (Mutikainen et al. 2017), pressure had a significant effect on delignification. For example, increasing the pressure from 280 kPa to 380 kPa had a clear increasing effect on delignification, see the arrow in the Figure 11. Together, pressure and bubble size determine the amount of dissolved oxygen, and, hence, the bubble size should also have an effect on delignification in this case.

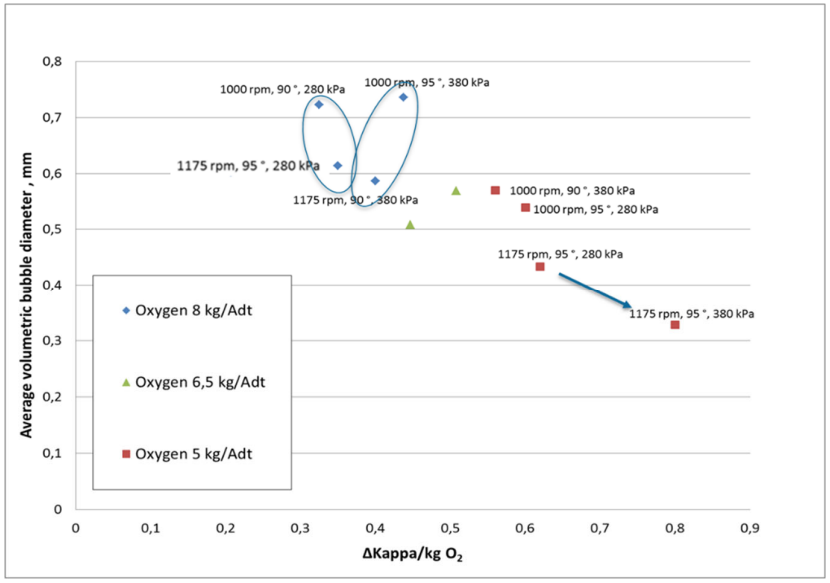


Figure 13: Effect of different factors on kappa reduction in experiments conducted in the hardwood line (Mutikainen et al. 2017)

Figure 14 presents the gas hold up level measured at the top of the reactor during the previously mentioned defoamer shut off test. The gas hold up level is the total volume of the detected bubbles and it gives an indication of the amount of oxygen gas leaving the reactor. It can be seen here that the gas hold up level clearly decreases when the defoamer is turned off. Also, during the shut off no large gas bubbles were present at the top of the reactor, see Figure 15. This all indicates that oxygen is consumed more by the delignification reactions and the reactor is working better.

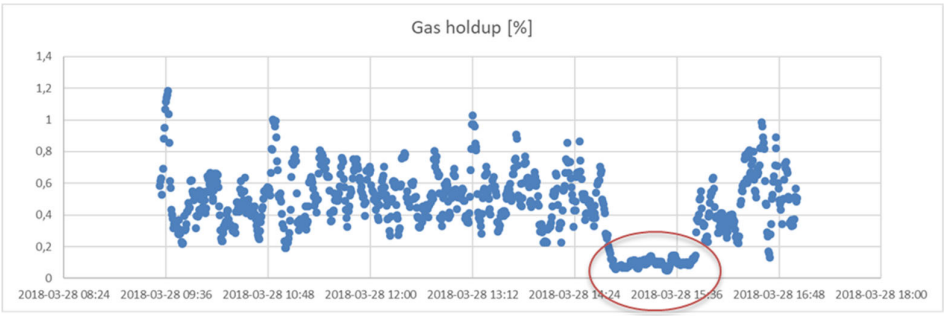


Figure 14. Gas hold up level measured at the top of the reactor during the defoamer shut off test (Käyhkö et al. 2019)

