Bleaching

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Assessment of Q(OP)D(PO) bleachability of softwood kraft pulp

<https://doi.org/10.1515/npprj-2021-0022>

Received March 29, 2021; accepted September 6, 2021; previously published online September 30, 2021

Abstract: Bleachability is evaluated as how easily a pulp sample is bleached and it depends on the structure of residual lignin and carbohydrates. Also, the bleachability varies depending on the bleaching sequence. ECF light sequences have been improved significantly in the recent years. However, we still don't fully understand how ECF light bleach plants are optimally run. This work studies the bleachability of softwood kraft pulp in an ECF light bleaching sequence, (OO)Q(OP)D(PO). Three pulp samples with brown stock kappa number 27, 32 and 35 were bleached and studied for residual lignin, hexenuronic acid and carbohydrate content. It was found that in the bleaching stages that are highly delignifying, it is beneficial with a higher kappa number for the delignifying bleachability. However, in the bleaching stages where the objective is brightness increase, the brightness gain bleachability is improved by a lower kappa number. We also intended to determine which of the three samples had the best suited kappa number for this particular bleaching sequence. According to our results, the bleaching was most effective with kappa number around 32. Although an even higher kappa number resulted in higher yield after cooking, it seemed that this bleaching sequence cannot preserve the yield gain.

Keywords: brightness gain; chlorine dioxide; delignification; ECF light bleaching; kappa number.

Introduction

Bleaching of chemical pulp is a process where residual lignin, chromophores and extractives are removed from the brown stock pulp to produce bright and clean products such as printing paper, tissue and packaging board. In order to maintain a high selectivity in the bleaching process, with high yield and pulp quality as a result, the bleaching is carried out in a sequence, alternating between bleaching stages. Modern bleaching sequences can be divided into either elemental chlorine free (ECF) or totally chlorine free (TCF) bleaching sequences. In ECF, the process is based on bleaching with chlorine dioxide of various charges (Björklund *et al.* 2002, Hart and Connell 2006, Lachenal *et al.* 2008). In TCF, the pulp is bleached with chemicals that do not contain any chlorine, but oxygen based chemicals such as oxygen, hydrogen peroxide (Brelid *et al.* 1997, Sjöström 1998), ozone and peracetic acid. Recently, a new type of bleaching sequence, ECF light, has been developed and implemented in a number of pulp mills (Stratton *et al.* 2004, Starrsjö *et al.* 2020). ECF light processes combine the efficiency and high selectivity of chlorine dioxide bleaching with more environmentally friendly oxygen based bleaching chemicals. However, better understanding of optimal bleach plant operating parameters is needed, in order to minimize the environmental impact and cost while assuring high pulp quality.

One approach to improve a bleaching process is to evaluate the bleachability, i. e. how well the pulp respond to the bleaching chemicals. What gives a good bleachability varies depending on the specific bleaching sequence and the treatment history of the unbleached pulp (Gustavsson *et al.* 1999, Ragnar 2004). The effect of pulp-plant conditions on the bleachability has been the object of much research. Cooking with a higher effective and residual alkali and temperature gives better bleachability, but do not favor yield and selectivity (Carnö *et al.* 1975, Sjöström 1998, Colodette *et al.* 2002, Axelsson *et al.* 2002, Gellerstedt and Wafa Al-Dajani 2003, Axelsson and Lindström 2004, Axelsson *et al.* 2004). Ionic strength and origin of raw material are also contributing factors (Sjöström 1999, Martino *et al.* 2013). Structures in the pulp can affect

