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MODELLING OF REAL OXYGEN DELIGNIFICATION PROCESSES

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SUMMARY

Previously, extensive work has been done on the modelling of oxygen delignification process, based on how the basic parameters i.e., temperature, kappa number, concentration of alkali and concentration of oxygen affect the delignification rate. However, these models are not used extensively to evaluate the performance of real processes primarily because they have not been able to properly consider all the essential issues affecting to delignification in practice. Such issues are the mass transfer and consumption of oxygen, which defines the concentration of dissolved oxygen in the process and effect of that concentration on the delignification rate. In this paper is used a new way to model the oxygen delignification process where these parameters, among other smaller things, are taken into account. An essential part of these studies was the information obtained from the oxygen concentration measured from the residual gas obtained from the top of the reactor. In the aid of this measurement, it was possible to define more accurately the consumption of oxygen and partial pressure of oxygen which define the concentration of dissolved oxygen in the reactor. By the aid of mill experiments the model was formed which predict the operation of that oxygen delignification process. Model was used to show how much process could be improved by optimizing the charge of oxygen. Also, mill experiments confirmed that mass transfer of oxygen is modelled correctly enough, except if the charge of oxygen is very low and/or the mixing is not efficient enough. In that case there is variation in the concentration of oxygen in the process which should be taken into account in the modelling.

Keywords: chemical pulping, delignification, mill process, modelling, oxygen

INTRODUCTION

There have been many studies related to oxygen delignification and the modelling of oxygen delignification process e.g. [1-3]. However, but on to this moment, there have not been much real attempt made to model the existing mill oxygen delignification processes. The main obstacle is that there has not been sufficient information related to the oxygen mass transfer that determines the concentration of dissolved oxygen, which in turn determine quite far the speed of delignification. Recent studies [4-6] related to oxygen bubble size in delignification processes, effect of bubble size on delignification and the relationship between oxygen bubble size and mass transfer provide the possibility to model real oxygen delignification processes more accurately. In these studies also other essential factors, g e.g. effect of carryover and usage of white liquor as alkali source were taken int account in the modelling. In this paper is used this semi mechanistic model for the numerical evaluation of the real oxygen delignification process.

The main aim of the studies described in this paper was to:

- Use and improve modelling by verifying those parameters which are related to oxygen.
- Develop and use new continuous measurements related to oxygen delignification process, mainly image-based bubble measurement, measurement of residual gas oxygen concentration and measurement of gas void fraction from the pulp.

Oxygen delignification is very important part of chemical pulping process. It is quite simple process but mainly because of uncertainties related to state and role of oxygen, complex connection of oxygen delignification to washing stages and control of process and residual gases in the process, the existing oxygen delignification processes are mostly not jet running in optimal way and there might be lot of room to improve these processes. These improvements may have big economic and environmental effects.

In the long term the purpose of modelling is to use it as a tool, which turn the data from the mill or laboratory tests to basic parameters that determine the delignification rate. By connected modelling to new continuous in- line measurements this give possibility to understand, develop, optimize, compare, improve and control existing processes.

EXPERIMENTAL

The results were obtained by making measurements and collecting information from Finnish two stage softwood oxygen delignification processes, making tests in the mill and modelling the process. The bubble measurement was made with the equipment delivered by Pixact Ltd [6]. The continuous gas void fraction (GWF) measurement was made with clamp on Echowise™ gas analyzer. The oxygen concentration measurement was made with Geotech 110 gas analyser.

In the modelling the delignification rate was calculated as:

$$\Delta K = -A(3*10^6/60)e^{-51000/(8,314T)}([OH^-])^{0.7}(C_{O2})^{0.7}(K)^2\Delta t \qquad (1)$$

Where:
K: Kappa number
T: Temperature, K
[OH-]: Hydroxide ion concentration, mol/l
C_{o2}: Concentration of dissolved oxygen, mol/l.
A: a constant which is set so that the modelling fits to experimental results.

The detailed description of modelling can be found from our previous publication [6].

RESULTS AND DISCUSSION

Earlier it was observed [6] that in this two-stage softwood oxygen delignification process the average bubble size of the oxygen in the feed of the reactors was very small, about 0,1 mm in the reactor I and 0,2 mm in the feed of reactor II. Also, there was clearly lot of residual gas in the top of the reactors and hence, the modelling indicated that both reactors are practically saturated with dissolved oxygen. If this is true, then the charge of the oxygen could be decreased without decreasing the kappa reduction. This was not the case in the mill tests, see figure 1. When the oxygen charge was decreased the kappa reduction also decreased and there was still lot of residual gas in the top of the reactor.