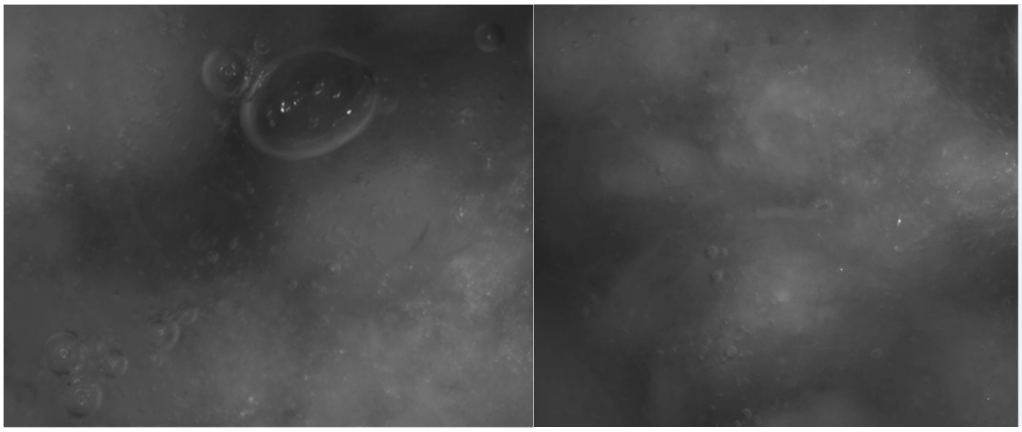


Figure 15. Example of the gas dispersion at the top of the reactor in the normal run (left) and during the defoamer shut off test (right) (Käyhkö et al. 2019)

Figure 16 presents the effect of the bubble size on the kappa reduction in the test made in the hardwood line. When the defoamer feed in the washer before oxygen delignification was shut off, the bubble size is decreased and the kappa reduction is increased from 20 % to 25 %. Without a defoamer, the washing efficiency decreased and the operator had to start the feeding of defoamer again. Because of that, the bubble size increased and in same time the kappa reduction decreased strongly, see sample point five in Figure 14. Increasing the oxygen charge improved the kappa reduction slightly. When the bubble size decreased, the amount of residual oxygen at the top of the reactor also decreased, see Figure 17.These results indicate that in this mill kappa reduction could be increased if the oxygen bubble size would be smaller.

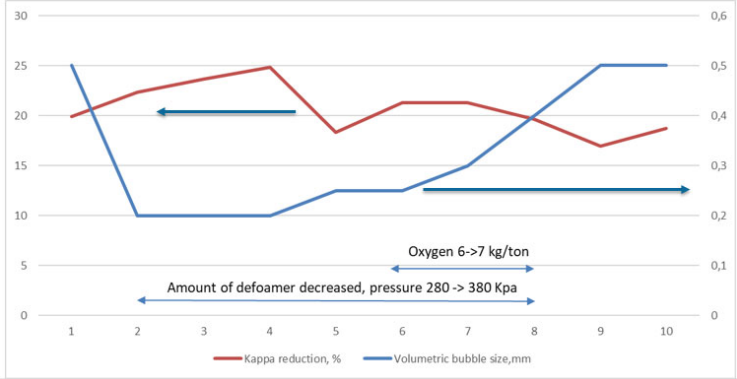


Figure 16. The effect of bubble size on the kappa reduction in the test made in the hardwood line (Käyhkö et al. 2019)

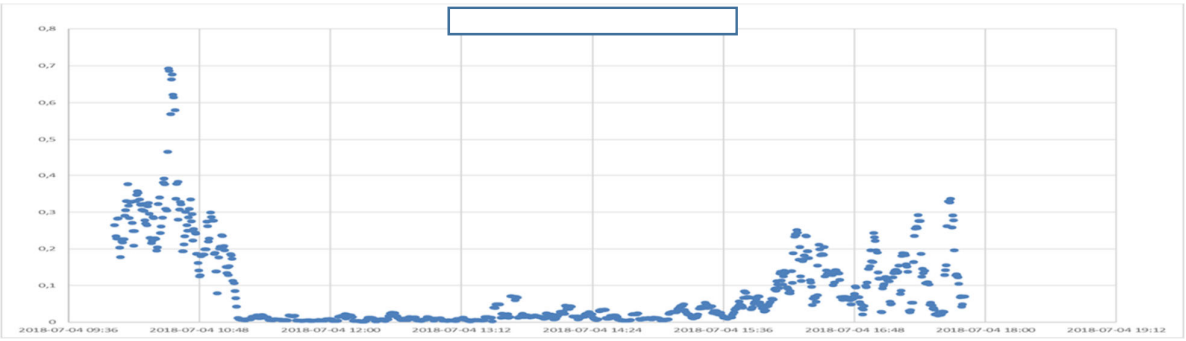
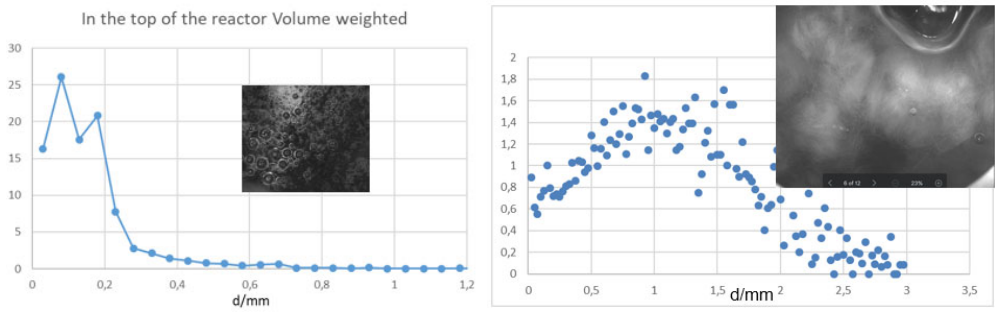


