Model development for real oxygen delignification processes

Jari Käyhkö, XAMK, FiberLaboratory
Kari Peltonen, Andritz Oy
Markus Honkanen, Pixact Ltd.
Antti Kokkonen, Buckman Inc. Finland
Adriaan van Heiningen, University of Maine

Modelling of real oxygen delignification processes: Outline of the presentation

- The motive of this study
- Modelling principles
- Materials, methods, laboratory and mill studies
- Modelling results based on the laboratory and mill studies
- Discussion and conclusions

The motive of this study

- Studies related to oxygen:
  - Development of new continuous in-linen bubble size measurement (Käyhkö et al. 2017)
  - Laboratory and mill studies based on this measurement (Käyhkö et al. 2019)
  - Connection between bubble size and oxygen mass transfer defined (Käyhkö et al. 2021)
  - -> This give possibility to model mill processes more accurately
- Modelling can be used to predict the performance of mill processes but also to extract from laboratory and mill data essential basic information or parameters related to modelling.
- We are mostly interested parameters related to oxygen consumption and mass transfer which determine the concentration of dissolved oxygen in the process and the effect of this concentration on the delignification rate.
  - Residual oxygen cause problems in subsequent process especially in the washing -> optimization of the feeding of oxygen.
  - Mill processes work in in average in 80 % efficiency compared to laboratory delignification (van Heiningen et al. 200x). They assumed that reason for this can be too low mass transfer of oxygen i.e. too big oxygen bubble size.

Modelling equations and constants

$$k_L a = \frac{12 D_{O^2} X_g}{B * ((1/X_g)^{1/3} - 1) {d_b}^2}$$

$$N = k_L a({C_{O^2}}^* - C_{O^2})\Delta t$$

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

$$\Delta[OH^-] = \frac{1{,}5 b_2}{40}\left(\frac{c}{100}\right)\Delta K \qquad r_{0^2} = \frac{1{,}5 b_1}{32}\left(\frac{c}{100}\right)\Delta K$$

D_{O^2}= Diffusion coefficient of oxygen, $5.7*10^{-9}$ m^2/s

B: constant which decrease $k_L a$ value because of different heterogeneities, 4,0

A: Constant which change reaction speed

b_1 = g O_2 consumed / g lignin reacted, 1,0

1,5 : one softwood kappa unit represents 1.5 grams of lignin in 1.0 kilogram of pulp

b_2: g NaOH consumed / g lignin removed. 0,9

Washing loss:

- Lignin in the water phase is assumed to be 1/3* COD value, 70 % oxidized non reactive, lignin behaves similarly as lignin in fiber
- Alkalinity coming with carry over is added to NaOH charge

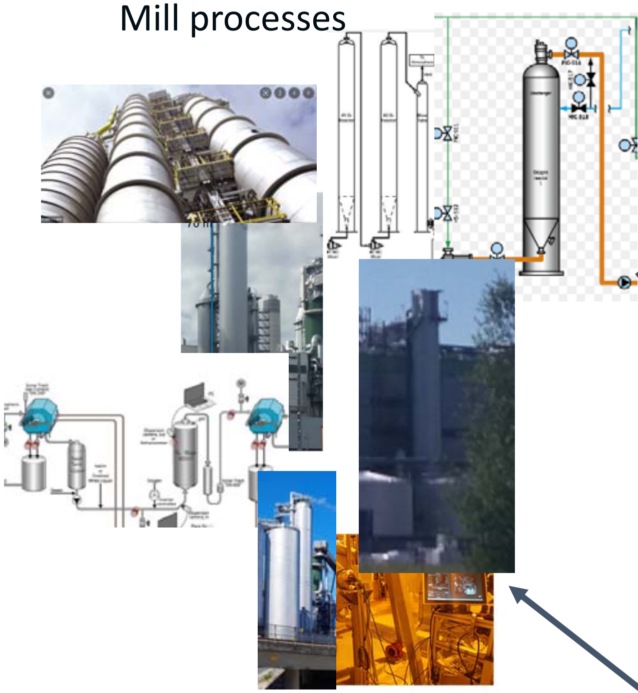
HW: HexA free kappa used in the calculation

${C_{O^2}}^*$= 0,2 g/l (8,3 bar, 95 °C)

Oxidised white liquor (OWL): 75 % oxidized so it will consume 0,13 kg oxygen/kg OWL, NaOH content = 0,56*OWL

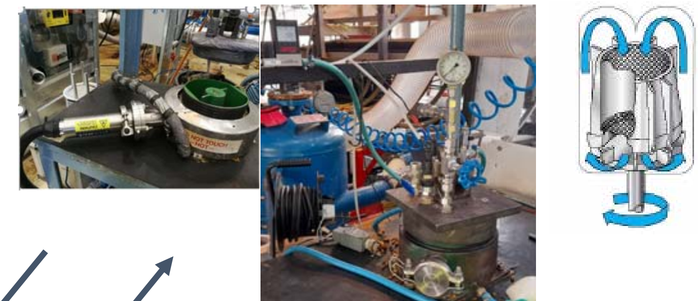
(Van Heiningen et al. 2003, Käyhkö et al. 2019)

Mill processes



Samples

Laboratory delignification and tests



Process data

Lab data

Predicting

Verification and improving the modelling

Literature and other sources

Modelling equations and constants

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Studing
Predicting
Optimization
Adjusting
Benchmarking