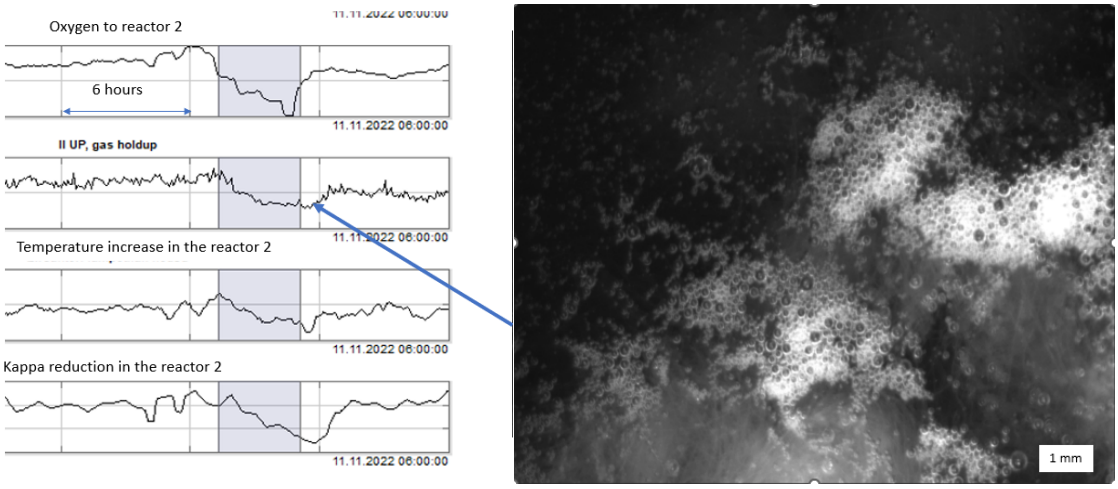

Figure 1. The effects of the oxygen charge in the reactor two.

This was very odd result. There was a possibility to take filtrate from the pulp in the top of the reactor, get the gas sample and measure its's oxygen concentration and it was nearly zero. It turned out that this mill in not using liquid oxygen. They have oxygen producing plant and the purity of oxygen is 93 +/- 0,5 %, so the nitrogen content of the gas is 7 %. This does not sound much but it has a clear effect on the process in this case. This means that using bubble measurement to measure the amount of residual oxygen is not working since there is always residual gas in the top of the reactors with varying concentration of oxygen.

Instead, existence of known amount of nitrogen in the process also gives possibility to quantify the amount of residual oxygen (kg/t) in the process by measuring the oxygen content from the purge gas. In this mill it was possible to obtain proper gas sample from the purge stream where residual gases from the white liquor oxidation and second reactor are connected, see Figure 2. According to mass balance the concentration of oxygen in the second reactor residual gas was 0 kg/t. Here could be also obtained information how far the white liquor is oxidized. This measurement indicate that it is 76 % oxidized. According to [7] the typical value is 75 % and that value was also used in the modelling.

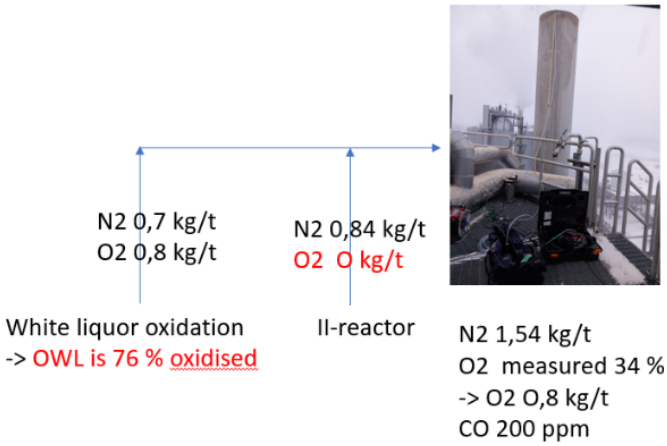

Figure 2. The mass balance of nitrogen and oxygen in the system.

