

Further insights into extended-impregnation kraft cooking of birch

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SUMMARY: Extended-impregnation kraft cooking (EIC) is a cooking concept that combines prolonged impregnation with modern improved modified kraft cooking. In the current investigation, the EIC cooking of birch was studied in relation to conventional kraft cooking. Specifically, the reject content and carbohydrate yield retention when terminating at a high cooking kappa number were examined. It was demonstrated that EIC cooking reduced the reject content. Unexpectedly, a high cooking kappa number led to no increase in carbohydrate yield, possibly due to the chemical composition of birch wood and the EIC cook lab procedure. A large amount of liquor was withdrawn after the impregnation, resulting in a loss of dissolved xylan that otherwise could have redeposited on the fibres and contributed to the carbohydrate yield. The effects of EIC cooking on extended oxygen delignification, bleaching chemical requirement in a D(OP)DP sequence, and strength properties were also examined. Compared with conventional lab cooking, EIC cooking resulted in a lower bleaching chemical requirement and similar strength properties.

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As a major part of the production cost in kraft pulping comes from the wood cost, high process yield is crucial for good production economics. The main objective when manufacturing bleached kraft pulp is to preserve the carbohydrates while removing the lignin and extractives during cooking and bleaching. Most carbohydrate yield loss occurs in the kraft cook rather than the oxygen delignification and bleaching. Because the kraft cook is the least selective stage in terms of carbohydrate retention versus lignin removal, it is the sub-process with the greatest potential for improved overall carbohydrate retention. Keys to higher carbohydrate retention would be process modifications aiming to retain carbohydrates, to prevent carbohydrate degradation reactions, to increase the delignification rate, and to enhance the impregnation

of cooking chemicals into the wood chips, reducing the quantity of knots and shives. Levelling-out the alkali profile (Nordén, Teder 1979; Teder, Olm 1981; Sjöblom et al. 1983), lowering the cooking temperature (Teder, Olm 1981; Kubes et al. 1983; Bäckström, Jensen 2001), and raising sulphidity (Teder, Olm 1981; Sjöblom et al. 1983; Lindgren 1997; Gustavsson et al. 1997) in the kraft cook have been demonstrated to be important process modifications to improve carbohydrate retention and increase the delignification rate.

A well-known way to increase the carbohydrate yield in the cook is to terminate cooking at a high cooking kappa number, though this approach is feasible only if the reject content can be kept low. It has fairly recently become possible to decrease the reject content for hardwood by using modern cooking technology (Näsman et al. 2007). To reduce the reject content further, extended-impregnation kraft cooking (EIC) has recently been developed and demonstrated very homogenous delignification, resulting in a low reject content for softwood (Karlström 2009) and for hardwood (Wedin et al. 2010). The EIC-cooking is a lab concept that combines extended impregnation with improvements of the modified kraft cooking concept. A similar kraft cooking concept has been brought to market by Metso Paper and marketed as Compact Cooking G2.

The extended impregnation exploits the phenomenon that the rate of diffusion of cooking chemicals is slower than the rate of alkali consumption (Hartler, Onisko 1962). A lower temperature during impregnation in combination with a longer time thus favours the diffusion of cooking chemicals into the wood chips. EIC cooking also uses a high liquor-to-wood ratio during impregnation. A high liquor-to-wood ratio is important to increase the number of hydroxide ions throughout the impregnation without increasing the alkali concentration. This is important to avoid critical low levels of alkali inside the core when the cooking temperature is increased and the consumption of alkali is accelerated through the delignification and carbohydrate degradation reactions.

In a recent study conducted in the present laboratory, the extended-impregnation kraft cooking (EIC) concept was used on *Eucalyptus urograndis*. It was demonstrated that this process could be used to increase the carbohydrate yield after the kraft cook and that part of the yield gain could also be preserved in the bleached end product (Wedin et al. 2010).

Although a carbohydrate yield gain was obtained for *E. urograndis* using the EIC concept (Wedin et al. 2010), it is not obvious that EIC cooking would increase the pulp yield for other hardwood species, such as birch, acacia, poplar, oak, and aspen, in a similar manner. Large differences exist between hardwoods in terms of, for example, chemical composition, the number, size, and shape of fibres, fibre wall thickness, and the number and

shape of vessels. These and other parameters affect the cooking and bleaching performance and/or product properties. Birch is a common hardwood pulping species in the Nordic countries and is the focus of this study. The carbohydrate composition of birch differs greatly from that of eucalypt. In the literature, cellulose values reported for Nordic birch wood (i.e. *Betula pendula* and *Betula pubescens*) are 40–42% (Sjöström 1993; Willför et al. 2005; Patt et al. 2006), while the neutral hemicellulose sugar (mainly xylan) and uronic acid content of Nordic birch wood are 28–32% and approximately 6%, respectively (Sjöström 1993; Pinto et al. 2005; Willför et al. 2005; Patt et al. 2006). *E. urograndis*, on the other hand, has a higher cellulose content and a lower hemicellulose content than does Nordic birch. The cellulose content of *E. urograndis* is reported to be 43–48% expressed as the cellulose and 48–52% expressed as the anhydrous glucose content of wood (Pinto et al. 2005; Patt et al. 2006; Colodette et al. 2007; Magaton 2008). The neutral hemicellulose sugar content is reported to be 12–17% and the uronic acid content approximately 5% of *E. urograndis* wood (Pinto et al. 2005; Patt et al. 2006; Colodette et al. 2007). Our recent study of *E. urograndis* demonstrated that approximately 60% of the carbohydrate yield gain was due to cellulose retention when the kraft cook was terminated at a high kappa number of 34 instead of kappa number 18. It would thus be interesting to investigate whether similar results could be obtained for birch or whether the higher xylan content of this wood would play a greater role in carbohydrate retention than would the cellulose content.

This study of birch investigates the potential to increase overall pulp yield by terminating the kraft cook at a higher than otherwise kappa number using the EIC concept. The effects of EIC cooking on extended oxygen delignification, bleaching chemical requirement, strength properties were also to be studied. In this study, a standard D(OP)DP bleaching sequence was used. A final P stage has displayed promising results in terms of higher brightness (Senior et al. 1998; Süß et al. 2000), lower brightness reversion (Colodette et al. 2004), and improved tensile index (Carvalho et al. 2008). In addition, a final alkaline stage is a very efficient means of ensuring a low organically-bound chlorine content in an ECF pulp (Ragnar, Törngren 2002). A conventional lab-cooked kraft pulp was used as a reference and conditions were chosen to obtain a defibration point close to what is standard in today's mills.

