Publication I

Mikhail Iakovlev, Timo Pääkkönen, and Adriaan van Heiningen. 2009. Kinetics of SO_2-ethanol-water pulping of spruce. Holzforschung, volume 63, number 6, pages 779-784.

Holzforschung, Vol. 63, pp. 779–784, 2009 • Copyright © by Walter de Gruyter • Berlin • New York. DOI 10.1515/HF.2009.109

Kinetics of SO_2-ethanol-water pulping of spruce

10th EWLP, Stockholm, Sweden, August 25–28, 2008

Mikhail Iakovlev[1,*], Timo Pääkkönen[1] and Adriaan van Heiningen[1,2]

[1] Department of Forest Products Technology, Helsinki University of Technology, Espoo, Finland

[2] Department of Chemical and Biological Engineering, University of Maine, Orono, ME, USA

*Corresponding author.
Department of Forest Products Technology, Helsinki University of Technology, PL 6300, 02015 TKK, Espoo, Finland
E-mail: mikhail.iakovlev@tkk.fi

Abstract

SO_2-ethanol-water (SEW) pulping is a promising fractionation process for lignocellulosics to produce pulp and value-added chemicals as a contribution to the concept of forest biorefinery. The presence of SO_2 leads to dissolution of hemicelluloses in high yield mostly as monomeric sugars, while lignin becomes soluble through sulfonation. After lignin removal, the dissolved sugars may be used as feedstock for fermentation to ethanol or butanol. SEW pulping may be considered a hybrid between solvent pulping (organosolv pulping by solvolysis) and acid sulfite pulping. Absence of an inorganic base leads to simplification of the recovery cycle. Furthermore, alcohol increases the impregnation rate of dissolved SO_2 into wood, so that a separate impregnation phase is not necessary. Also, the presence of SO_2 allows cooking of softwoods, while ethanol pulping is limited to hardwoods. Thus, SEW pulping may be applied to a wide variety of lignocellulosics at lower temperatures and similar cooking times than those used in kraft pulping. In the present study, SEW pulping experiments were performed on spruce chips at cooking temperatures of 135–165°C with a 12% SO_2 solution at a liquor-to-wood ratio of 6:1 $l\ kg^{-1}$. The effect of cooking temperature and time on kappa number, yield, and intrinsic viscosity of the pulp was determined. Based on these results, the kinetics of delignification, hemicelluloses removal, and cellulose hydrolytic destruction were established.

Keywords: biorefinery; cellulose degree of polymerization; delignification; ethanol; kinetics; organosolv pulping; sulfur dioxide.

Introduction

Kraft pulping became the preferred process in the last seven decades because of its advantages in pulp quality, efficient chemical recovery, and applicability to all wood species. However, kraft-based pulp and paper mills in the temperate-climate regions are presently under great economic pressure due to competition from new producers in tropical and subtropical regions, where the largest possible units are established based on the latest technologies. The costs for wood and labor are low in these regions. In temperate-climate regions, modified and alternative pulping processes are needed which would allow forest products companies to obtain additional revenue from lignocellulosics besides the traditional products (van Heiningen 2006). Another key driver for innovative developments in this field is the concern about climate change and the notion/legislation that renewable fuels and chemicals derived from biomass are needed to address this global problem.

In the past, the ALCELL pulping process was developed based on ethanol/water (1:1) as delignification solution. This process already follows the biorefinery concept as cellulosic fibers, hemicelluloses, and lignin are obtained in separate streams. Other advantages are a relatively simple chemical recovery and a higher pulp yield. The ALCELL process is limited to hardwood pulping and requires high temperatures and pressures (Pye and Lora 1991). Other organosolv processes (Acetosolv and Acetocell, Formacell, Organocell, ASAM, Milox) have also been explored. However, due to the problems related to the feedstock (wood species, presence of silica, moisture content, etc.), solvent losses and process difficulties (e.g., complex recovery operations), none of these are presently commercialized.