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the bleachability, including residual lignin characteristics and lignin-carbohydrate complexes. A high β -aryl ether content in the residual lignin after the cook contribute to a better bleachability in alkaline peroxide bleaching (Gustavsson *et al.* 1999, Gellerstedt and Wafa Al-Dajani 2000). The amount of delignification in the cook and oxygen delignification also affects the bleachability with higher brown stock lignin content being beneficial (Pascoal Neto *et al.* 2002, Axelsson *et al.* 2004, Bourbonnais *et al.* 2004, Hart and Connell 2006, Segura *et al.* 2016). The optimal brown stock kappa number for pulping and bleaching costs depends on the sequence and the brightness target (Hart and Connell 2006). Hexenuronic acid (HexA), is formed in the cook from 4-O-methylglucuronic acid units on the xylan chain, and is known to contribute to the kappa number, consume bleaching chemicals and cause brightness reversion of bleached pulp (Buchert *et al.* 1995, Bergnor-Gidnert *et al.* 1998, Granström *et al.* 2002). Bleachability is used with various definitions in the literature. The concept of oxidation equivalents (OXE) was defined by Grundelius (1993) as the combined oxidizing power of all bleaching chemicals in a sequence. It is often converted to OXE per kappa number units to reach a certain brightness. However, the OXE concept has been criticized for not taking into account the differences in reaction pattern between the numerous bleaching chemicals (Ragnar 2004).

To summarize the findings in the bleachability literature, many studies show that the bleachability depends

on the preceding treatment of the pulp. This is due to the difference in composition and structure of the lignin and carbohydrates present in the unbleached pulp. However, what exactly gives a good bleachability depends on the specific pulping conditions and bleaching process. None of the published work cover the above mentioned new type of ECF light bleaching sequence for softwood kraft pulp. In this study, we aim at filling part of this research gap.

We intend to evaluate the bleachability in the ECF light bleaching sequence (OO)Q(OP)D(PO). (OO) is oxygen delignification in two stages, Q is a chelating treatment, (OP) and (PO) are hydrogen peroxide reinforced alkaline oxygen stages and D is bleaching with chlorine dioxide. Here, we define bleachability as the delignifying bleachability (1) and brightness gain bleachability (2). The delignifying bleachability is defined as kappa number units reduced per kilo of bleaching chemical for each bleaching stage. The brightness gain bleachability is defined as units of brightness increases per kilo bleaching chemical for each bleaching stage. They are arranged so that a higher value means better bleachability. Three softwood kraft pulp samples with brown stock kappa number 27, 32 and 35 have been lab bleached and analyzed in regards to yield, pulp viscosity, carbohydrates and brightness ceiling. Using the above bleachability definitions, we intend to determine the best suited kappa number level for this particular bleaching sequence. The study is illustrated in Figure 1.

Figure 1: Schematic illustration of pulp samples and laboratory procedure.

Delignifying bleachability:

$$\frac{-(\text{kappa number of pulp after stage X} - \text{kappa number of pulp before stage X})}{\text{Charge bleaching chemical in stage X [kg/odt]}} \quad (1)$$

Brightness gain bleachability:

$$\frac{\text{ISO brightness of pulp after stage X [\% ISO]} - \text{ISO brightness of pulp before stage X [\% ISO]}}{\text{Charge bleaching chemical in stage X [kg/odt]}} \quad (2)$$

Experimental

Materials

The starting material were brown stock softwood kraft pulp from the SCA Östrand pulp mill, Table 1. Upon collection the pulp samples were washed with deionized water, dewatered to 30 % consistency, homogenized and stored in polyethylene bags at 5 °C.

Methods

The laboratory two-stage oxygen delignification, O1 and O2, as well as the bleaching sequence Q(OP)D(PO) were carried out according to Table 2. The pressurized bleach-

ing stages (O1, O2, OP and PO) were carried out in teflon-lined autoclaves in a preheated rotating polyethylene glycol bath. The oxygen delignification was configured to remove 60 % of the unbleached kappa number. The sodium hydroxide (NaOH) charge was varied to achieve the desired kappa number and final pH. The Q and D stages were done in the same way for all pulp samples, in polyethylene bags in a preheated water bath. The hydrogen peroxide (H₂O₂) charge in the OP stage was varied in order to achieve the same incoming kappa number to the D stage. A series of pretrial OP stages were carried out in order to find the H₂O₂ charges. In the last bleaching stage, PO, five charges of H₂O₂ were applied, to reach a final brightness in the interval 87–92 % ISO, and to find the brightness ceiling for all pulp samples. Interpolation was used to calculate the values at 88 % ISO.