Materials and Methods

Mill-chipped birch wood chips (a mixture of *B. pendula* and *B. pubescens*) were supplied by the Metsä-Fibre Äänekoski mill in Finland. The chips were hand screened and the 2–8-mm thickness fraction was used; chips containing bark and knots were removed by hand.

Conventional circulation kraft cook (CK)

Screened wood chips (1.8 kg oven dried [o.d.]) were placed in a 15.4-dm³ forced circulation digester (Calor Industri AB, Karlstad, Sweden) and pre-steamed for 5 min at 110°C at a steam pressure of 1 bar(g). The cooking trials were performed conventionally, in that all

white liquor was added at the beginning of the cook. The sulphidity was 40%, effective alkali (EA) 18%, and liquor-to-wood ratio 3.5:1 for all CK cooks. To obtain pulps with different kappa numbers, the temperature was varied. The time to reach cooking temperature was approximately 10 min and the retention time at the cooking temperature was 80 min. After the cook, the pulp was disintegrated, screened, and centrifuged. The cooking temperature, EA measured as NaOH, and residual alkali measured as NaOH are reported in *Table 1*.

Extended-impregnation kraft cook (EIC)

Screened wood chips (1.8 kg o.d.) were placed in the same circulation digester as used for CK and pre-steamed for 5 min at 110°C at a steam pressure of 1 bar(g). The EIC cooking concept consists of three consecutive steps: an extended impregnation step followed by cooking at an elevated cooking temperature in two further steps, i.e. step 1 and step 2 corresponding to the upper and lower zones in a continuous mill digester (*Fig 1*). To level out the alkali profile, the addition of cooking liquor was split between the impregnation and the first cooking step, whereas no liquor was charged in the second cooking step. The impregnation was performed with black liquor at 110°C for 90 min and at a liquor-to-wood ratio of 7:1 dm³ kg⁻¹ o.d. wood chips. EA was 13.0–14.5% (measured as NaOH) and sulphidity was 55% in the impregnation liquor. The black liquor was collected from a previous cook and adjusted to the correct EA and sulphidity before being charged to the next cook. The first cooking step was performed at a sulphidity of 40% for 120 min using a liquor-to-wood ratio of 4:1 dm³ kg⁻¹ o.d. wood chips. To obtain pulps with different kappa numbers, the temperature and EA were varied. The second cooking step was performed for an additional 120 min at the same cooking temperature without adding any cooking chemicals and using a liquor-to-wood ratio of 3.5:1 dm³ kg⁻¹ o.d. wood chips. Thereafter, the pulp was disintegrated, screened, and centrifuged. The cooking temperature, EA, and residual alkali in all stages are reported in *Table 1*.

Oxygen delignification and bleaching

Selected pulps were subjected to oxygen delignification and bleaching. The bleaching was carried out in a D₀(OP)D₁P sequence in the laboratory. A standard low-temperature D₀ stage in the initial position rather than a hot D stage was chosen, since the latter has so far not been implemented industrially in Nordic countries. Stainless steel autoclaves internally coated with Teflon were used for the O and the (OP) stages; the autoclaves were heated while rotating in a polyethylene glycol bath. The D₀, D₁ and P stages were performed in sealed plastic bags in a water bath. The chlorine dioxide dosage in the D₀ stage was based on kg ClO₂ per BDT of pulp = 0.76 × kappa number. In the D₁ stage, the chlorine dioxide charge was varied to give three sample points, sufficient to obtain a curve to interpolate or extrapolate the bleaching chemical requirement to achieve a target ISO brightness of 90% after bleaching. Trial conditions are summarised in *Tables 2* and *3*.

Table 1. Cooking conditions.

Cook no.	Cooking temp °C	EA % (as NaOH)	Residual EA g l ⁻¹
1	158	18.0	5.3
CK 2	155	18.0	6.7
3	151	18.0	8.0
		imp/step1/step2	imp/step1/step2
4	141	14.5/9.0/-	5.5/11.5/8.0
5	140.5	13.0/9.0/-	4.0/11.0/7.7
EIC 6	137	13.5/9.0/-	5.7/13.8/10.6
7	137	13.5/9.0/-	4.4/11.6/8.4
8	135	13.5/9.0/-	5.4/13.2/10.0

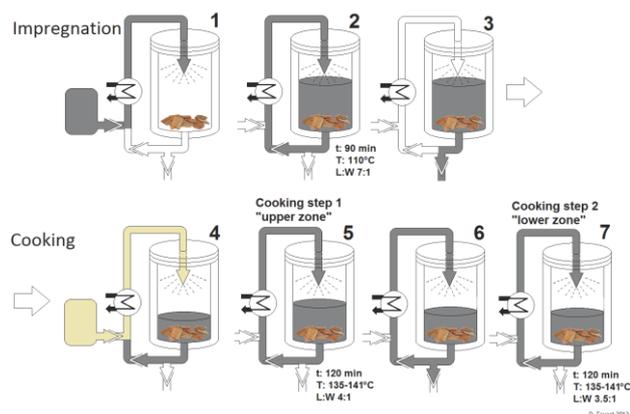


Fig 1. 1) Addition of cooking liquor, 2) impregnation, 3) extraction of black liquor after impregnation, 4) addition of cooking liquor, 5) cooking step 1, 6) extraction of black liquor, 7) cooking step 2.

Analysis

The total yield was determined gravimetrically. Screening was performed in two stages: the coarse material was first removed in a water-jet disperser (Nordiska armaturfabriken, Sweden) with perforations of 1.5 mm at a water pressure of 1.5 bar(g); residual shives were then separated on a vibrating flat screen with 0.15-mm slots. The reject content was determined by combining the shives from the NAF and the flat screening devices after drying at 105°C overnight. Residual hydroxide ion concentration in the spent cooking liquor samples was determined according to SCAN N 33:1994.