SO_2-ethanol-water (SEW) pulping was introduced by Schorning (1957). Later on, it was demonstrated that ethanol concentration around 50% (by vol.) is optimal and the concentration of SO_2 could be between 1% and 15%. Without the presence of a base, the initial pH is approximately 1. The temperature range between 130°C and 160°C was tested (Eliashberg et al. 1960; Primakov 1961; Primakov et al. 1979; Westmoreland and Jefcoat 1991). The chemistry of delignification is very similar to that of acid sulfite pulping. By sulfonation, lignosulfonic acids arise. Subsequently, the solid lignosulfonic acids undergo solvolytic destruction resulting in dissolution of lignin fragments (Tsypkina et al. 1981; Vishnevskaya et al. 1981; Kushko and Primakov 1984). It is known that the solubility of lignosulfonic acids in ethanol is several times higher than that in water (Primakov et al. 1979). However, the main role of ethanol is to facilitate impregnation of SO_2 into the chips. The pH of the pulping solution decreases with time because of the formation of strong lignosulfonic acids. The presence of ethanol reduces the acidity somewhat, thereby reducing the carbohydrates hydrolysis.

SEW pulping can also be considered as fractionation process for the biorefinery concept by separating the feedstock into: (1) cellulosic fibers and (2) mostly undegraded monosugars from hemicelluloses, and (3) low-sulfonated lignin precipitates obtained from the sugar solution when ethanol is evaporated. Additional treatment of the ethanol-free spent liquor leads to precipitation of (4) higher-sulfonated lignin. Recovery of the pulping chemicals (SO_2 and ethanol) is possible by simple distillation and washing due to the absence of a base (Mg, Na, etc.). The absence of bisulfite in the pulping liquor explains the limited degradation of the dissolved sugars, and decrease in sulfur consumption compared to sulfite pulping (Primakov and Barbash 1989). Ethanol does not take part in the delignification reactions and can almost totally be recovered (Primakov et al. 1979).

The SEW process permits the cooking of softwoods, such as spruce and even pine. The monomeric sugars set free can be fermented to alcohols (ethanol, butanol, etc.) and acids (succinic acid, lactic acid, etc.). The advantage of SEW over the traditional acid sulfite process, which can also be classified as biorefinery fractionation, is that the presence of ethanol leads to fast impregnation of the chips so that the impregnation phase may be eliminated. Like sulfite pulp, SEW pulp is very bright and more easily bleached than kraft pulp.

Of course, the SEW pulping also has disadvantages. The pulp quality is similar to that of sulfite pulp (Eliashberg et al. 1960), which primarily means lower tear strength than that of kraft pulp. The efficiency of ethanol recovery from the pulp suspension must also be very high to minimize costly ethanol losses. Other drawbacks include flammability of ethanol, corrosiveness of the liquor, and potential sulfur dioxide losses to the atmosphere. These disadvantages prevented commercial implementation in the past. However, with the renewed interest in the biorefinery concept, and the potential of the SEW process to fractionate all lignocellulosic biomass, including agricultural and municipal waste, further investigation of the fundamental chemical kinetics of this fractionation process is needed.

In the present study, the kinetics of SEW pulping of spruce are determined in terms of delignification, hemicelluloses removal, and cellulose hydrolytic destruction.

Experimental

The pulping liquor was prepared by injecting gaseous sulfur dioxide into ethanol/water (1:1, v/v). Deionized water and ethanol ETAX A (96.1 v/v%) were used. The concentration of SO_2 in the liquor was 12% (by weight). A total of 25 o.d. g of screened (// 2–4 mm) air-dried spruce chips and liquor at a liquor-to-wood ratio of 6 l kg^{-1} were placed in 220 ml bombs. Heating was done in silicon oil bath at temperatures 135°C, 145°C, 155°C, and 165°C (±1°C). After rapid quenching in cold water, the pulp was removed from the bombs and placed into a washing sock. After squeezing the spent liquor, the pulp was washed several times with 50 ml of the solvent at 60°C and finally two times with 500 ml of deionized water at room temperature. The resulting pulp was analyzed for yield, kappa number by SCAN-C 1:00, and intrinsic viscosity in cupriethylenediamine (CED) solution using SCAN-CM 15:99. Pulps with a kappa number higher than 35 were exposed to chlorite delignification prior to viscosity measurement according to T230 om-66. The pulp yield was determined with a reproducibility of ±0.3% based on the original wood weight.