Basic information about oxygen delignification
-> Role of Oxygen

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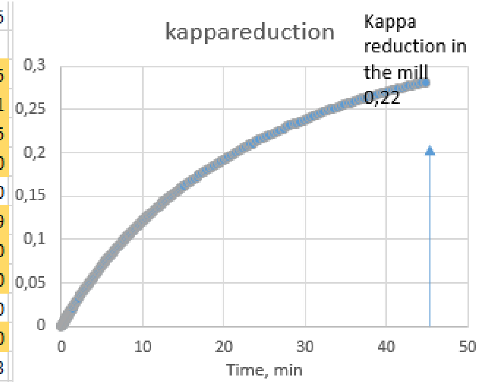
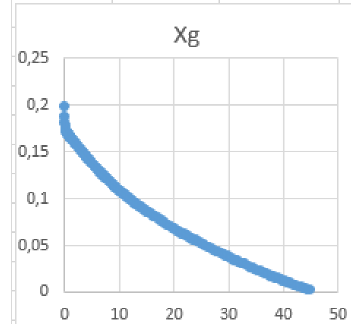
Example of the excel sheet used for the modelling: Hardwood

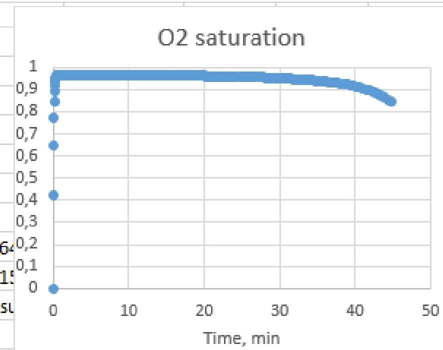
tank d	m	3,880956
tank PA	m2	11,82353
tank h	m	34
tank V	m3	402
production	Adt/d	1500
Pulp C	%	12
Flow	m3/h	12500
dwell time	min	46,3104
pulp speed	m/min	0,012236
average bubble size		0,15
	Potenssit	
	tai arvo	
NaOH	0,7	
O2	0,7	
Kappa	2	
Kappra red. Fixing	6	
b1 (O2 consumed)	0,8	
b2 (OH consumed)	0,9	
D, O2 Diff, coeff.	5,7E-09	
Kla B coefficient	4	

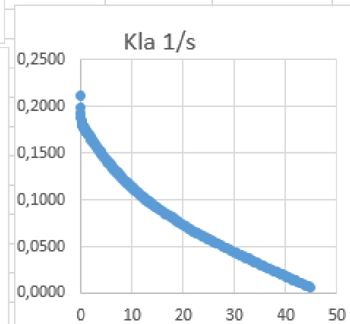
Hexa	6,5
	In
kappa	17,5
Hexa free Kappa	11
Pressure, bar	6,5
Alkaline leaching	0
temperature average, oC	90
O2, kg/ton	9
NaOH charge, kg/Adt	20
Washing loss OH kg/Adt	10
Total NaOH, kg/Adt	30
washing loss, COD, kg/Adt	100
dissolved lignin kg/Adt	33,3333333
Dissolved kappa	20,8
dissolved unoxid kappa	6,9

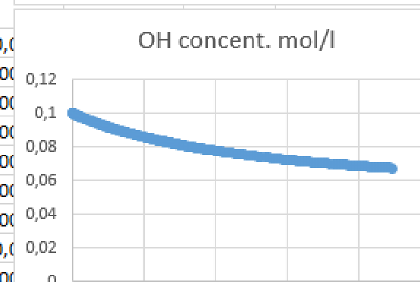
								9,64
			32,88	3,21		O2		1,15
	time	Time	height	pressure	Xg	saturat conc.	dissolution	consu
	min	s	m	bar		g/l	g/l	g/l
2	0	0	0,0	6,5	0,198749	0,160	0,06764574	
2	0	2	0,0	6,50	0,187865	0,160	0,03658744	0,(
2	0	4	0,0	6,50	0,182006	0,160	0,02175282	0,0(
2	0	6	0,1	6,49	0,178548	0,160	0,01374712	0,0(
2	0	8	0,1	6,49	0,176385	0,160	0,00916465	0,0(
2	0	10	0,1	6,49	0,174965	0,159	0,0064523	0,0(
2	0	12	0,1	6,49	0,173984	0,159	0,00481385	0,0(
2	0	14	0,2	6,48	0,173268	0,159	0,00381101	0,0(
2	0	16	0,2	6,48	0,172714	0,159	0,00319152	0,(
2	0	18	0,2	6.48	0.172261	0.159	0.00280603	0.0(