Table 1: Starting pulp samples collected at SCA Östrand pulp mill.

Sample	Date, time	Kappa number	ISO brightness, %	Viscosity, ml/g
K27	2020-03-17, 10:30	26.6	29.5	1091
K32	2020-03-24, 10:55	31.9	26.8	1123
K35	2020-02-18, 17:30	34.9	27.8	1085

Table 2: Laboratory parameters for oxygen delignification (O1O2) and bleaching (Q(OP)D(PO), odt=oven dry ton. In O1, the sodium hydroxide charge was 26 kg/odt for K27, 31 for K32, and 30 for K35. The same denotation goes for the hydrogen peroxide charge in the OP stage. In PO, five hydrogen peroxide charges between 2 and 15 kg/odt were applied to all pulps.

		O1	O2	Q	OP	D	PO
O ₂	MPa	1	0.5		0.5		0.5
NaOH	kg/odt	26/31/30					
MgSO ₄	kg/odt	2			1		0.5
ClO ₂	kg/odt					8	
Active Cl	kg/odt					21	
H ₂ O ₂	kg/odt				3/6/8		2, 3.5, 5, 10, 15
EDTA	kg/odt			1.5			
Time	min	20	60	70	120	60	140
Temperature	°C	85	100	85	95	80	100
Consistency	%	12	12	10	12	12	12
Final pH			11–11.5	4.5	10.5–11	3	10–11

The pulp yield was measured gravimetrically for laboratory oxygen delignification and bleaching stages. The oxygen delignification yield was measured with seven replications. The bleaching yield was measured with two replications. The cook yield was estimated based on laboratory cooking data from a previous study, where kappa number was plotted against total gravimetric yield.

Analysis

The pulp samples were analyzed as per the standard methods ISO 3688 (1999), ISO 2470 (2016), ISO 302 (2004), ISO 5351 (2010) and SCAN-CM 71:09 to prepare hand-sheets and measure ISO brightness, kappa number, limiting viscosity and carbohydrate composition, correspondingly. The hemicellulose fractions were calculated from the monosaccharides according to Matthews (1974). The lignin content was calculated from the kappa number, with the factor 0.153 (Dence and Reeve 1996). The HexA content was calculated from the kappa number contribution of HexA. The kappa number of the samples was measured before and after acid hydrolysis according to the work by Vuorinen *et al.* (1999) with modifications according to the work by Chakar *et al.* (2000). The contribution of HexA to the kappa number was used to calculate the content of HexA in the pulp, 10 μmol of HexA correspond to 0.86 kappa number units (Li and Gellerstedt 1998). Brightness reversion was measured for seven days of thermal yellowing according to Sevastyanova (2005). Diffuse reflectance UV-Vis-spectrophotometry (DRUVIS) was carried out according to Ragnar (2001), with a Varian Cary 1 equipped with a diffuse reflectance accessory.

Results and discussion

Bleaching results

The bleaching results are summarized in Table 3. Three brown stock pulp samples with kappa number 27, 32 and 35 were collected at the pulp mill and used for laboratory bleaching. The difference in unbleached kappa number between the three pulp samples was reduced gradually throughout the bleaching sequence, in order to resemble pulp mill practice. In the oxygen delignification, kappa number reductions between 60.2 and 61.1 % were obtained. Instead of aiming at the same kappa number after oxygen delignification for the three pulp samples, the desired degree of delignification was set to 60 % with varying kappa numbers as a result. This was chosen in order to maintain a high selectivity in the delignification. The oxygen delignification of K35 would otherwise have to be carried out with very harsh conditions, in order to reach the same kappa number as K27. This would probably have caused unnecessary viscosity loss (Annergren *et al.* 1998, Poukka *et al.* 1999).