If the concentration of oxygen in the top of the reactor is low then increasing the charge of oxygen should speed up reactions, increase the consumption of oxygen and hence also increase the temperature in the top of the reactor. In the test made in the second reactor this was the case, see Figure 3. When the oxygen charge was increased by 3 kg/t the temperature in the top of the reactor increased about 1 °C. The amount of residual gas in the top of the reactor also increased, but only a bit, which indicate that additional oxygen was mainly consumed.

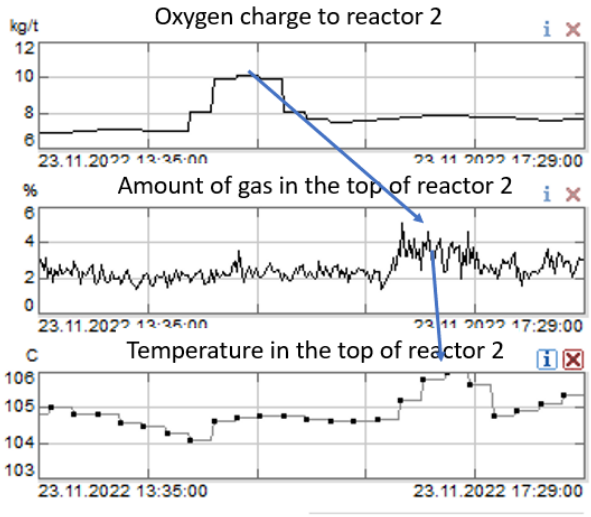

Figure 3. The effect of oxygen charge on the amount of residual gas and temperature in the top of the second reactor.

According to oxygen delignification modelling following result for the concentration of dissolved oxygen in relation to saturation concentration in the reactors is obtained, see Fig 4. When the oxygen charge to reactor two is increased by 3 kg/t, the concentration of dissolved oxygen in the top of reactor two is multiplied. According to modelling this should increase delignification by 0,9 kappa unit and increase temperature by 1,0 °C.

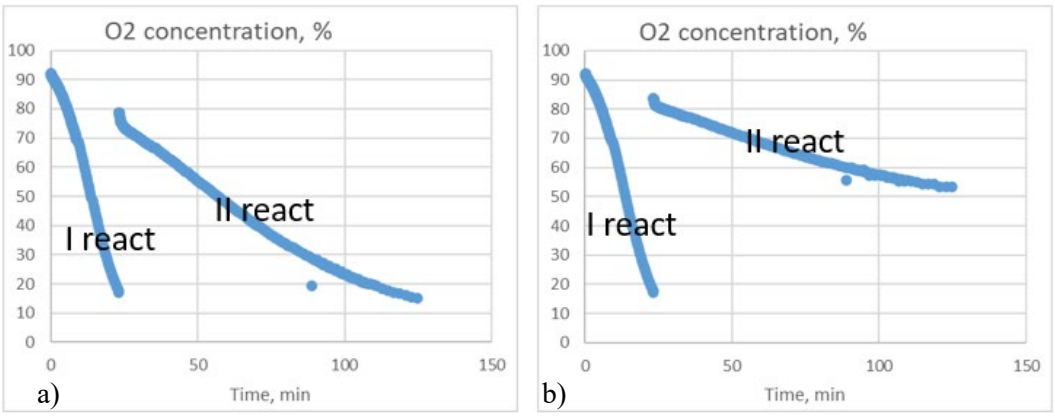

Figure 4. Concentration of oxygen according to modelling in relation to saturation concentration in the reactors without oxygen charge increase (a) and with oxygen charge increase by 3 kg/t to reactor two (b).

According to these results it would be beneficial in this process to increase the charge of oxygen. Residual gases cause some vibrating problems in the reactor one and the residual gases from the reactor two cause problems in the subsequent washing stages. Because of these problems mill want to keep the charge of oxygen as low as possible.

Lately mill has made investments which make possible to remove residual gases from the pulp in the top of the reactors. In same time there was made to both reactors sample points to obtain sample from the residual gas, see figure 5. This give possibility to get new essential information from the process to be used in the modelling. Oxygen concentration tells what is the partial pressure of oxygen in the top of the reactor which then defines the amount of dissolved oxygen. Also, since the amount of nitrogen fed to the process is known, the amount of residual oxygen (kg/t) can be calculated and the exact amount of oxygen consumed in the reactor is then also obtained.

Figure 5. Sampling point and measurement for the residual gas in the reactor two.