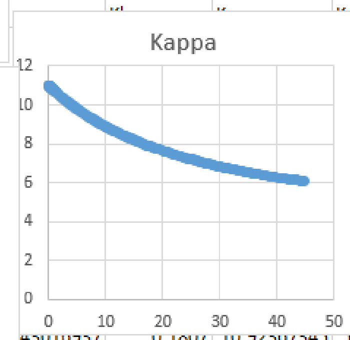




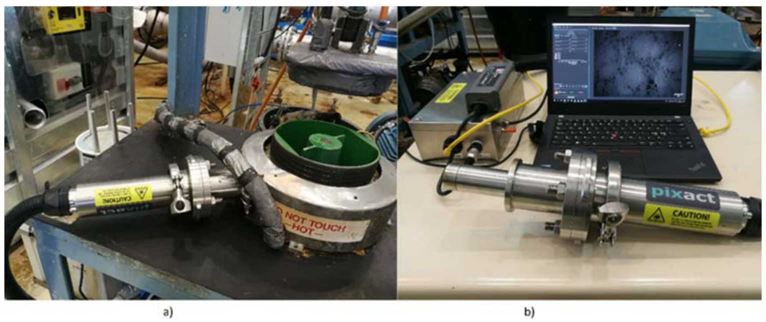




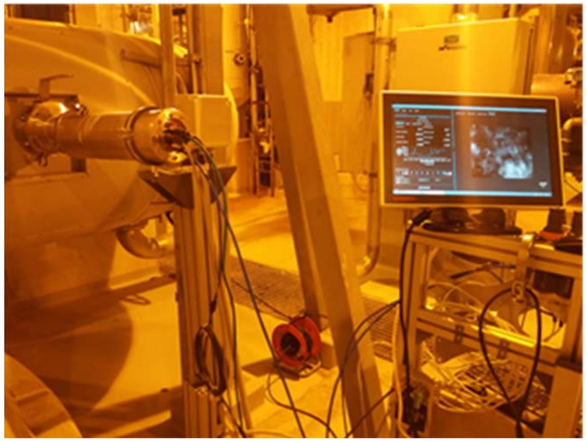




Materials, methods, laboratory and mill studies



Mark reactor (a) and bubble size measurement (b) used in the laboratory delignification.



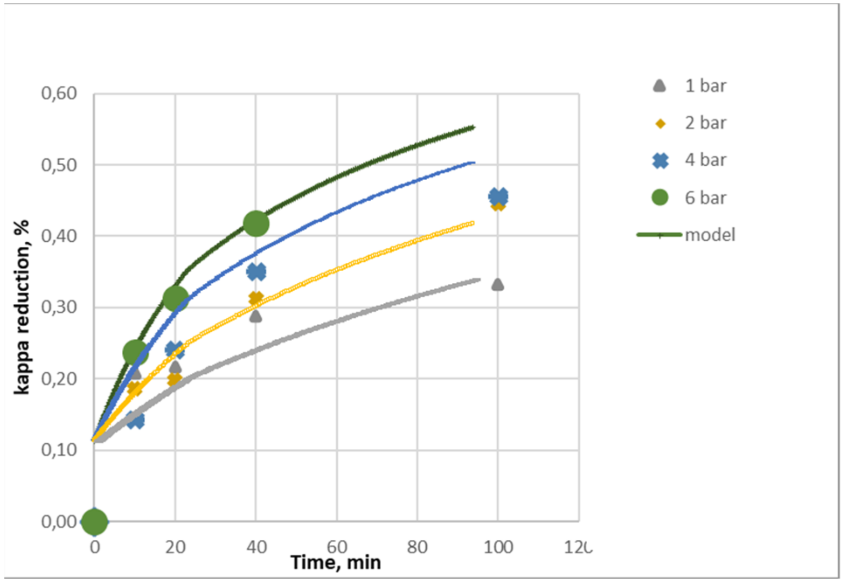
Bubble size measurement in the feed of the reactor.

Two stage oxygen delignification process

Softwood process, two stage, feed kappa 26-31

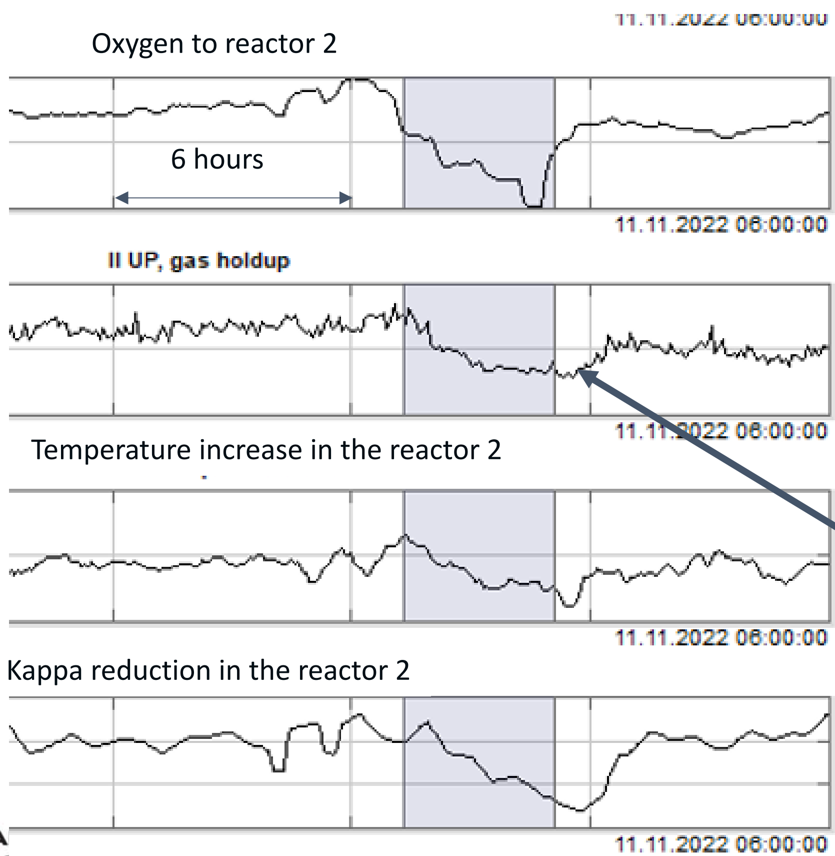
-> Feed pulp samples and process data collected mill in same time
-> In Mark delignification strong and repeted mixing -> Bubbles are small and reactor is all the time saturated with oxygen.