The pulp brightness was consistently increased throughout the fibre line. In the OP stage, however, the brightness increased unevenly for the three pulp samples, Figure 2, due to the varying charges of H_2O_2 that were used to even out the kappa numbers. Since a higher dosage of H_2O_2 was needed to reach kappa number 7 for K35, we observed the highest brightness increase with this pulp. However, the viscosities are similar for all pulp samples after the OP stage, Figure 3. Here emerges an advantage with ending the cook at a higher kappa number; a brighter pulp can be obtained after OP when comparing

Table 3: Bleaching results – kappa number, brightness and intrinsic viscosity.

Kappa number										
Pulp	Unbleached	Ox. del.	OP	D	PO 2	PO 3.5	PO 5	PO 10	PO 15	PO 88
K27	26.6	10.6	6.9	1.7	0.64	0.58	0.58	0.51	0.48	0.62
K32	31.9	12.4	7.1	1.7	0.66	0.61	0.57	0.53	0.49	0.65
K35	34.9	13.6	7.9	2.0	0.84	0.79	0.73	0.67	0.65	0.80
Brightness (% ISO)										
Pulp	Unbleached	Ox. del.	OP	D	PO 2	PO 3.5	PO 5	PO 10	PO 15	PO 88
K27	29.5	41.7	59.9	73.4	87.3	88.7	89.6	90.8	92.0	88.0
K32	26.8	40.2	65.6	75.6	87.6	89.4	90.6	91.5	92.3	88.0
K35	27.8	40.0	67.5	75.3	86.9	88.4	89.3	91.3	91.9	88.0
Viscosity (ml/g)										
Pulp	Unbleached	Ox. del.	OP	D	PO 2	PO 3.5	PO 5	PO 10	PO 15	PO 88
K27	1091	910	877	863	854	841	819	748	784	848
K32	1123	918	887	875	853	845	831	775	791	851
K35	1085	914	872	858	831	798	777	716	635	806

Figure 2: Kappa number (kn) and brightness (ISO) development through the fibre line to PO 88 % ISO.

Figure 4: Brightness development in PO stage.

Figure 3: Intrinsic viscosity and brightness through the fibre line to 88 % ISO.

at the same kappa number and viscosity. This is in accordance with earlier studies that achieved similar results. Röst *et al.* (2000) observed higher brightness after oxygen delignification, when comparing at the same kappa number and viscosity. However, after bleaching to full brightness, the brightness ceiling is highest for K32, although the difference between the three pulp samples is very small, Figure 4.

The intrinsic viscosities were reduced with increasing brightness and bleaching oxidation, Figure 3. The viscosity is similar for the three unbleached pulp samples, and are following the same reduction pattern through oxygen delignification and the OP stage. After the D stage, there is an indication that K32 has a higher viscosity than the other two pulp samples. After bleaching to full brightness, it is clear that the pulp with the lowest intrinsic viscosity is K35. Contrary to expectations (Hart and Connell 2006) it seems that this pulp is more liable to the viscosity loss in the PO

stage. An unexpected viscosity loss could be explained by a difference in the metal ion profile in the pulp samples. Manganese, copper and iron are detrimental for H_2O_2 , reacting with superoxide anions forming hydroxyl radicals (Dence and Reeve 1996). However, it seems that transition metal ions are not the reason for the viscosity loss that we observe for K35, since the metal ion content in the pulp samples are similar after the D stage, Table 4. Another possible explanation for the viscosity loss is that this bleaching sequence is not potent enough to reduce the higher unbleached kappa number 35 without overcharging bleaching chemicals and damaging the fibres. Perhaps an optimum is obtained around kappa number 32. A similar optimum was found by Poukka *et al.* (1999) for D(EOP)DD-bleached softwood kraft pulp, but at a higher kappa number.