Oxygen charge to reactor 1 was increased from 11 to 14 kg/t and same time the concentration of oxygen was measured from the top of the reactor and it increased from 15 % to 55 %, see figure 6. Same time the temperature in the top of the reactor was increased about 0,7 ºC and kappa decreased about 1,3 kappa units.

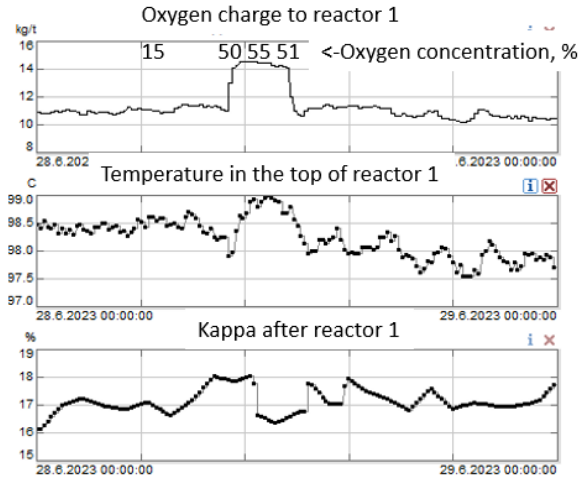

Figure. 6. Oxygen charge to reactor, kappa after reactor, oxygen concentration and temperature in the top of reactor during mill trial.

Model was fixed so that concentration of oxygen in the residual gas was set to 15 % in the top of the reactor and the kappa reduction after both reactors were same in the model as observed in the mill. Concentration of oxygen in the reactors according to modelling is shown in the Figure 7.

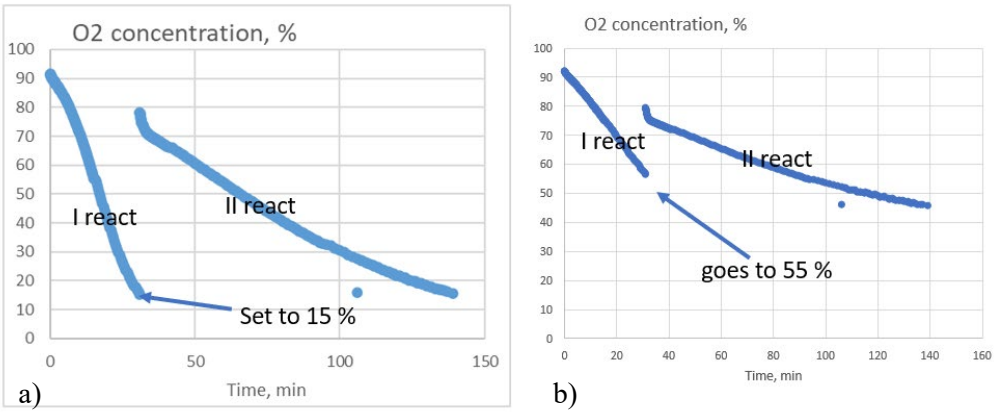

Figure 7. Concentration of oxygen in the reactors without oxygen charge increase (a) and with oxygen charge increase to reactor I by 3 kg/t (b).

According to modelling, 3 kg/t charge increase to first reactor should decrease kappa after first reactor 2,0 kappa units which is quite same as observed in the process. Also, oxygen concentration in the top of the reactor I should rise to 55 % which is same as measured in the mill.

In another test, charge increase, temperature increase and kappa decrease were quite same as shown in the Figure 6, but the oxygen concentration in the top of the reactor increased only to 25 %, see figure 8. Also, according to the modelling it should have been raised to 47 %, see figure 9.

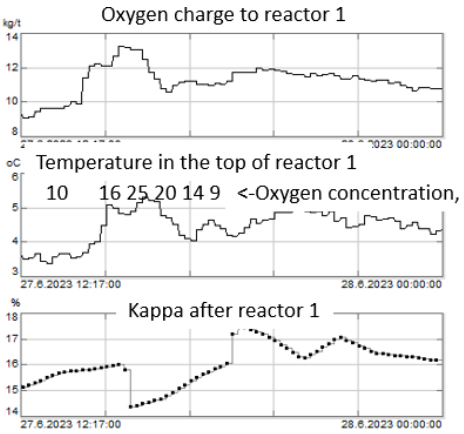

Figure 8. Oxygen charge to reactor, kappa after reactor, oxygen concentration and temperature in the top of reactor during mill trial.