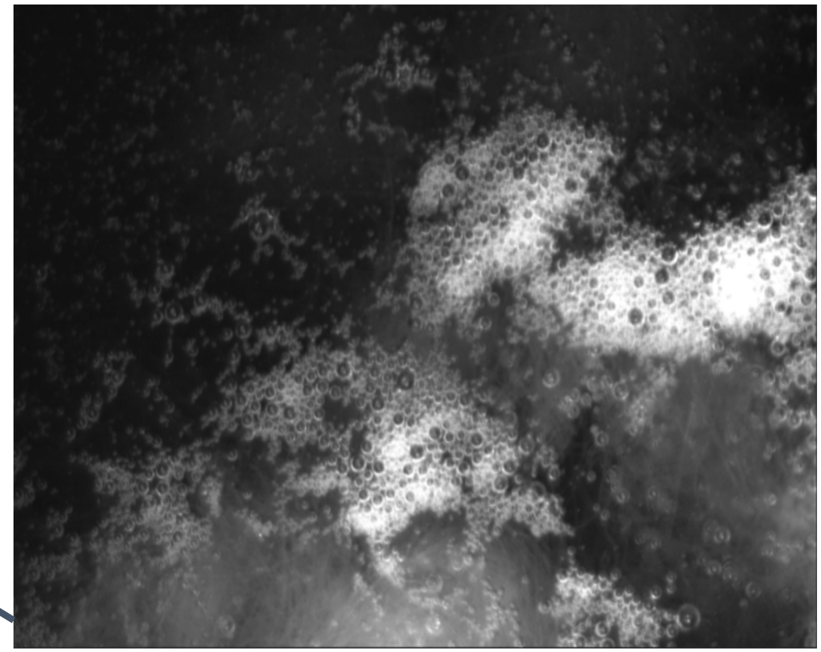
The effect of oxygen pressure on the delignification obtained in laboratory tests and according to modelling.



-> modelling seems to predict quite well the effect of oxygen pressure, i.e. the concentration of dissolved oxygen on the delignification.

Effects of the oxygen charge in reactor 2.





Lot of small bubbles left in the top of the reactor and it should be saturated with dissolved oxygen -> Why Kappa reduction goes down ?

1 mm

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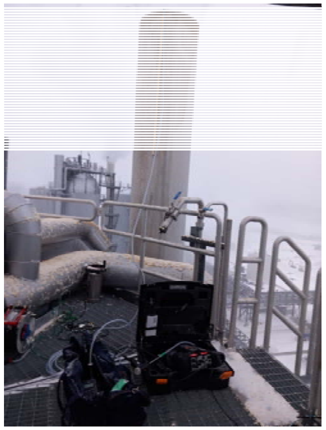
-> There is no oxygen left in gas phase -> purity of oxygen used in the process is 93 %

Oxygen (93 %) and nitrogen flows



N2 0,7 kg/t
O2 0,8 kg/t

N2 0,84 kg/t
O2 0 kg/t

White liquor oxidation
-> OWL is 76 % oxidised

II-reactor

N2 1,54 kg/t
O2 measured 34 %
-> O2 O,8 kg/t
CO 200 ppm

-> Concentration of oxygen can be very low in the top of the reactor

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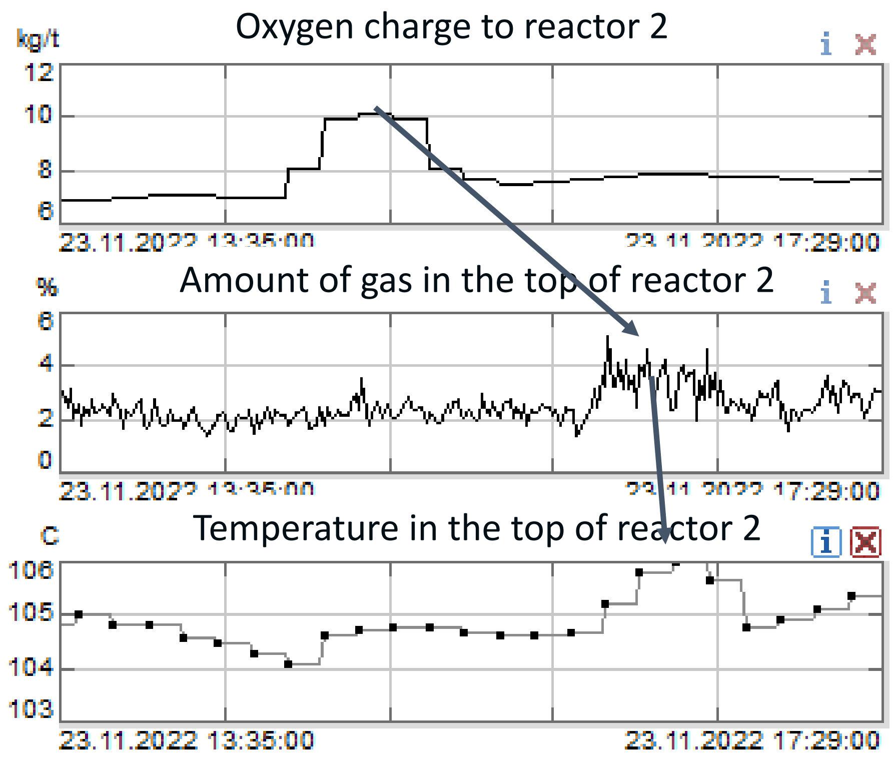
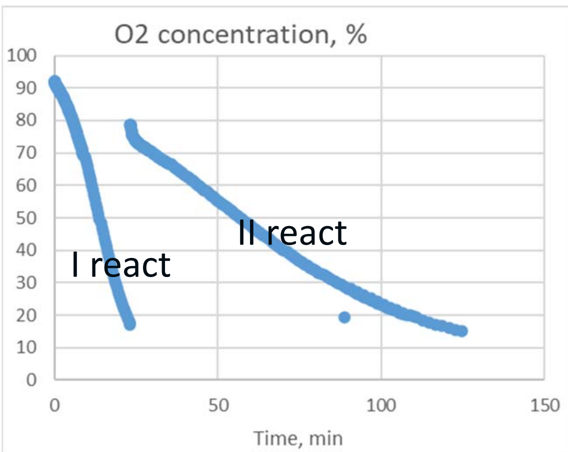
Effect of oxygen charge on the amount of residual gas and temperature in the top of the second reactor.