The brightness stability is presented in Figure 5. In accordance with the literature, it was found that pulp samples with a lower unbleached kappa number had a higher brightness stability (Röst *et al.* 2000). The difference in

Table 4: Bleaching results – metal ion content and hexenuronic acid content.

Metal ion content in pulp (mg/kg)						
Pulp	After Q stage			After D stage		
	Fe	Mn	Cu	Fe	Mn	Cu
K27	3.9	0.7	<0.1	3.6	0.06	<0.1
K32	3.1	0.5	<0.1	3.8	0.05	<0.1
K35	5.0	0.7	<0.1	3.7	0.06	<0.1
Hexenuronic acid (μml/g)						
Pulp	Ox. del.	OP	D			
K27	29.1	30.6	4.2			
K32	38.1	37.3	4.5			
K35	37.7	37.8	6.5			

Figure 5: Brightness loss after treatment for one and seven days, for OP, D and PO pulp samples. PO samples were chosen at ca 88 % ISO (K27 PO 3.5, K32 PO 2, K35 PO 3.5).

brightness stability between the samples is large after the OP stage, reduced after the D stage, and small after the PO stage. The difference in brightness stability is most likely due to differences in lignin and HexA content. H_2O_2 and O_2 cannot degrade HexA, which means that the differences in HexA that originate from the cook, is still present in the pulp samples and affect the brightness stability after the OP stage, as seen in Table 4. The HexA contents in K35 and K32 are similar after oxygen delignification and OP stage. However, there is more lignin left in K35, increasing the brightness loss for that sample. ClO_2 is known to readily degrade HexA, which is why the difference in brightness stability is reduced after the D stage. The small variation in brightness stability after the PO stage is most likely due to the lingering variations in residual lignin content.

Bleachability

The bleachability results are presented in Table 5–6 and Figure 6–7. The pulp samples were collected at similar residual and effective alkali in the cooking, so that this parameter would not influence the bleachability. Also, the temperature and final pH in the bleaching stages were kept at the same levels for all pulp samples. However, pulp mills are very complex and there is no warranty that the unbleached kappa number is the only parameter having an effect on bleachability that varied during the sampling period.

In Table 5, the total OXE and OXE bleachability is presented. The chemical charge and OXE/odt increases with increasing kappa number, as expected due to a higher H_2O_2 charge. In addition, the overall OXE bleachability is improved by a higher unbleached kappa number. However, the calculation is not perfect, since we have not taken

Table 5: Chemical charges in oxygen delignification and bleaching with (OP)D(PO) to 88 % ISO. For OXE calculation 74.12 OXE/kg ClO_2 , 58.79 OXE/kg H_2O_2 and 125.0 OXE/kg O_2 were used (Grundelius 1993).

			K27	K32	K35
Ox. del.	O_2	kg/odt	155	155	155
Ox. del.	NaOH	kg/odt	26	31	30
OP	O_2	kg/odt	77.5	77.5	77.5
OP	H_2O_2	kg/odt	3	6	8
D	ClO_2	kg/odt	8	8	8
PO	O_2	kg/odt	77.5	77.5	77.5
PO	H_2O_2	kg/odt	2.3	2.7	3.1
Σ OXE		OXE/odt	39654.5	39854.4	39995.5
OXE/ Δ kappa number		OXE/odt. ΔK	1525.2	1277.4	1172.9

Figure 6: Effect of unbleached kappa number on the delignifying bleachability. A higher bleachability value means better bleachability.

Figure 7: Effect of unbleached kappa number on the brightness gain bleachability. A higher bleachability value means better bleachability.

Table 6: Bleachability results, including summary of bleachability results. A higher unbleached kappa number is positive (+), negative (–) or neutral (/) for the bleachability.