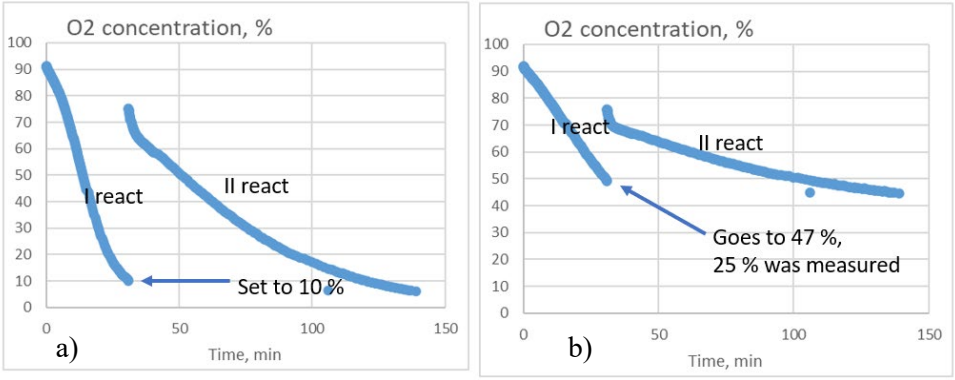

Figure 9. Concentration of oxygen in relation to saturation concentration according to modelling in the reactors without oxygen charge increase (a) and with oxygen charge increase by 3 kg/t.

In the test made in the reactor two similar result was obtained, see figure 10. The charge of oxygen was raised 3 kg/t, temperature was increased and kappa decreased but the concentration of oxygen was not increased at all. This is very odd since if the concentration of oxygen is not increased in the gas phase in the top of the reactor, then, according to modelling, the concentration of dissolved oxygen is not increased hence there is no driving force for increased delignification reactions and nothing should happen.

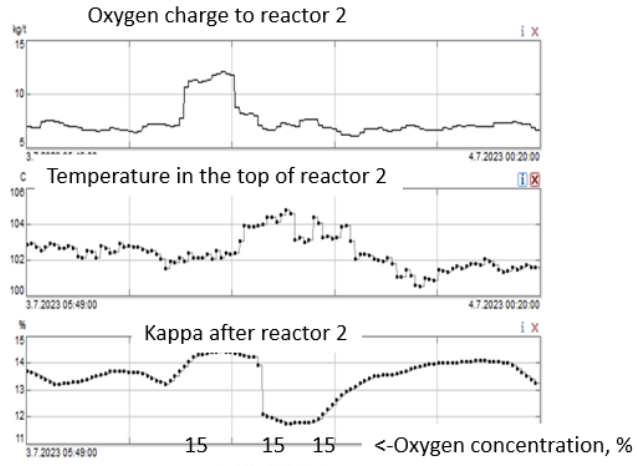

Figure. 10. Oxygen charge to reactor, kappa after reactor, oxygen concentration and temperature in the top of reactor during mill trial.

One explanation for this is that some reason we don't get representative sample for the oxygen concentration measurement. Another interesting explanation is that there is heterogeneities in the reactor. I.e. the consumption of oxygen and/or distribution of oxygen gas in the reactor is not even and there is places where the concentration of oxygen is very small or zero. This seem to be case especially in the reactor two. The motor in the oxygen mixer in the reactor two is much smaller compared to reactor one which may explain this difference. Also, the bubble size of oxygen in the feed of the reactor one was about two times bigger compared to reactor I [6] and bubbles are also forming flocs, see Figure 1, and this may decrease the mass transfer of oxygen.

Residual gases have a negative effect on the performance of the washers after oxygen delignification. There was installed two gas measurements to the feed of DD-washer after oxygen delignification. In the figure 11 is shown the gas content based on the Echowise and bubble imaging-based measurement and example of the bubble image. These measurements give quite similar results and they also indicate that gas content in the feed of DD washer can be quite high.