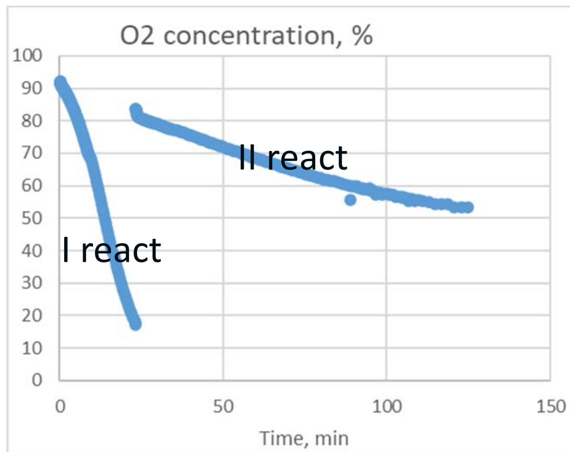
According to the modeling, temperature should increase 1.0 °C and kappa decrease 0.9 kappa units



Concentration of oxygen in the reactors without oxygen charge increase (a) and with oxygen charge increase by 3 kg/t to reactor 2 (b).



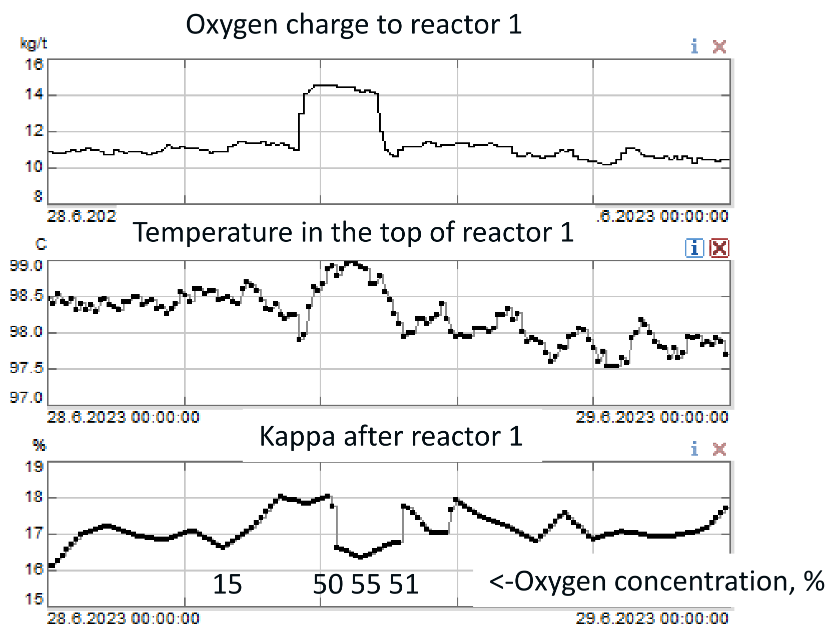
a



b

Sampling point and measurement for the residual gas in reactor 2.

Oxygen charge to reactor 1, kappa after reactor, oxygen concentration and temperature in the top of the reactor during the mill trial.