The pulping conditions for establishing the washing procedure were 145°C, 40 min pulping time and 12% SO_2. The solvents studied were water, ethanol/water (4:6 and 7:3, v/v) and dioxane/water (9:1, v/v). The washing efficiency was optimized based on kappa numbers of the pulps obtained. Additional cooking experiments were done with chips fractions // 6–8 mm and // 2–4 mm to compare pulp properties. For these experiments, a different batch of spruce chips was used.

Results and discussion

Effect of pulp washing and chip thickness

An effective washing procedure is a prerequisite for reliable pulping kinetics. Hemicelluloses are better removed with polar solvents (water) and lignin with less-polar solvents (dioxane, ethanol, etc.). As a compromise, washing was performed with ethanol/water mixtures. Ethanol warrants an easy recovery of the pulping liquor. Washing with dioxane/water (9:1) was tested to determine the maximum amount of lignin which could be removed from the pulp, as this mixture is well known to be an excellent lignin solvent (Browning 1967). Table 1 summarizes the washing experiments. It shows that washing with water does not remove all the dissolved lignin, while washing with ethanol/water solution results in nearly the same kappa number as obtained with dioxane/water washing. There is no significant difference in kappa numbers when washed in ethanol/water solutions (4:6 or 7:3), and no further improvements are obtained after the second stage of washing. Thus, in the subsequent experiments, the pulp was washed twice with 50 ml of ethanol/water (4:6) at 60°C followed by washing twice with 500 ml water at room temperature.

As sulfite plants practically operate with chips of thickness up to 8 mm, the impregnation rate of relatively thin (// 2–4 mm up to // 6–8 mm) chips should be investigated in terms of the properties of resulting pulps (Table 2). It is obvious that the pulp properties are not affected by chips thicknesses in the range indicated.

Delignification kinetics

Table 3 shows the kappa numbers of pulps obtained at different temperatures and total elapsed cooking times (including heat-up time being ~10 min). Obviously, the

Table 1 Comparative washing of the spruce pulps obtained by SO_2-ethanol-water (SEW) pulping (145°C, 40 min).

Solvent washing at 60°C		Water washing at 20°C	Kappa number
Solvent	Frequency		
–	–	Twice	49.4
–	–	Thrice	40.5
Water	Twice	Twice	48.1
Ethanol/water (4:6)	Once	Twice	36.4
Ethanol/water (4:6)	Twice	Twice	35.6
Ethanol/water (4:6)	Thrice	Twice	35.7
Ethanol/water (7:3)	Once	Twice	40.2
Ethanol/water (7:3)	Twice	Twice	34.8
Ethanol/water (7:3)	Thrice	Twice	35.6
Dioxane/water (9:1)	Thrice	Twice	34.2

Table 2 Influence of chip thickness on spruce SO_2-ethanol-water (SEW) pulping (80 min at 135°C).

Chip thickness (mm)	Pulp properties		
	Yield (%)	Kappa number	Viscosity $[\eta]^a$ (ml g^{-1})
2–4	52.2	36.1	1050
6–8	51.2	35.7	1042
6–8	51.5	36.5	–

[a]Intrinsic viscosity in CED.

delignification proceeds very fast. At the lowest temperature (135°C) a pulp with 30 kappa number is obtained in 80 min. At 165°C, such a pulp is obtained with a cooking time between 15 and 20 min.

The delignification kinetics is first order in terms of lignin removal, as the main reactions of lignin follow the monomolecular nucleophilic substitution S_N1 mechanism (Figure 1, Sixta et al. 2006, p. 409):

$$-\frac{d\,[Lig]}{dt}=k'_{Lig}(T)[Lig]^a[H_3O^+]^b=k_{Lig}(T)[Lig], \qquad (1)$$

where $[Lig]$ – lignin content of pulps,% based on original dry wood; t – duration of pulping, min; k'_{Lig} and k_{Lig} – real and composite (includes proton concentration) delignification rate constants; T – temperature, K; $[H_3O^+]$ – concentration of H_3O^+ in the solution; a and b – reaction orders in lignin and H_3O^+. The simplification of the right-hand side of Eq. (1) by assuming a constant proton concentration during pulping is justified due to the high concentration of the sulfur dioxide in the liquor.