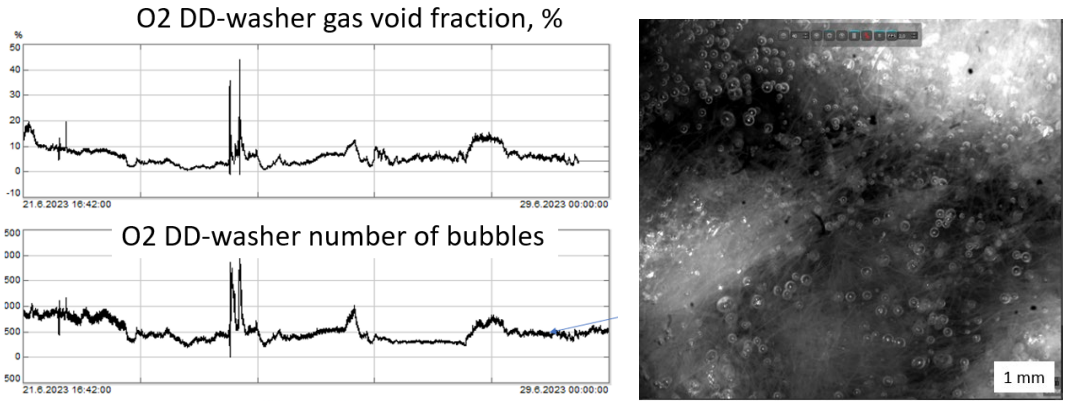

Figure 11. Gas content in the DD-washer feed pulp based on the Echowise and bubble imaging-based measurements and example of the bubble image.

During the mill test the aim was also to get information how increasing of oxygen charge increase the gas content in the feed of DD-washer, see figure 12. This information was not obtained since the oxygen charge increased the temperature in the top of the reactor II, this increased vaporization of water and hence removal of gases from pulp and the gas content in the washer decreased.

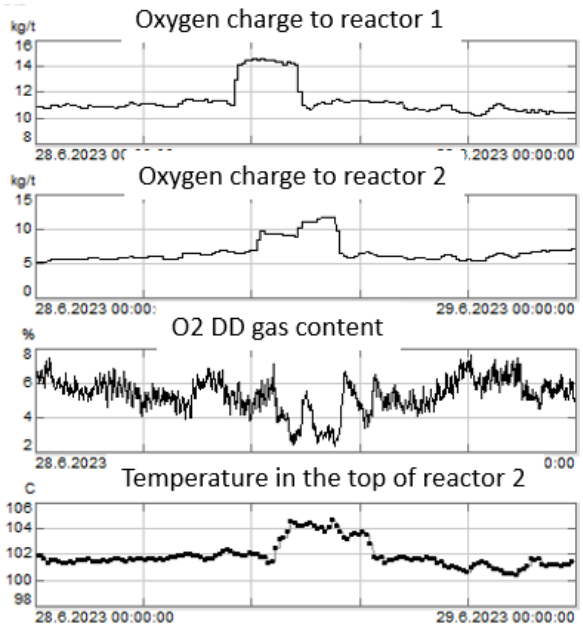

Figure 12. The effect of oxygen charge to the gas content in the feed of DD-washer pulp and to the temperature in the top of the second reactor.

Next good questions are that are the new gas removal systems in the top of the reactors working so well that oxygen charges could be increased and even so well that removal of residual gases by flashing is not necessary any more and process temperatures could be decreased. The heating of pulp before reactor II is made with steam. If the temperature in the reactor could be decreased 2 °C the production of electric energy could be increased in this mill about 4 MW.

CONCLUSIONS

In this paper, the modelling of real oxygen delignification processes was developed further, connected to new continuous in-line gas measurements and used to analyse mill results.

The concentration of oxygen in the residual gas was taken as a new measurement to the modelling of the oxygen delignification processes. On the base of this measurement the oxygen gas partial pressure and the consumption of oxygen and hence the concentration of dissolved oxygen in the reactor could be modelled more precisely and measurement could be used to optimize the feeding of oxygen in practice. Continuous oxygen concentration measurement is in this moment under development and testing. Also, continuous gas content measurement could be used to monitor the amount of residual gases from oxygen delignification in the washing.

Results indicate that modelling of oxygen mass transfer may work enough well. In addition, in some cases, especially when the charge of oxygen is low and when the mixing of oxygen is not very strong the concentration of oxygen in the reactor may vary so much that this has a negative effect on the delignification and modelling is not working as such.

There are still lot of open questions related to modelling. However, modelling provides a base to extract the essential information from laboratory tests and mill processes. Therefore, it can also be used to analyse and predict the operation of mill processes and to further develop the modelling itself.

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