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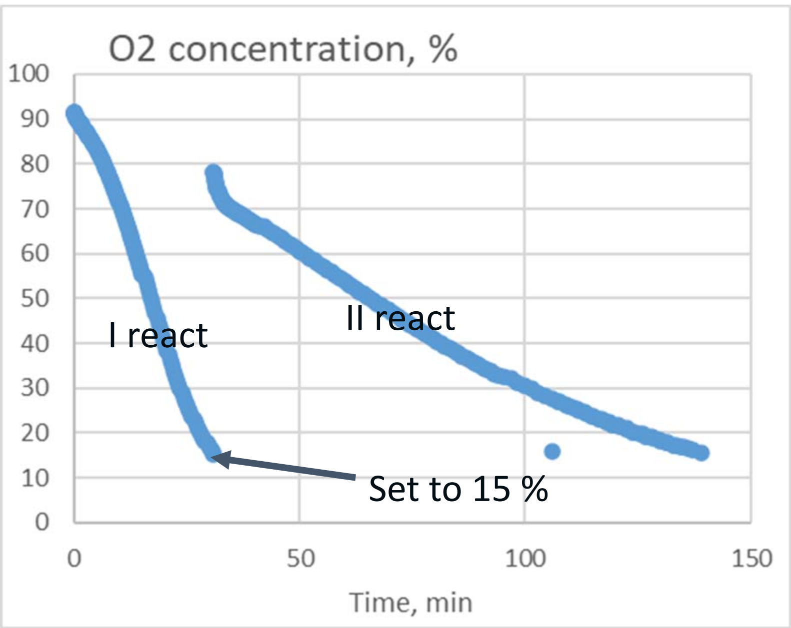
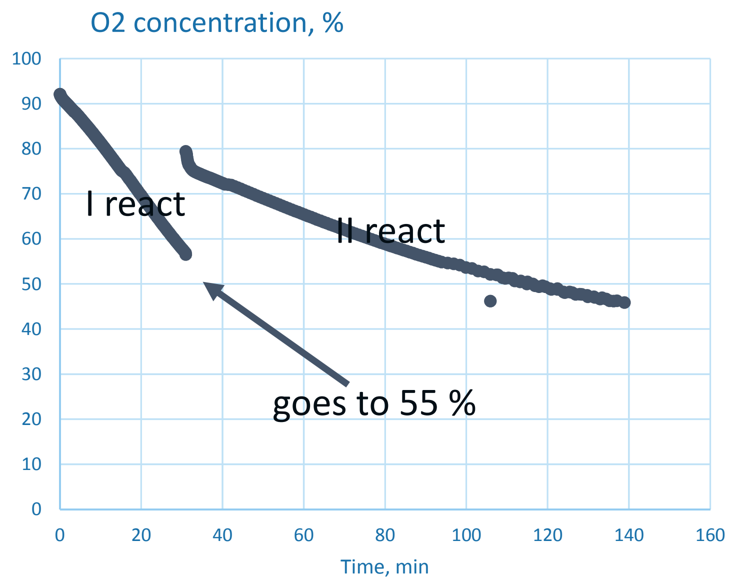
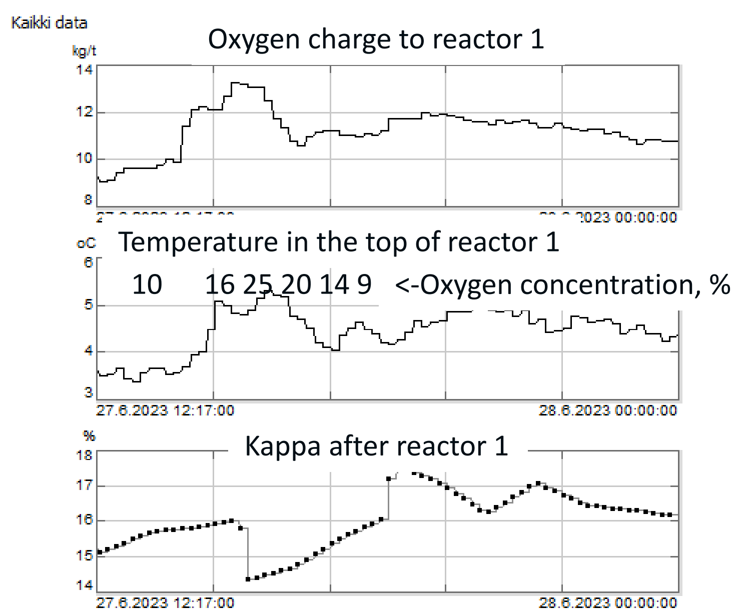
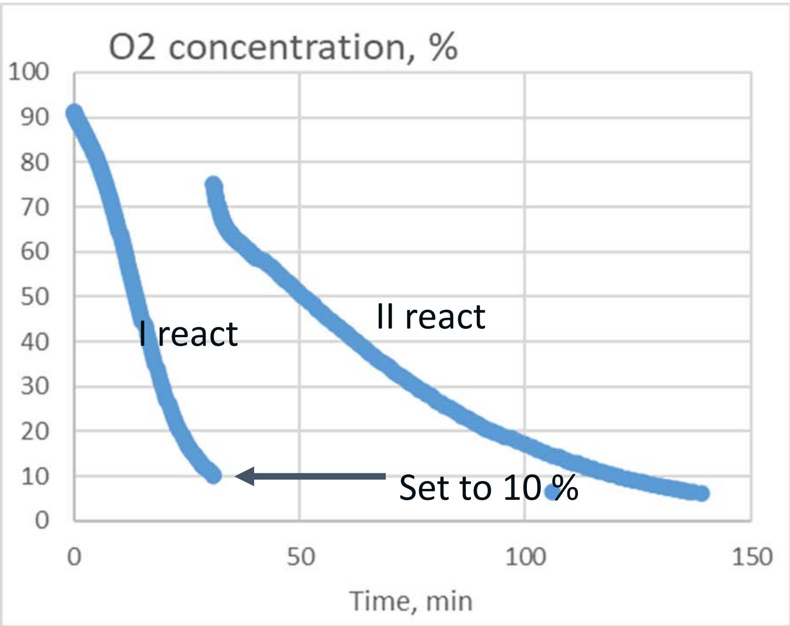


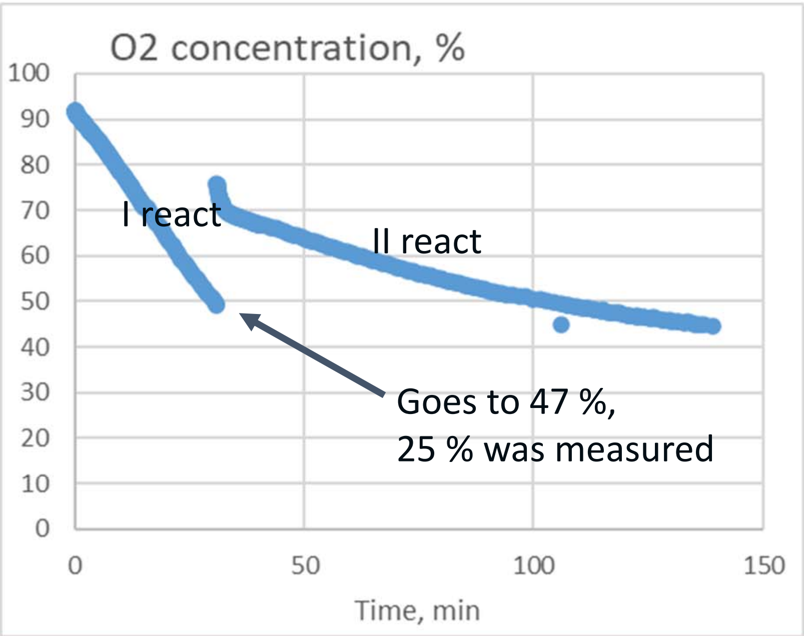


Oxygen charge to the reactor 1, kappa after reactor, oxygen concentration and temperature in the top of the reactor during the mill trial.