Kappa number (ISO 302:2004), limiting viscosity number (ISO 5351:2004), ISO brightness (ISO 3688:1999 and ISO 2470:1999), and chemical oxygen demand (COD) (ISO 15705:2002) were analysed according to the ISO standards. The COD content in the bleaching was analysed on combined liquors collected from all bleaching stages. The total yield after oxygen delignification and bleaching was determined gravimetrically. 30 g of unbleached pulp was O and OD(OP)DP bleached; after bleaching, the pulp sample was dried and weighed. Tests were conducted in duplicate. The coefficient of variation of the gravimetric yield was 0.3–1.3% expressed as % of pulp. The yield after the oxygen delignification was also estimated using the expression that 17 kg COD corresponds to 1 % yield loss, a correlation based on a number of data from gravimetric yield determination by Metso, Paper (Sundsvall, Sweden).

Table 2. Oxygen delignification conditions.

	CK17.4	CK21.4	EIC17.8	EIC21.9	EIC27.0
Target kappa number	10	10	10	10	10
Pulp consistency, %	12	12	12	12	12
Temperature, °C	~95	~100	~100	~100	~98
Time, min	90	90	90	90	120
O ₂ pressure, bar(g)	8	8	8	8	8
NaOH, kg BDT ⁻¹	18	26	18	26	30
Final pH measured at 25°C	10.8	11.9	10.8	11.3	11.8

¹ Adjusted temperature of pulp; temperature was approximately 5°C higher in the polyethylene glycol bath.

Table 3. Bleaching conditions.

	D ₀	OP	D ₁	P
Pulp consistency, %	10	12	12	12
Temperature, °C	55	80	75	85
Time, min	60	60	120	120
Final pH at 25°C	2.5–2.8	10.5–11.4	3.8–4.4	10.4–11.1
O ₂ pressure, bar(g)	-	2	-	-
Chemical charge, kg BDT ⁻¹	ClO ₂ : 7.0–9.1 H ₂ SO ₄ : 2.0–2.5	H ₂ O ₂ : 3.0 NaOH: 10.0 MgSO ₄ : 2.0	ClO ₂ : 0.8–4.6 H ₂ SO ₄ : 0.0–2.5 NaOH: 0.0–1.0	H ₂ O ₂ : 3.0 NaOH: 4.5 MgSO ₄ : 1.0

Acid hydrolysis combined with gas chromatography was used to analyse the glucose content of wood according to Sundberg et al. (2003) while methanolysis combined with gas chromatography was used to analyse the quantity of neutral and acid sugar units in the hemicellulose and pectin according to Willför et al. (2005) and Willför et al. (2009). Prior to methanolysis, the wood samples were first cooled with liquid nitrogen and then ball-milled for 20 min at 420 revolutions per minute (rpm). The ball mill was a Planetary Mono Mill Pulverisette 6 (Fritsch, Idar-Oberstein, Germany) equipped with a tungsten carbide grinding bowl. The cellulose content was determined using cotton linters and sorbitol as external and internal standard respectively while the hemicellulose content was the sum of all methylated sugars converted to anhydrous sugars using a factor of 0.88 for xylose and arabinose, 0.89 for glucose, rhamnose and mannose and 0.91 for the uronic acids. The neutral sugar units in the pulps were analysed after acid hydrolysis according to SCAN-CM 71:09 using a high-performance anion exchange chromatograph equipped with pulsed amperometric detection (HPAEC-PAD) and a CarboPac PA1 column (Dionex, Sunnyvale, CA, USA). The Klason lignin was filtered after acid hydrolysis according to SCAN-CM 71:09, oven dried at 105°C, and then gravimetrically determined; the Klason lignin analysis used 600 mg of pulp. The coefficient of variation for the Klason lignin data was 1–7% as % of pulp.

Table 4. Monosaccharide composition of the tested wood.

Carbohydrate composition, wt% of wood	Birch wood
Cellulose ¹	37.0
Hemicellulose + pectin ²	33.5
Neutral monosaccharide	
Glucose	42.9
Methylated monosaccharide (anhydrous)	
Glc	6.2
Xyl	20.8
Rha	0.4
Ara	0.3
Man	1.3
Gal	1.0
4-O-MeGlcA	1.4
GalA	1.9
GlcA	0.3

¹ Cellulose = based on glucose content (acid hydrolysis) using cotton linter and sorbitol as external and internal standard respectively.

² Hemicellulose + pectin = $\Sigma(\text{Xyl}, \text{Rha}, \text{Ara}, \text{Gal}, \text{Glu}, \text{Man}, \text{4-O-MeGlcA}, \text{GalA}, \text{GlcA})$

The hexenuronic acid (HexA) content was determined according to Gellerstedt and Li (1996). A mercury acetate solution was charged into the pulp, and after 1 h of reaction, the HexA in the hydrolysate was quantified on a reversed-phase HPLC equipped with an Ascentis C18 column (250 mm \times 4.6 mm \times 5 μm ; Sigma-Aldrich, St. Louis, MI, USA) and a photodiode array detector. The mobile phases were A: 1% trifluoroacetic acid in water, and B: acetonitrile. The flow was set to 1 ml min⁻¹ and started with isocratic conditions using 10% of solvent B

for 2 min. Thereafter, the proportions were linearly increased to 100% of solvent B for 5 min. After 12 min at 100% of solvent B, the proportions were changed linearly to 10% for 1 min followed by 10 min of isocratic conditions of 10% of solvent B. The total cycle time was 23 min. A benzoic acid solution with a concentration of 4 mmol dm⁻³ was used as a monitor standard and mixed with the sample in a ratio of 1:1 prior to injection. The column effluent was monitored using a wavelength of 236 nm. An oxygen-delignified birch kraft pulp containing a known amount of HexA was used as a reference. The coefficient of variation of HexA was 0.2–5% when expressed as $\mu\text{mol g}^{-1}$ pulp. The contribution of HexA to the kappa number was calculated according to the relationship: 1 kappa number unit = 11.6 $\mu\text{mol g}^{-1}$ of o.d. pulp (Li, Gellerstedt 2002).

Accelerated yellowing was measured by means of dried heat-induced brightness reversion using the sheets used for the ISO brightness measurement after the sheets had been heat-treated in an oven at 105°C for 3 h. The brightness reversion was reported as normalised ISO brightness reversion units at an ISO brightness of 90% according to (Ragnar 2007).

Results

Cooking

In this study, five kraft cooked EIC pulps were compared with three CK pulps cooked from the same birch wood chips in a range of kappa numbers from 17 to 34. The sugar composition of the wood and the chemical data for the cooks are presented in *Tables 4* and *5*, respectively.