Delignifying bleachability (–ΔK/kg chemical)								
Pulp	Ox. del. (NaOH)	OP (H ₂ O ₂)	D (ClO ₂)	PO 2 (H ₂ O ₂)	PO 3.5 (H ₂ O ₂)	PO 5 (H ₂ O ₂)	PO 10 (H ₂ O ₂)	PO 15 (H ₂ O ₂)
K27	0.62	1.23	0.65	0.53	0.32	0.22	0.12	0.08
K32	0.63	0.88	0.68	0.52	0.31	0.23	0.12	0.08
K35	0.71	0.71	0.74	0.58	0.35	0.25	0.13	0.09
Summary	+	–	+	/	/	/	/	/
Brightness gain bleachability (–ΔISO/kg chemical)								
Pulp	Ox. del. (NaOH)	OP (H ₂ O ₂)	D (ClO ₂)	PO 2 (H ₂ O ₂)	PO 3.5 (H ₂ O ₂)	PO 5 (H ₂ O ₂)	PO 10 (H ₂ O ₂)	PO 15 (H ₂ O ₂)
K27	0.47	6.07	1.69	6.95	4.37	3.24	1.74	1.24
K32	0.43	4.23	1.25	6.00	3.94	3.00	1.59	1.11
K35	0.41	3.44	0.98	5.80	3.74	2.80	1.60	1.11
Summary	/	–	–	–	–	–	–	–

the residual chemicals into account in the calculations, but used the total charge of the bleaching chemicals. This means that the oxygen charges are extreme, since an excess of O₂ is used in the laboratory method. Hence, the sum of OXE is large. In addition, the OXE bleachability does not take into account that the bleaching chemicals react in different ways with the pulp.

When we instead use the delignifying and brightness gain bleachability, Table 6, the results show that in the bleaching stages that are highly delignifying (oxygen delignification and D stage) it is beneficial with a higher unbleached kappa number for the delignifying bleaching.

In the bleaching stages that are mainly brightness increasing (OP and PO) it is favorable with a lower unbleached kappa number for the brightness gain bleachability. Thus, it is possible to compare the effect of different bleaching stages and to adjust the bleach plant parameters according to delignifying or brightness target.

The DRUVIS reflectance spectra, Figure 8, are helpful for visualizing the overall performance of the bleaching sequence. When presented as difference spectra, Figure 9–10, where the spectrum of the preceding pulp is subtracted from the spectrum after a given stage, the bleaching work of the given stage can be evaluated.

Figure 8: Reflectance spectra, development of bleaching. PO samples at ca 88 % ISO (K27 PO 3.5, K32 PO 2, K35 PO 3.5).

Figure 9: Difference spectra, bleaching work of oxygen delignification and D.

Figure 10: Difference spectra, bleaching work of OP and PO. PO samples at ca 88 % ISO (K27 PO 3.5, K32 PO 2, K35 PO 3.5).

Oxygen delignification

In the oxygen delignification, the delignifying bleachability is slightly better with increasing unbleached kappa number, Figure 6. The NaOH charge was the lowest for K27, as is expected due to lowest kappa number reduction. However, the NaOH charge was slightly higher for K32 than K35, even though the kappa number reduction was lower. This results in a better delignifying bleachability for K35 than K32. This is also visible in the DRUVIS difference spec-

tra, Figure 9, where the bleaching effect of K35 is larger than K32.

The unbleached kappa number does not affect the brightness gain bleachability in the oxygen delignification, Figure 7. This is expected since the main objective of the oxygen delignification stage is not brightness increase. O_2 can oxidize deprotonated phenolic structures in the lignin, depolymerizing and increasing the hydrophilicity via the formation of superoxide anion, $O_2^{\bullet-}$. Brightness improvement is moderate, but occurs when superoxide anion is turned into H_2O_2 .

OP stage

In the OP stage, the delignifying and brightness gain bleachability is better with lower unbleached kappa number. The hydroperoxide anion, HOO^- , attacks and eliminate colored structures in the lignin and depolymerize phenolic lignin structures. In combination with O_2 , the objective of this stage is both delignification and brightness increase. In the DRUVIS spectra, Figure 10, it can be seen that the lower H_2O_2 charge for K27 resulted in a lower bleaching effect in the OP stage than for the other two pulp samples. However, the lower charge should be beneficial for the bleachability in this stage.