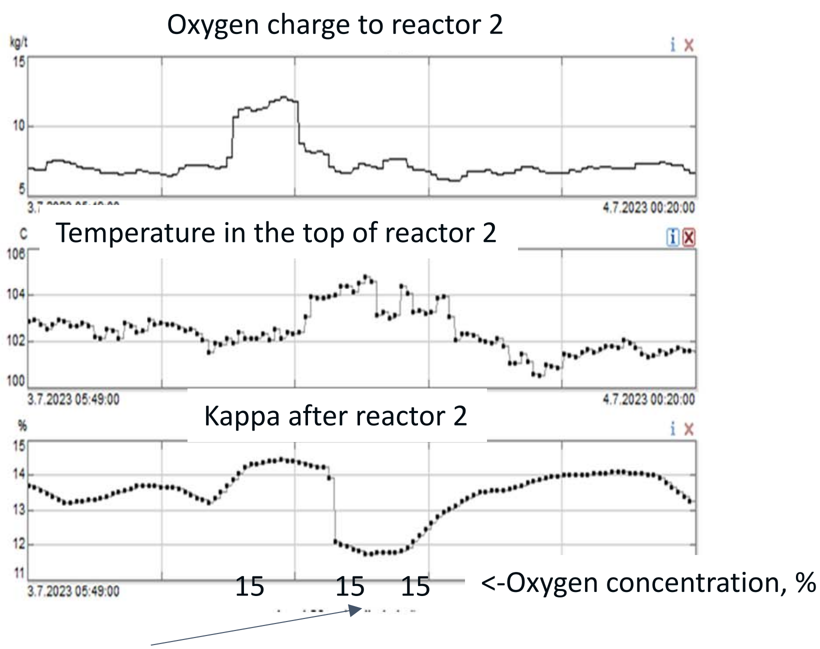


Concentration of oxygen in the reactors without oxygen charge increase (a) and with oxygen charge increase to reactor 1 by 3 kg/t according to modelling.





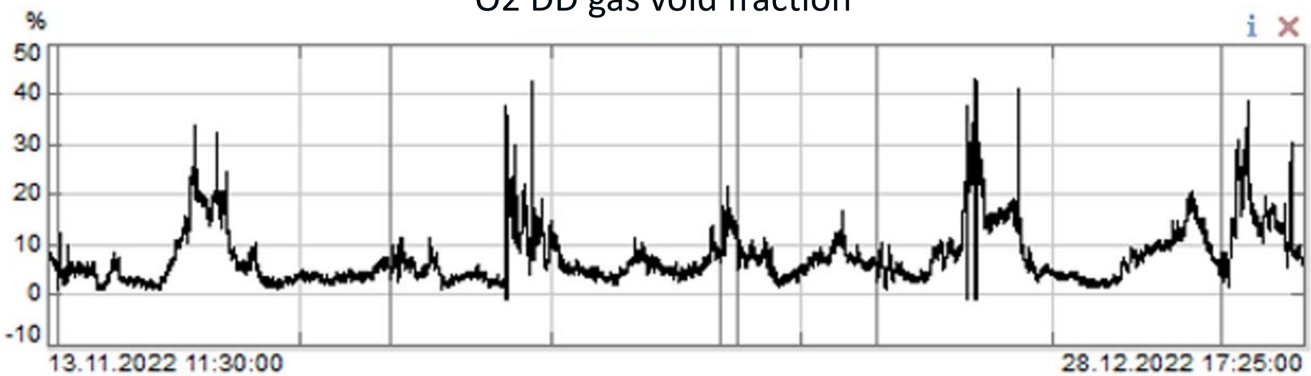
Oxygen charge to reactor 2, kappa after reactor, oxygen concentration and temperature in the top of the reactor during the mill trial.



Why this is not increasing -> heterogeneities in the concentration of oxygen gas ?

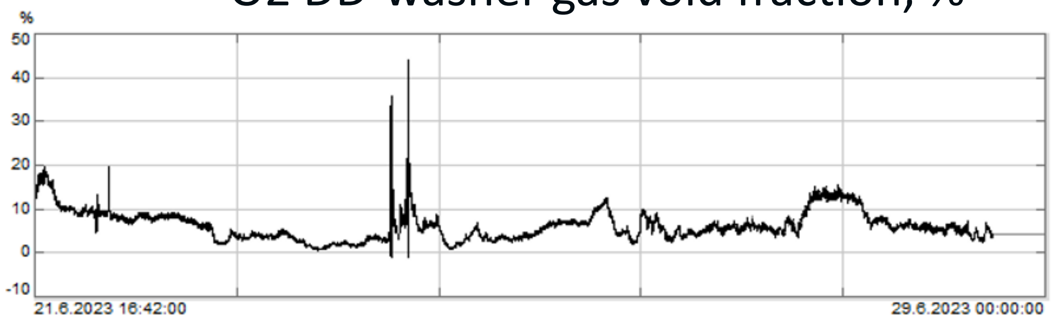
Gas content in the feed of the DD-washer measured with Echowise gas measurement.