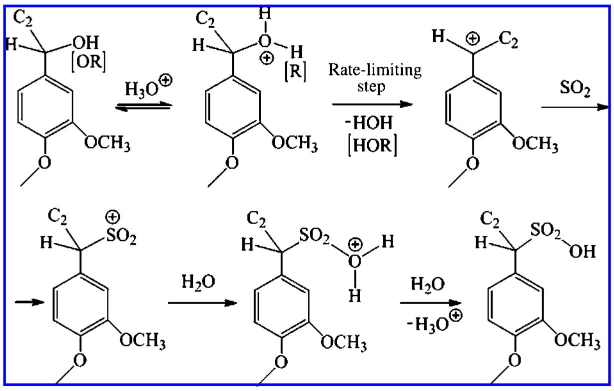

Figure 1 S_N1 mechanism for the sulfonation of lignin: the rate-limiting step is dissociation of the oxonium cation to produce the carbocation.

The pulp lignin content (% based on original wood) was calculated by Eq. (2):

$$[Lig]=0.21Y\kappa, \qquad (2)$$

where Y – pulp yield,%; κ – pulp kappa number.

Table 3 Pulping kinetics data of spruce wood by SO_2-ethanol-water (SEW) pulping.

Temp. (°C)	Duration of pulping (min)	Pulp characteristics						
		Yield, (%)	Kappa number	Lignin content[a] (%)	Lignin free yield (%)	Hemicelluloses content[a] (%)	Intrinsic viscosity in CED, (ml g^{-1})	Cellulose degree of polymerization (DP)
135	40	65.0						
	50	59.9	87.3	11.0	48.9	8.90	1128	6657
	60	56.3	62.5	7.40	48.9	8.90	1085	5943
	70	53.6	43.5	4.90	48.7	8.70	1094	5677
	80	51.2	29.4	3.10	48.1	8.10	1058	5197
	80	51.8	32.2	3.50	48.3	8.30	1083	5404
	100	48.4	17.0	1.70	46.7	6.70	982	4501
	120	47.9	9.1	0.90	47.0	7.00	884	3949
145	25	62.3						
	30	57.9	76.9	9.30	48.6	8.60	1086	6140
	35	53.1	52.5	5.80	47.3	7.30	1020	5202
	40	51.1	35.6	3.80	47.3	7.30	1089	5364
	40	51.7	38.8	4.30	47.4	7.40	1007	4978
	50	48.4	17.4	1.80	46.6	6.60	875	3952
	60	46.9	10.5	1.00	45.9	5.90	776	3340
155	15	66.6						
	20	55.7	76.2	8.90	46.8	6.80	1001	5379
	25	49.9	29.1	3.00	46.9	6.90	904	4241
	30	47.1	17.2	1.70	45.4	5.40	784	3395
	30	47.3	14.3	1.40	45.9	5.90	744	3213
	40	44.7	8.1	0.80	43.9	3.90	554	2176
	50	42.8	6.4	0.50	42.3	2.30	438	1602
165	10	74.3						
	15	54.3	68.4	7.80	46.5	6.50	948	4922
	20	46.5	16.0	1.60	44.9	4.90	671	2815
	25	43.7	7.4	0.70	43.0	3.00	458	1721
	30	42.7	6.5	0.60	42.1	2.10	353	1255
	35	41.7	5.4	0.50	41.2	1.20	295	1004

[a]Based on wood.

The coefficient 0.21 was found by comparing the kappa number and Klason lignin content of some pulps. By plotting the natural logarithm of the lignin content (% based on wood) versus cooking duration, two phases of delignification can be observed at 155 and 165°C: bulk and residual (Figure 2). Residual delignification occurs when lignin content of pulp drops below 1% (b.o. wood). From the slopes of the bulk delignification linear plots, the delignification rate constants were calculated for different temperatures (Table 3). The delignification rate of kraft pulping at 170°C ($k=0.04$ min^{-1} at 1 N NaOH; Sixta et al. 2006, p. 204) is comparable to that of SEW pulping at 135°C.