One possible reason for the differences in bleachability between the pulp samples in the OP stage is the variation in metal ion content after the Q stage, Table 4. However, the differences are small and this is most likely not the complete explanation. The differences in HexA content in the pulp samples after oxygen delignification, Table 4, can also affect the bleachability. A high HexA content will retain more metal ions in the pulp, decreasing the selectivity of the OP stage. Whether the decreased bleachability with higher unbleached kappa number depends on HexA and lignin structures or harmful metal ions in the pulp is unknown. However, it seems that the higher H_2O_2 charge used in the OP stage to compensate for the higher kappa number 35, was an overcharge.

D stage

In the D stage, the delignifying bleachability is slightly better with increasing kappa number and the brightness gain bleachability is better with decreasing kappa number. ClO_2 reacts fast with phenolic lignin structures, slowly with non-phenolic lignin structures, can degrade HexA (Bergnor-Gidnert *et al.* 1998) and increase brightness via chlorination of double bonds. ClO_2 works as a radical scavenger so that the selectivity of the D stage remains very high. Even though this D stage is an intermediate D stage, i. e. a single D stage at the middle of the sequence (Starrsjö *et al.* 2020), it is more delignifying than one could expect, with kappa number reductions around 20 % for all pulp samples. This is due to the low final pH of the D stage, which in this study was kept at pH 3. An intermediate D stage such as this can be used to manage changes in the bleaching process, such as varying incoming kappa numbers or lack of brightness. It is not a designated delignifying stage such as a D_0 stage, but can be used in favor of delignification when needed.

PO stage

In the PO stage, the brightness gain bleachability (compared at H_2O_2 charge of 3.5 kg/odt) is better with lower unbleached kappa number. The delignifying bleachability in PO is the same for all pulp samples and is the lowest of all bleaching stages, which is expected since the objective of the final bleaching stage is brightness increase and to reduce brightness reversion of the product. According to the DRUVVIS difference spectra, it seems that the PO stage of K27 is most effective in removing colored content, and the PO stage of K35 is the least effective, which is in agreement with the bleachability results.

Yield and chemical composition

Bleached pulp yield plays an important role in the total bleached pulp cost. For bleachable pulp grades, the idea is to avoid the residual delignification phase of the cooking, where the selectivity for lignin removal is lost (MacLeod 2007). The gravimetric yield in this study is given in Table 7. As expected in the cook (Annergren *et al.* 1998, Poukka *et al.* 1999), a higher unbleached kappa number resulted in a higher yield, as less lignin and hemicelluloses were removed from the wood. In the oxygen delignification, a higher unbleached kappa number gave lower yield, as a constant delignification degree at 60 % means more lignin removal. The bleaching yield follows the same pattern, with lower yield for the samples with higher unbleached kappa number. The question regarding the yield is: Will the higher yield obtained in the cook with the higher unbleached kappa number be maintained throughout this particular bleaching sequence? For the sequence (OO)Q(OP)D(PO), the yield gain from cooking to kappa number 35 does not seem to be preserved after the bleaching. However, the results indicate that K32 obtains a higher total yield after the bleaching than K27, i. e. it seems there is an optimum in total pulp yield around kappa number 32 for this bleaching sequence.

The gravimetric yield is supported by the chemical composition, given in Table 8. As expected for unbleached pulp samples, lower kappa number correlates with less hemicellulose in relation to cellulose, as the cook is driven longer and degrades more lignin as well as hemicellulose, in accordance with Esteves *et al.* (2021). However, after bleaching, the pulp with the most hemicellulose in relation to cellulose is K32, not K35. It seems this bleaching sequence cannot maintain the higher hemicellulose content that was achieved after the cook, as the higher lignin

Table 7: Gravimetric yield (%) for laboratory cooking, oxygen delignification and bleaching to 88 % ISO.