Table 5. Data for the investigated extended-impregnation kraft cook (EIC) and conventional circulation kraft cook (CK) pulps.

	CK				EIC			
	1	2	3	4	5	6	7	8
Cook no.	1	2	3	4	5	6	7	8
H factor	465	332	238	305	280	205	204	168
Kappa number	17.4	21.4	28.0	17.8	21.9	25.4	27.0	34.3
Klason lignin, % of pulp	1.9	2.5	3.3	1.8	2.6	2.9	3.2	4.4
Total yield, % of wood	54.0	55.1	56.2	53.0	53.9	54.4	55.0	54.9
Reject, ¹ % of wood	0.56	1.09	3.04	0.02	0.17	0.52	0.74	4.02
Reject-free yield, % of wood	53.4	54.0	53.2	53.0	53.7	53.9	54.3	50.9
Lignin ² and reject-free yield, % of wood	52.4	52.7	51.4	52.0	52.3	52.3	52.5	48.6
HexA, $\mu\text{mol g}^{-1}$	59	59	57	66	64	61	62	57
HexA, kappa number	5.1	5.1	4.9	5.7	5.5	5.2	5.3	4.9
ISO brightness, %	34.8	34.7	33.0	38.9	38.4	37.3	35.1	32.9
Limiting viscosity number, dm ³ kg ⁻¹	1310	1350	1380	1440	1510	1510	1540	1530
Xyl, ³ rel % of pulp	27.3	28.0	28.0	27.1	27.0	26.0	27.7	26.6
Glu, ³ rel % of pulp	72.3	71.5	71.4	72.7	72.7	73.7	71.9	73.1
Man, ³ rel % of pulp	0.4	0.5	0.5	0.3	0.3	0.3	0.4	0.3
Ara, ³ rel % of pulp	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Gal, ³ rel % of pulp	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	0.1	<0.1
Hemicellulose contribution to yield, ⁴ % of wood	14.7	15.3	15.0	14.4	14.5	13.9	15.0	13.0
Cellulose contribution to yield, ⁵ % of wood	37.7	37.4	36.4	37.7	37.9	38.4	37.6	35.4

¹ Slot size = 0.15 mm

² Lignin content measured as Klason

³ Anhydrous monosaccharide

⁴ Hemicellulose = $\Sigma(\text{Xylan}, \text{Rhamnan}, \text{Arabinan}, \text{Galactan}, 2 \times \text{Mannan})$

⁵ Cellulose = Glucan – Mannan

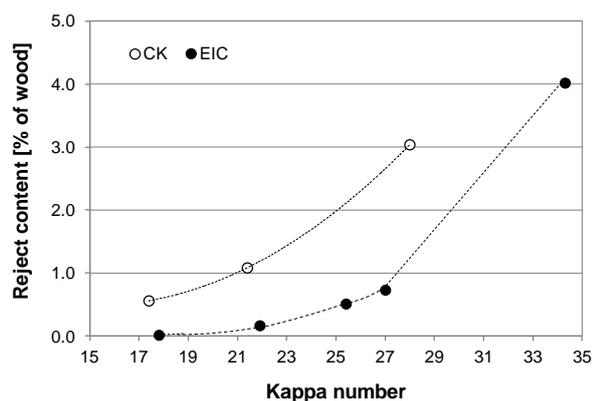


Fig 2. Reject content (shives) versus kappa number in birch kraft pulps, lab-cooked using extended-impregnation kraft cook (EIC) and conventional circulation kraft cook (CK).

The cellulose and hemicellulose contents of the wood were 37.0% and 33.5%, respectively. During the EIC and CK cooking, the hemicellulose (i.e. mainly xylan) accounted for the major yield loss: on average 57% and 55% of the initial hemicellulose content of the wood was lost from the EIC and CK pulps, respectively, whereas almost no cellulose was lost during the EIC and CK cooks.

The influence of the EIC cooking concept on the reject content at different cooking kappa numbers is shown in Fig 2. The EIC concept succeeded in reducing the reject content for birch. The defibration point often appears at a 1% reject content for wood, after which the reject content starts to rise markedly.

As seen in Fig 2, the defibration point seemed to appear at higher kappa number 28 for the EIC cooking, whereas for the conventional cooking the defibration point seemed to appear at kappa number 21.

Fig 3 shows the carbohydrate yield after the cook, in which the carbohydrate yield is the yield corrected for the lignin and the reject contents.

The EIC birch cooking produced no significant increase in carbohydrate yield (lignin and reject-free yield) when terminating the cook at a kappa number of 27 instead of 18. The carbohydrate yield for EIC cooking was 52.5% and this was no higher than the yield of conventional cooking. As seen in Figs 2 and 3, termination of the EIC cook at a kappa number higher than 27 led to a markedly higher reject content, which negatively affected the carbohydrate yield.

The conditions applied in the EIC cooking concept, such as lower cooking temperature and levelled-out alkali profile, also affect the hexenuronic content (HexA), ISO brightness, and limiting viscosity number. As shown in Table 5, EIC cooking of birch at a given kappa number resulted in a HexA content that was 5–7 $\mu\text{mol HexA odg}^{-1}$ higher than did the CK cooking. At a given Klason lignin content, the ISO brightness was approximately 2–4 percentage points higher and the limiting viscosity number was approximately 130–160 $\text{dm}^3 \text{kg}^{-1}$ higher for EIC cooking than for CK cooking.

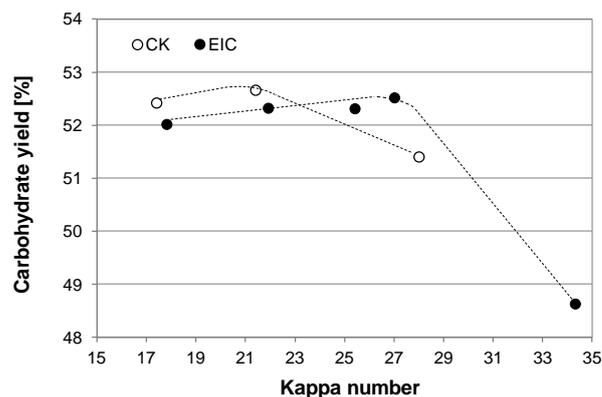


Fig 3. Carbohydrate yield (lignin and reject-free yield) versus kappa number in birch kraft pulps, lab-cooked using extended-impregnation kraft cook (EIC) and conventional circulation kraft cook (CK).