Figure 17. The gas holdup in the top of the reactor during the test shown in the Figure 16.

Another and more fundamental way to quantify the effect of bubble size on kappa reduction is through physical modelling of the delignification process. In earlier modelling studies (Van Heiningen et al. 2003), there was no direct physical basis to model the mass transfer of oxygen from the bubbles to the liquid phase. However, this is now possible based on measured data of the oxygen bubble size in the reactor. In addition the bubble size measurement can answer important questions which are needed for the modeling e.g. does coalescence of bubbles occur in the reactor and does the oxygen bubble pass through the reactor faster than pulp. Figure 18 shows the bubble size distribution measured at the top of the reactor in the softwood and hardwood lines. In the softwood line, the bubble size at the top of the reactor is slightly larger, compared to the feed (see Figure 5), which can result from the dissolution of the smaller bubbles leaving, leaving only the larger bubbles. In the hardwood line, there are much larger bubbles at the top, compared to those in the feed of the reactor. This shows that there has been some coalescence of the bubbles in the reactor. This can also be seen clearly in the images (not shown in here) taken from the top and the bottom of the reactor in the hardwood line. At the top of the reactor there are large, odd-shaped bubbles which do not exist in the feed of the reactor. According to these results, it can be concluded that if the bubbles are small enough, e.g. smaller than 0.5 mm, no severe coalescence of bubbles occurs in the reactor. All of the bubble size measurements shown in here, especially in the case of softwood, but also for hardwood, indicate that in these cases the oxygen gas is passing through the reactor at the same speed as the pulp.



Softwood Hardwood

Figure 18: Volume weighted bubble size distribution and an example of the image at the top of the reactor in the softwood and hardwood fiber lines.

Figure 19 displays an example of the effect of the oxygen mass transfer rate, k_La, on the kappa reduction rate.

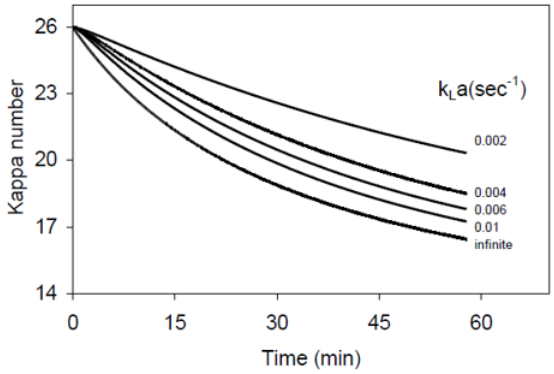


Figure 19. Development of kappa number in the tower as a function of mass transfer rate. Softwood pulp, NaOH charge 2,0 %, Oxygen charge 2,0 %, Pulp Consistency 10 %, oxygen pressure at reactor inlet 8,3 bar, height of the reactor 38 m and temperature 95 °C (Van Heiningen at al. 2003)

Now the question is of course, what is the relationship between the k_La and the oxygen bubble size, d_b. Based on a preliminary analysis the following equation has been derived:

$$k_La = \frac{12\, D_{O2} X_g}{((1/X_g)^{1/3} - 1) d_b^2} \qquad \text{eq. (2)}$$

where:
k_La : mass transfer rate, 1/s
D_{O2}: Diffusion coefficient of oxygen, m^2/s
X_g : Gas void fraction
d_b : bubble diameter, m

In the reactor, oxygen is consumed and hence k_La is decreasing. Figure 20 presents the k_La values in the inlet and discharge of the tower, based on the values listed in the Table 1.