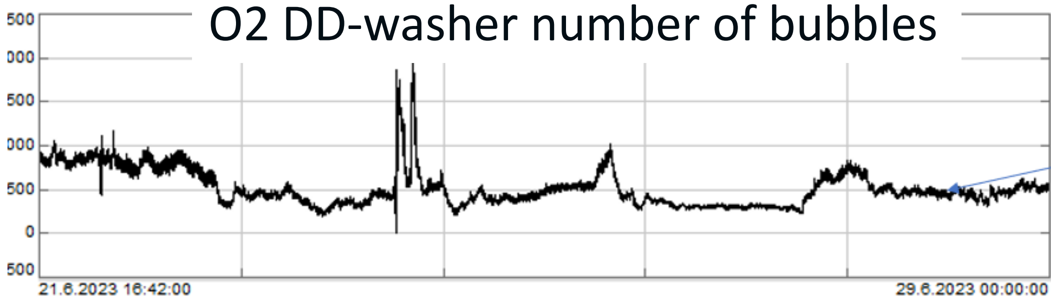
O2 DD gas void fraction

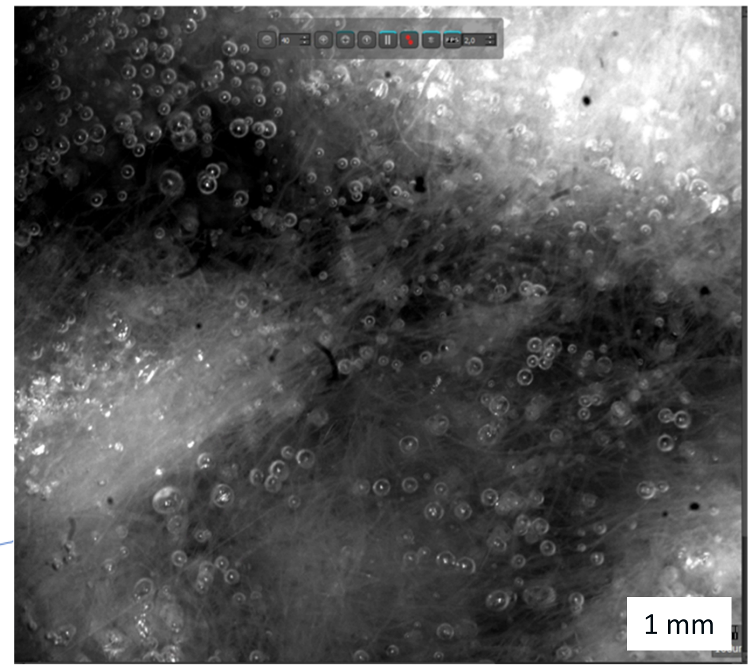


Gas content in the DD-washer feed pulp based on the Echowise and bubble imaging-based measurements and an example of the bubble image.

O2 DD-washer gas void fraction, %

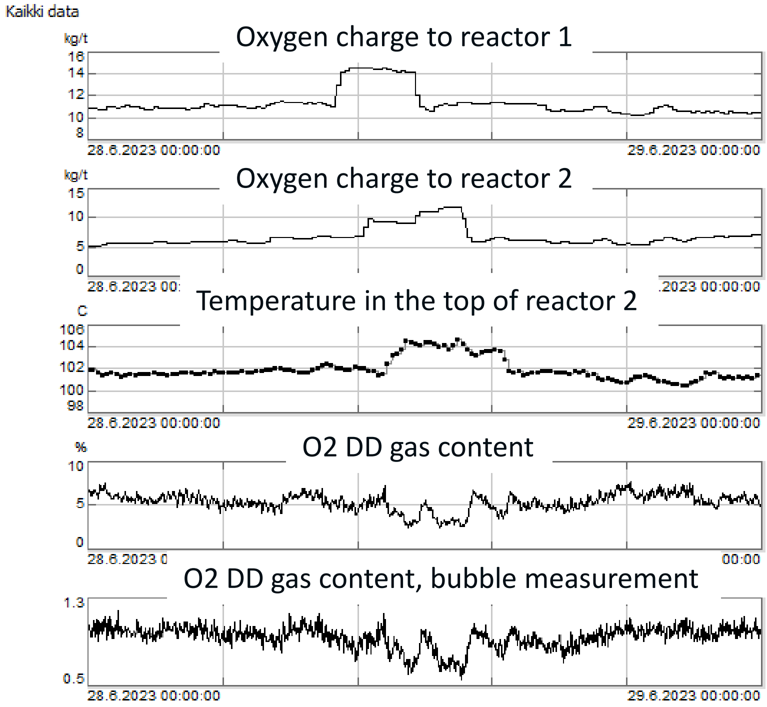






Effect of oxygen charge on the gas content in the feed of the DD-washer pulp and the temperature in the top of the second reactor.

-> Temperature is increased, this improve gas removal and gas content in the washer is decreased



DISCUSSION AND CONCLUSIONS

- Modelling is useful tool to study and evaluate the performance of mill processes and basic phenomena related to oxygen delignification process.
- In this process:
  - The concentration of oxygen in residual gas was taken as a new measurement to be used in the studies and it could even be used to optimize the feeding of oxygen in practice.
  - The concentration of oxygen in the top of the reactors was very small. So, this process could be improved by increasing charge of oxygen and decreasing charge of alkali.
  - This could be possible:
    - If the improvements made lately for the removal of residual gases in the top of the reactors are working enough well.
    - By the aid of new continuous measurements related to gases, especially the measurement of gas void fraction in the feed of O2 DD washer.
  - There might be severe heterogeneities (in large or small scale) related to oxygen gas in rectors which have a negative effect on the delignification.

Thank you

Acknowledgements: These studies were financed mainly by ERD fund through South Savo Regional Counsil.