The Arrhenius equation was applied to establish the dependence of pulping reactions rate constants on temperature:

$$\frac{d\ln k}{dT}=\frac{E_A}{RT^2}, \tag{3}$$

where k – rate constant of the particular reaction at fixed temperature; E_A – activation energy for this particular reaction, kJ mol^{-1}; R – gas constant, $R=8.314$ J mol^{-1} K^{-1}.

An activation energy of 114 kJ mol^{-1} was calculated (Table 4) by plotting the natural logarithm of the delignification rate constant versus the inverse of the temperature using the data of cookings at 135°C, 145°C, and 155°C. This value is lower than that of kraft delignification (134 kJ mol^{-1}, Vroom 1957) but higher than that of acid sulfite delignification (88 kJ mol^{-1}, Richards and van Heiningen 2004).

Kinetics of hemicelluloses removal

The development of the pulp yield during pulping is shown in Table 3 and Figure 3. At kappa number 30, the yield is 51.5% at 135°C. The yield at constant kappa number decreases with increasing temperature because of the higher rate of hemicelluloses removal compared to delignification. The higher pulp yield (at levels of similar kappa numbers) than that of kraft pulp (~46% for kappa number 30; Sixta et al. 2006, p. 289) may be explained by the absence of carbohydrates peeling-off reactions and higher retention of hemicelluloses due to the relatively short pulping time.

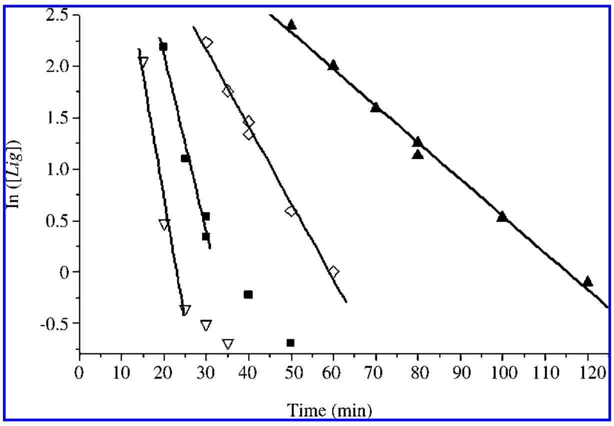

Figure 2 Natural logarithm of lignin content of pulps, % on wood {ln([*Lig*])}, versus pulping duration (*t*): ▲, 135°C; ◇, 145°C; ■, 155°C; ▽, 165°C.

Table 4 Kinetics of spruce pulping by the SO_2-ethanol-water (SEW) process: reaction rate constants and activation energies.

	Reaction rate constants at different temperatures, min^{-1}					
	Delignification		Hemicelluloses losses		Cellulose hydrolytic destruction	
	$k_{Lig}\times10^3$	R^2	$k_{Hemi}\times10^3$	R^2	$k_{Cel}\times10^6$	R^2
135°C	35.7	0.99	4.43	0.83	1.45	0.99
145°C	74.7	0.99	11.2	0.92	4.58	0.96
155°C	171	0.98	38.0	0.95	14.9	0.99
165°C	241	0.97	84.5	0.99	40.5	1.00
	Activation energies, kJ mol^{-1}					
	$E_{A(Lig)}$	R^2	$E_{A(Hemi)}$	R^2	$E_{A(Cel)}$	R^2
	114	1.00	150	0.99	166	1.00

R^2, pair correlation coefficient.

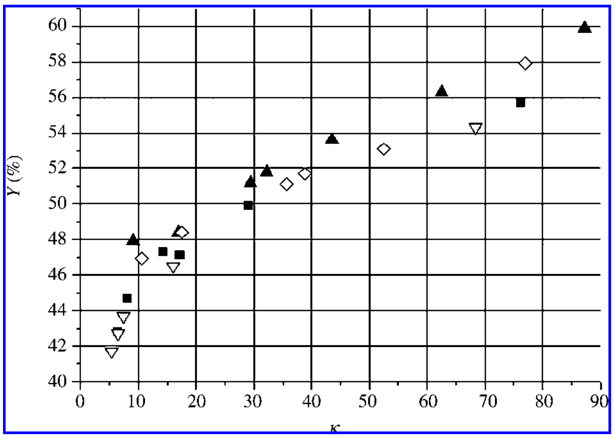

Figure 3 Pulp yield (*Y*) versus kappa number (*κ*): ▲, 135°C; ◇, 145°C; ■, 155°C; ▽, 165°C.