Table 6. Data after oxygen delignification for extended-impregnation kraft cook (EIC) and conventional circulation kraft cook (CK) pulps.

O delignification	CK17.4	CK21.4	EIC17.8	EIC21.9	EIC27.0
Kappa number after O delig.	9.7	9.9	9.6	9.2	10.1
Limiting viscosity number, $\text{dm}^3 \text{kg}^{-1}$	970	940	1070	1030	1030
Brightness, % ISO	55.9	58.2	63.0	63.7	60.4
COD, kg BDT^{-1}	43.9	56.7	39.9	67.4	76.4
Yield, COD, ¹ % of pulp	97.4	96.7	97.7	96.0	95.5
Yield, gravimetric, % of pulp	97.2	95.9	96.2	95.0	97.6

¹ Estimated yield determined from COD, 17 kg COD corresponds to 1% yield loss.

Oxygen delignification

For oxygen delignification and bleaching trials, kraft cooked pulps with acceptable cooking reject contents were chosen: EIC17.8, EIC21.9, EIC27.0, CK17.4 and CK21.4, where the abbreviation number represents the unbleached kappa number of the EIC and CK pulps. The target kappa number was ten for all pulps. The results of the oxygen delignification are shown in Table 6.

As can be seen in Table 6, it was possible to reach the target kappa numbers for all the pulps. Remarkably, the extended oxygen delignification of EIC pulp at a cooking kappa number of 27 reached kappa number 10 without excessively lowering the limiting viscosity number, as it was still 1030 $\text{dm}^3 \text{kg}^{-1}$. At a kappa number of approximately 10, the EIC pulps displayed higher ISO brightness of approximately 60–64% than did the CK pulps, with ISO brightness of 56–58%. Lower gravimetric yield and higher COD indicate more dissolved carbohydrates during oxygen delignification. Comparing the EIC with the CK pulps at a given cooking kappa number, a slightly lower gravimetric yield was seen for the EIC pulps; however, the yield based on COD values did not indicate one cooking concept led to greater carbohydrate loss in the oxygen delignification than the other. It should be noted that the highest gravimetric yield was seen after the extended oxygen delignification of EIC at a cooking kappa number of 27.

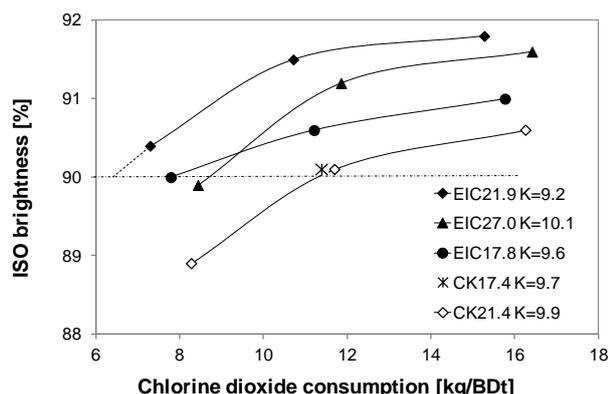


Fig 4. ISO brightness versus total chlorine dioxide consumption in an OD(OP)DP bleaching sequence for birch kraft pulps. (EIC =extended-impregnation kraft cook, CK= conventional circulation kraft cook, K= for kappa number into bleaching).

Bleaching

The oxygen-delignified pulps were bleached using a D(OP)DP sequence to a target ISO brightness of 90%. The chlorine dioxide was varied in the second D stage to achieve the target ISO brightness. This was done for all the oxygen-delignified pulps except for the CK17.4 pulp, which was only bleached using one charge of chlorine dioxide due to an insufficient amount of pulp. In Fig 4, the ISO brightness is plotted against the total chlorine dioxide consumption. Chlorine dioxide consumption was evaluated at an interpolated or extrapolated ISO brightness of 90.0%, apart from the CK17.4 pulp which was reported at an ISO brightness of 90.1%. The results are shown in Fig 5.

At an ISO brightness of 90%, the EIC pulps consumed less chlorine dioxide than did the CK pulps, i.e. 6.4–8.7 kg of chlorine dioxide per BDt for the EIC pulps versus 11.3–11.4 kg of chlorine dioxide per BDt for the CK pulps.

The overall yields of the pulps with a kappa number close to ten after oxygen delignification are shown in Table 7. All the EIC pulps produced slightly less overall yields than did the conventional pulp. The overall yields were 50.7–50.9% of wood for the EIC pulps versus 52.2 and 51.0% of wood for the CK17.4 and CK21.4 pulps. Table 7 also shows the limiting viscosity number, HexA, and neutral sugar composition for the bleached pulps. The bleached EIC pulps had higher limiting viscosity numbers of 960–1010 $\text{dm}^3 \text{kg}^{-1}$ versus 860 and 880 $\text{dm}^3 \text{kg}^{-1}$ for the CK pulps. The HexA content was three to four times higher for the bleached EIC pulps (25–31 $\mu\text{mol g}^{-1}$) than the conventional pulp (7–8 $\mu\text{mol g}^{-1}$). The neutral sugar composition did not differ between the EIC and CK bleached pulps.

The yellowing tendency was determined after dried heat-induced treatment of the bleached pulps. CK17.4 was used as a reference, since kappa number 17 is more common today in mills than is kappa number 21. A more standardised number is obtained by normalising the brightness reversion to an ISO brightness of 90%, y_{90} (Ragnar 2007). The normalised brightness reversion values shown in Table 8 were 1.2–1.4 percentage point higher for the EIC pulps than the CK pulp.

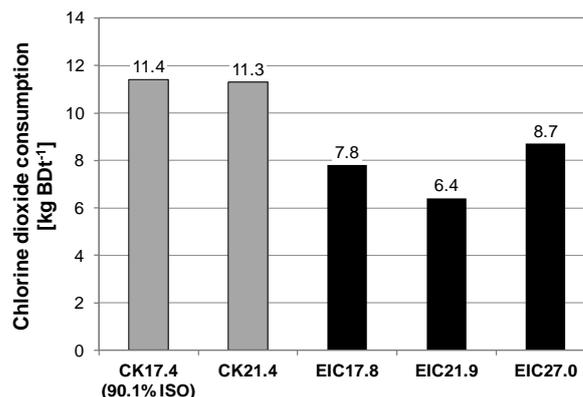


Fig 5. Total chlorine dioxide consumption in the D₀ and D₁ stages for D(OP)DP bleached kraft pulps at an ISO brightness of 90.0%. The kappa number into bleaching is 9.7 ± 0.5 . (EIC =extended-impregnation kraft cook, CK= conventional circulation kraft cook).