	Inlet of reactor	Top of reactor
O_2 , kg/ton	20	1
P, bar	7	3.5
Xg	0.2	0.02

Table 1. Values used in the k_La calculation, the used D_{O2}value was 5.7 $*10^{-9}$ m^2/s

Figure 20 shows the calculated mass transfer coefficient (k_La) as a function of bubble diameter. In order to also obtain maximal kappa reduction at the top of the reactor, the k_La value should be larger than about 0.01 1/s (see Figure 19). This is achieved when the bubble size at the top of the reactor is smaller than 0.23 mm and less than 0.5 mm in the feed of the reactor.

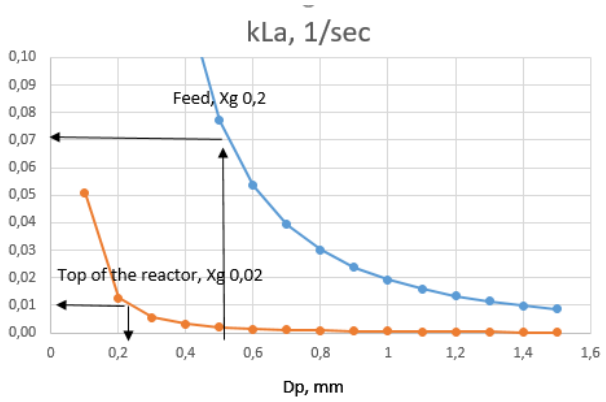


Figure 20. The mass transfer coefficient (k_La) in the function of the bubble diameter in the typical delignification conditions shown in the table 1.

However, the present analysis does not account for several phenomena which result in an even smaller required bubble size, e.g.

- Due to fiber flocculation, the consistency at the bubble size scale is non-uniform
- Instead of using the average volumetric bubble size, the bubble size distribution should be used in the modelling which would yield lower k_La values..
- Even if no coalescence of the bubbles takes place, they might form aggregates which may then decrease the mass transfer.
- The consumption of oxygen in practice may be greater due to reaction with carried over organics which then would decrease the required oxygen bubble size. Another additional consumption of oxygen may be due to use of incompletely oxidized white liquor (Goncalves et al. 2019).

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 equation (2).

Thus the above fundamental modelling of the mass transfer rate shows that the average bubble size should be below a certain level to achieve maximum oxygen delignification, and that this predicted maximum bubble size is in the same range as that measured by the present analytical technique. However, there are still a number of unanswered questions and the presented modelling approach must be incorporated in the overall model of an oxygen delignification tower (van Heiningen, 2003). This comprehensive model which uses the measured bubble size distribution and other operating data as input will be an important tool for control, troubleshooting and further improvement of industrial oxygen delignification. The modelling work is continuing and will be verified through on-going mill and laboratory experiments with the aid of the on-line bubble size measurement technique.

CONCLUSIONS

In the present study it was shown that:

- The new continuous on-line bubble size measurement is working very well
- In the softwood lines, the average volumetric bubble size was about 0.1 mm and in the hardwood line it was almost ten times larger. The mixing of oxygen in these lines was very similar, so it is likely that the difference must come from different surface chemistries in these two lines.
- In both 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 had a clear decreasing effect on the bubble size and the oxygen charge had a clear increasing effect on the bubble size.

- Coalescence of bubbles in the reactor was not observed in the softwood line, but in the hardwood line some coalescence of larger bubbles certainly occurred in the reactor.
- In the test in the hardwood line, the usage of a defoamer had a clear increasing effect on 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 modelling approach, it was concluded, that in practice the volumetric average oxygen bubble size should be around 0.2 mm or smaller.

With the new developed on-line bubble size measurement and new modelling approach it may be possible to better understand, monitor, control and design the oxygen delignification process. The integration of the present modelling approach with the overall model of an oxygen delignification tower (van Heiningen, 2003)may provide a totally new route to improve the oxygen delignification process. The present studies are continuing through modelling and mill studies, e.g. studying how the usage 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 in different production lines will also be collected. One particular interest is to conduct measurements and tests in a eucalyptus pulping line.

ACKNOWLEDGMENTS

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