Sample	Cook	Ox. del.	Std. dev.	Bleaching	Std. dev.	Total yield
K27	44.9	96.6	0.022	96.6	0.07	41.9
K32	46.5	95.9	0.015	96.6	0.07	43.1
K35	47.5	95.6	0.021	94.1	0.21	42.7

Table 8: Chemical composition, percent of pulp, and relation hemicellulose to cellulose of unbleached and bleached pulp at ca 88 % ISO.

Sample	Cellulose	Glucomannan	Xylan	Galaktoglucomannan	Lignin	Hemi/cell
K27	79.0	7.7	8.9	0.3	4.1	0.215
K32	78.0	7.6	9.1	0.4	4.9	0.220
K35	77.4	7.8	9.0	0.4	5.3	0.223
K27 PO 3.5	82.6	8.1	9.0	0.2	0.1	0.209
K32 PO 2	82.3	8.1	9.3	0.2	0.1	0.214
K35 PO 3.5	82.7	7.8	9.2	0.2	0.1	0.208

content of K35 required a high bleaching chemical charge to reach a sufficiently high brightness.

Unbleached kappa number for (OO)Q(OP)D(PO)

In this study, we intended to determine the best suited kappa number, out of three brown stock pulp samples, for this particular bleaching sequence. According to our results, the ECF light bleaching sequence (OO)Q(OP)D(PO) is most effective for the brown stock pulp sample with kappa number around 32. Although a higher kappa number than 32 resulted in a higher yield after cooking, it seems that this bleaching sequence cannot preserve the yield gain. Out of the three pulp samples, kappa number 32 also gave the best results in regards to brightness ceiling and viscosity. This kappa number region has been found to be beneficial also for other bleaching sequences with similar brightness targets (Annergren *et al.* 1998, Poukka *et al.* 1999, Hart and Connell 2006). On the other hand, in this study, kappa number 27 was the most favorable in regards to brightness reversion and chemical charge.

Increasing the unbleached kappa number has traditionally proven to be beneficial for yield and fibre strength (MacLeod 2007). However, eventually the kappa number limit will be reached, where increasing the kappa number is no longer beneficial; the bleaching cannot preserve the gains. It is likely that ECF light sequences reaches the limit earlier (in terms of kappa number) than traditional ECF sequences. Lower charges of delignifying bleaching agents (i. e. ClO_2), means that less residual lignin can be removed.

Even though oxygen and hydrogen peroxide also can degrade and dissolve lignin to some extent, the delignification is not as selective when the sequence contains fewer bleaching stages (Annergren *et al.* 1998). It could be that the “lighter” (i. e. the lower the ClO_2 charges) the ECF, the lower the optimal unbleached kappa number.

Conclusions

The delignifying and brightness gain bleachability can be used to evaluate the bleachability of the stages separately in a bleaching sequence, so that it is possible to distinguish the bleaching efficiency in each stage. For the ECF light sequence Q(OP)D(PO), the bleachability depends on the purpose of the stage. In the bleaching stages that are highly delignifying (OO and D) it is beneficial with a higher unbleached kappa number for the delignifying bleachability, although the brightness gain is not improved. However, in the bleaching stages where the objective is brightness increase (OP and PO) the brightness gain bleachability is improved by a lower unbleached kappa number.

The bleaching of three softwood kraft pulp samples with this specific ECF light sequence was most effective for brown stock kappa number around 32. Although a higher kappa number than 32 resulted in higher yield after cooking, it seems that this bleaching sequence cannot preserve the yield gain. Kappa number 32 also gave the best results in regards to brightness ceiling and viscosity. On the other hand, kappa number 27 was the most favorable in regards to brightness reversion and chemical charge.

Funding: This study was supported by the Knowledge Foundation, org.nr.802400-4213 (KK-stiftelsen) through the industrial graduate school FORIC+ and by Treesearch.se.

Conflict of interest: There is no conflict of interest.

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