Table 7. Data after bleaching for extended-impregnation kraft cook (EIC) and conventional circulation kraft cook (CK) pulps. The pulps are compared at an ISO brightness of $90\% \pm 0.6$.

OD(OP)DP	CK17.4	CK21.4	EIC17.8	EIC21.9	EIC27.0
Kappa no. after O delig.	9.7	9.9	9.6	9.2	10.1
Brightness, % ISO	90.1	90.3	89.7	90.3	90.4
Limiting viscosity number, $\text{dm}^3 \text{kg}^{-1}$	860	880	1000	960	970
HexA, $\mu\text{mol g}^{-1}$	8	7	31	27	25
Total gravimetric yield, %	97.6	97.1	96.1	94.7	93.4
COD, ¹ kg BDt^{-1}	30.8	40.3	25.1	24.8	38.1
Total overall yield, %	52.2	51.0	50.9	50.9	50.7
Xyl, ² rel %	26.3	26.5	26.1	25.6	26.0
Glu, ² rel %	73.3	73.0	73.7	74.1	73.7
Man, ² rel %	0.4	0.5	0.4	0.4	0.4
Ara, ² rel %	<0.1	<0.1	<0.1	<0.1	<0.1
Gal, ² rel %	<0.1	<0.1	<0.1	<0.1	<0.1

¹ Only D(OP)DP

² Anhydrous monosaccharide

Table 8. Normalised brightness reversion at an ISO brightness of 90.0%.

OD(OP)DP	CK17.4	EIC17.8	EIC21.9	EIC27.0
Kappa no. after O delignification	9.7	9.6	9.2	10.1
Normalised yellowing tendency, % ISO units, y_{90}	2.5	3.6	3.5	3.3

Strength properties

In pulp mills, it is important that any change in kraft cooking conditions should not degrade the strength properties of the pulp. The strength properties are evaluated as the tensile index and tensile stiffness index at various sheet densities. To obtain these densities, the pulps were beaten in a PFI mill at 500, 1000, and 2000 rpm. The results are shown in Figs 6 and 7.

As seen the EIC pulps had tensile indexes and tensile stiffness indexes similar to those of the conventional pulp. At an interpolated tensile index value of 90 Nm g^{-1} , the EIC pulps required 338–399 PFI mill revolutions to reach 90 Nm g^{-1} , whereas the conventional CK17.4 required 387 revolutions. The tensile stiffness index values at the interpolated tensile index value of

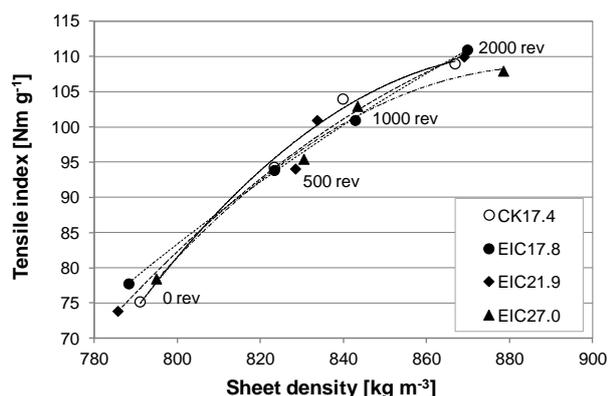


Fig 6. Tensile index versus sheet density for D(OP)DP bleached birch kraft pulps at $90\% \pm 0.4$. EIC stands for extended-impregnation kraft cook and CK for conventional circulation kraft cook.

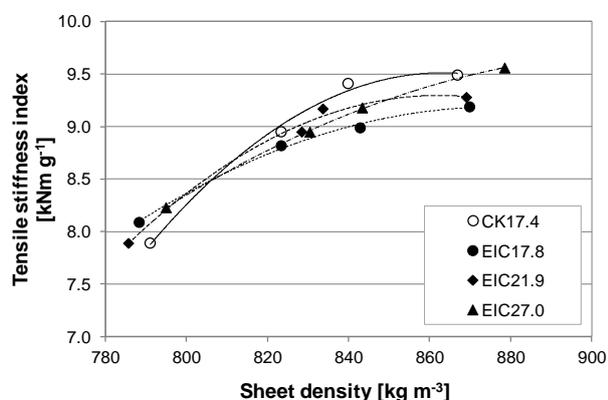


Fig 7. Tensile stiffness index versus sheet density for D(OP)DP bleached birch kraft pulps at $90\% \pm 0.4$. EIC stands for extended-impregnation kraft cook and CK for conventional circulation kraft cook.

90 Nm g^{-1} were 8.6–8.7 kNm g^{-1} for the EIC pulps and 8.7 kNm g^{-1} for the CK17.4 pulp.

Discussion

The underlying aim of this study was to investigate the possibility of obtaining a higher carbohydrate yield by terminating the cook at a higher cooking kappa number for birch wood pulp. It should be pointed out that the results of EIC cooks presented here represent a combination of prolonged impregnation and improved modified kraft cooking. The levelled-out alkali profile and lower cooking temperature, and not the exact effects of the extended impregnation, were the prime targets of this study. The alkali profile probably has the greatest impact on the reject content. This implies that the hydroxide ions have to reach the inner part of the chips during impregnation and that sufficient alkali must be present in the core of the chips before the delignification occurs. The choice of impregnation time in this study was based on literature data. According to Inalbon et al. (2009), 45–60 min of impregnation at 110°C is needed for hydroxide ions at a concentration of 0.5 mol dm^{-3} to completely deacetylate a 4.4-mm-thick *Eucalyptus grandis* wood chip. Based on this literature result and the facts that the wood chips were up to 8 mm thick in the present study and that the initial hydroxide ion

concentration was approximately 0.5 mol dm^{-3} , together with the practical limits of an impregnation vessel, an impregnation time of 90 min seemed reasonable. Whether 90 min was the most optimal impregnation time for the birch chips is a question for further investigation.

Influence of EIC cooking on reject and yield

Clearly, the EIC concept leads to a reduced reject content for birch and enables termination of the kraft cook at a higher than otherwise cooking kappa number. Termination at a higher cooking kappa number using the EIC concept led to no significant increase in carbohydrate yield and the carbohydrate yield was no more than that obtained using conventional cooking. This is in contrast to what has been reported for *E. urograndis*, in which a carbohydrate yield gain of 3.6 percentage points was obtained using the EIC concept when terminating at a higher cooking kappa number (Wedin et al. 2010). The reasons underlying our poor outcome in terms of carbohydrate yield gain when terminating at a higher cooking kappa number could be found in the quantity and structure of the birch wood components and in the procedure for performing the EIC cook in the lab. Recently, Pinto et al. (2005) found that birch and eucalypt (i.e. *E. urograndis* and *E. globulus*) differed in carbohydrate dissolution behaviour during the kraft cook. They reported that a considerable loss of xylose, approximately 25% of the initial xylose content of the wood, was already seen in birch at 75°C , whereas the eucalypt species displayed only a minor xylose loss of approximately 10%. This loss was probably related to the higher amount of xylan originally present in the wood, and to the fact that birch xylan has a lower molecular weight and a less branched structure than does the eucalypt xylan. The fact that much of the birch xylan is lost during the initial delignification phase has also been observed by Danielsson and Lindström (2005). Approximately 40% of the originally present birch xylan dissolved after a brief cooking time, and half of that was degraded to low-molecular-weight molecules. In the present study, the liquor-to-wood ratio after impregnation decreased from 7:1 to 4:1, which meant that about half of the black liquor had to be extracted to achieve the desired liquor-to-wood ratio in the first cooking step. Assuming that much of the birch xylan was already dissolved during impregnation, the large early extracted amount after the impregnation probably removed much of the dissolved xylan, preventing part of it from precipitating later on in the kraft cook. As can be seen in Table 5, the xylan contribution to the yield was in fact slightly less for the EIC than the CK pulps.

Pinto et al. (2005) also observed no glucose loss for birch during the initial phase of delignification, whereas glucose was largely dissolved ($\sim 5\%$, wood basis) for the two eucalypt species. They explained that the glucose loss was probably due to degraded amylopectin present in eucalypt wood rather than to cellulose. In the present study, the cellulose content of wood (Table 4) and the cellulose amount contributing to the yield after the cook (Table 5) were similar, indicating that almost no cellulose was lost during the birch cook. In other words, the maximum limit of cellulose yield for birch has already

been reached. Interestingly, for the birch cook, the cellulose contribution to the yield did not decrease with lower cooking kappa numbers. Thus, with the cooking conditions used for the EIC birch pulps in this study, the cellulose seems to be quite stable in the 27–18 kappa number range, resulting in similar amounts of cellulose in the pulps. The strategy for birch EIC cooking would thus be to focus entirely on higher xylan retention to improve the carbohydrate yield. However, a higher cooking kappa number may still be an option for birch cooking, since lower cooking temperatures yield other benefits, such as a lower requirement for medium steam pressure.

The influence of EIC cooking on HexA and viscosity

EIC cooking led to a slightly higher HexA content in the unbleached pulp than did the CK cooking. The higher HexA content is probably related to the cooking temperature and the energy of activation of HexA formation and degradation rather than to the xylan content, since a similar xylan content was obtained for the EIC and the CK pulps. According to Danielsson et al. (2006), the energy of activation for HexA formation is 129 kJ mol^{-1} , whereas the energy of activation for HexA degradation is 141 kJ mol^{-1} . The lower cooking temperature of EIC cooking would thus reduce the degradation of HexA, resulting in a higher HexA content.

EIC cooking led to a higher limiting viscosity number after the cook and also after the bleaching than did the conventional cooking. It is known that a decrease in cooking temperature leads to a higher limiting viscosity number at a given kappa number (Stockman, Sundkvist 1958; Bäckström, Jensen 2001). Hence, the improved modified kraft cooking using a lower cooking temperature probably accounts for the higher viscosity numbers.

Influence of EIC on oxygen delignification, bleaching, and overall yield

Although the carbohydrate yield was similar after the cook for the EIC and CK pulps at a kappa number of approximately 17, it seemed that the EIC17.8 pulp lost 1.5 percentage points more carbohydrates than did the CK17.4 pulp during oxygen delignification and bleaching, leading to a lower overall yield for EIC17.8. However, this overall yield of 52.2% for the CK17.4 pulp seemed to be unrealistic high as the yield after oxygen delignification was approximately 51.9% of wood (i.e. lignin included). The reason for this was probably the uncertainty in the yield determination. It would be expected that the overall yield of the CK17.4 pulp would be similar as the CK21.4 pulp of approximately 51%, and thus no significant difference compared to the EIC pulps of 50.7–50.9%.

The results of the extended oxygen delignification of EIC cooking at kappa number 27 displayed that it was possible to prolong the oxygen delignification to reach kappa number 10 and still obtain an overall yield similar to that obtained with EIC cooking at cooking kappa number 18. Moreover, after bleaching, the limiting viscosity number, bleaching chemical requirement, and strength properties of EIC27 were similar to those of the EIC18 pulp. Thus, the stronger conditions in the extended

oxygen delignification of birch did not substantially affect the bleaching performance and pulping properties. It was noted in *Table 6* that extended oxygen delignification resulted in a higher gravimetric yield after the oxygen stage. This may be due to an increased amount of oxidised lignin, since oxidised lignin weighs more than native lignin due to the introduction of carbonyl and carboxylic groups. Gravimetric yield determination including an oxygen delignification stage prior to bleaching can cause overestimation of yield (Rööst, Jönsson 2001).

In the literature, it has been shown that birch kraft pulp with a higher brightness after oxygen delignification consumes less bleaching chemicals in a D(EOP)DD sequence with the same “lignin”-kappa number after oxygen delignification (Axelsson, Lindström 2004). This finding was explained to be related to a high hydroxide ion concentration during kraft cooking, resulting in a bright and low-molecular-weight lignin structure presumably bound to carbohydrates (Axelsson et al. 2005). Moreover, eucalypt pulp with a high HexA content has been shown to have high ISO brightness and consume less bleaching chemicals in a D*(OP)D sequence than a low-HexA eucalypt pulp at an equal kappa number into bleaching (Gustavsson and Ragnar 2007). This is logical because HexA is colourless, whereas lignin is coloured, and the bleaching chemicals in a D*(OP)D sequence would preferentially react with coloured lignin rather than with HexA, which instead is substantially degraded hydrolytically in the D* stage (due to the low pH and high temperature). Based on these findings, a lower bleaching chemical requirement for the EIC pulps compared to that for the CK pulps in this study would thus be expected because the EIC pulps obtained higher ISO brightness after oxygen delignification and also had a higher HexA content at a given kappa number.

In the present study, the higher ISO brightness number for the EIC pulps after oxygen delignification correlated linearly with lower chlorine dioxide consumption in the bleaching (at an ISO brightness of 90%), as shown in *Fig 8*.

Thus, the levelled-out alkali profile in the EIC cooking and the slightly higher HexA content in the EIC pulps

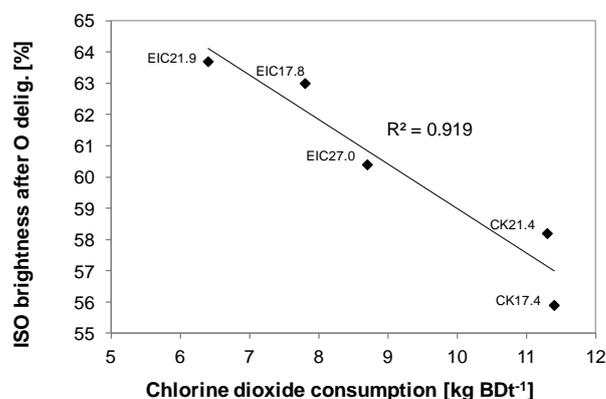


Fig 8. ISO brightness after oxygen delignification correlates with total chlorine dioxide consumption in a D(OP)DP bleaching sequence, at an ISO brightness of 90%, for EIC and CK birch pulps.

may explain the higher ISO brightness after oxygen delignification and hence the lower bleaching chemical requirement in the D(OP)DP sequence.

The importance of HexA for accelerated yellowing has been thoroughly discussed for thermal drying-induced yellowing (Vuorinen et al. 1999; Silva et al. 2011) and thermal wet-induced yellowing (Granström et al. 2001; Sevastyanova et al. 2006; Silva et al. 2011). It has also been reported that the use of oxidising bleaching chemicals such as chlorine dioxide in itself induces HexA-related accelerated yellowing (Ragnar et al. 2007). The causes underlying yellowing are very complex. In the present study, in which drying-induced yellowing was applied, the higher HexA content of the bleached EIC pulps probably largely affected the yellowing. Optimising the bleaching sequence, for example, changing the D₀ stage to a hot D stage, is one alternative to reduce the yellowing tendency (Ragnar 2005).

Influence of EIC cooking on strength properties

The strength results indicated only a small difference in the tensile index and tensile stiffness index between the bleached EIC and bleached conventional pulps. This may be explained by the similar cellulose and hemicellulose contents of the pulps, as a lower cellulose-to-hemicellulose ratio at a given sheet density is directly proportional to a higher tensile index for unbleached spruce kraft pulps (Molin, Teder 2002). Moreover, Laine and Stenius (1997) have reported that a higher charge of bleached kraft fibres correlates with more fibre swelling and higher fibre flexibility, which will improve the tensile strength. However, the higher HexA content of the bleached EIC pulps seemed not to be high enough to affect the tensile index and tensile stiffness index.

Process consideration

A high liquor-to-wood ratio during impregnation is beneficial for a more homogenous delignification. However, a high liquor-to-wood ratio of 7:1 led to a large extraction volume after the impregnation in the EIC cooking process that probably prevented dissolved xylan to precipitate and increase the xylan yield for birch. Two alternatives will be presented that reduce the extraction volume after the impregnation and may improve xylan retention in a continuous cooking mill system. The first is to convey part of the liquor withdrawn after impregnation to a later stage of the cook with the help of a central pipe in the digester. Danielsson and Lindström (2005) have demonstrated increased birch xylan retention and improved tensile index by taking part of the black liquor withdrawn from a birch cook after a short retention time and adding it back at a later position of a softwood cook. In this way, the high liquor-to-wood ratio in the impregnation can be maintained. However, this way may increase the load on the second screen section. The second alternative is to minimise the extracted amount after impregnation, which would be possible if a somewhat lower liquor-to-wood ratio were used in the impregnation, and maintain close to the same liquor-to-wood ratio in the upper cooking zone; a liquor-to-wood ratio of 4–5:1 would probably work. This may, however, decrease the liquor-to-wood ratio in the impregnation and

increase the load on the first screen section of the digester since more liquor would have to be withdrawn after the first screen section.

Conclusions

The results clearly demonstrated that the EIC cooking concept reduced the reject content at a given kappa number for birch wood and shifted the defibration point towards a higher cooking kappa number. However, terminating the EIC cook at a high cooking kappa number did not improve the overall yield. The amount of originally present cellulose was little affected by either EIC cooking or CK cooking, leading to almost no cellulose loss. Hence, the limit of cellulose yield has already been reached in the kraft cooking of birch wood. On the other hand, on average 57% of the initially present hemicellulose (i.e. mainly xylan) in wood was dissolved during EIC cooking, and much of that was probably already dissolved during impregnation. The large amount of early extraction of spent impregnation liquor in EIC cooking may have contained dissolved xylan that was prevented from precipitating later in the cook. Furthermore, the EIC cooking concept leads to a slightly higher HexA content than does the conventional cooking, probably because the lower cooking temperature reduces HexA degradation. By using a longer retention time and higher alkali charge in the oxygen delignification, it was possible to extend the EIC-cooked pulp from kappa number 27 to 10 while maintaining an acceptable limiting viscosity number. Bleaching in a D(OP)DP sequence to an ISO brightness of 90% resulted in less bleaching chemical consumption in EIC than in the conventional kraft pulp. The lower bleaching chemical requirement for the birch EIC pulps was linearly correlated with higher brightness after oxygen delignification. Finally, the strength properties of the bleached EIC birch pulps were similar to those of the conventionally cooked pulp, which may be explained by the similar cellulose-to-hemicellulose ratio of the bleached pulps.

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