The main hemicelluloses dissolution reaction is acid hydrolysis following an S_N1 mechanism, so the kinetics of hemicelluloses removal from pulp can be expressed by the equation:

$$\begin{aligned}-\frac{d\,[Hemi]}{dt} &= k'_{Hemi}\,(T)\,[Hemi]^c\,[H_3O^+]^d\\ &= k_{Hemi}\,(T)\,[Hemi],\end{aligned} \tag{4}$$

where [*Hemi*] – hemicelluloses content of pulp, % based on original wood; k'_{Hemi} and k_{Hemi} – real and composite rate constants for hemicelluloses removal; c and d – reaction orders in hemicelluloses and H_3O^+.

The hemicelluloses content of pulps was calculated by subtracting the contents of cellulose and lignin from the pulp yield. Cellulose was assumed to be totally retained in the pulp because of its high resistance to acid hydrolysis and the random nature of the hydrolytic cleavage reaction. The natural logarithm of the hemicelluloses content (% b.o. wood) was plotted versus cooking time (Figure 4). The reaction rate constants were calculated from the slopes of the straight lines (Table 4). Figure 4 reveals that the correlation lines obtained at the different temperatures converge at a hemicelluloses content of around 11% (b.o. wood). Therefore, it may be concluded that a part of the hemicelluloses dissolves very fast in the SEW solution during the heat-up period. This fast dis-

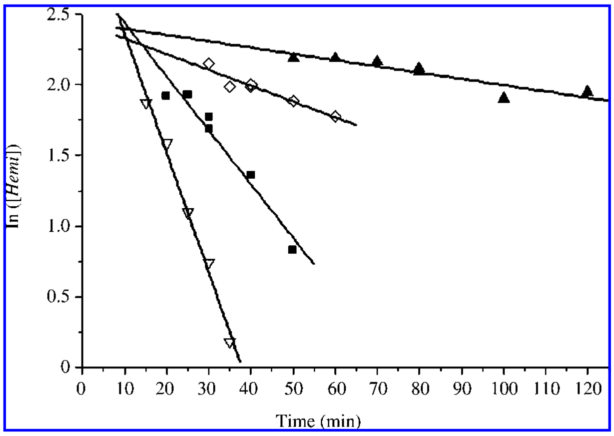

Figure 4 Natural logarithm of hemicelluloses content of pulps, % on wood {ln([*Hemi*])} versus pulping duration (*t*): ▲, 135°C; ◇, 145°C; ■, 155°C; ▽, 165°C.

solution likely includes the cleavage of galactose side units and deacetylation of glucomannan.

According to the Arrhenius Eq. (3), the activation energy of hemicelluloses dissolution was calculated to be 150 kJ mol^{-1} (Table 4). The higher value of the activation energy for hemicelluloses losses in comparison to that of delignification implies that with increasing temperature the delignification selectivity ($=k_{Lig}/k_{Hemi}$) decreases: at 135°C $k_{Lig}/k_{Hemi}=8.1$, while at 165°C $k_{Lig}/k_{Hemi}=2.9$. This explains the lower yield at higher temperature and at the same kappa number level.

Kinetics of cellulose hydrolytic destruction

The selectivity plot in Figure 5 and the data in Table 3 show that the intrinsic pulp viscosity remains high down to a kappa number of approximately 30 (at 135°C a 30 kappa number pulp has an intrinsic viscosity around 1050 ml/g).

Under acid conditions, protons randomly attack the glycosidic bonds along the cellulose chains leading to a rapid decrease in the average degree of polymerization (DP) of cellulose. However, because the DP of the degraded cellulose chains is still in the order of 1000, cellulose is retained in high yield in the pulp. The hydrolytic attack proceeds again via the S_N1 mechanism, so the kinetics of this process could be expressed by the equation:

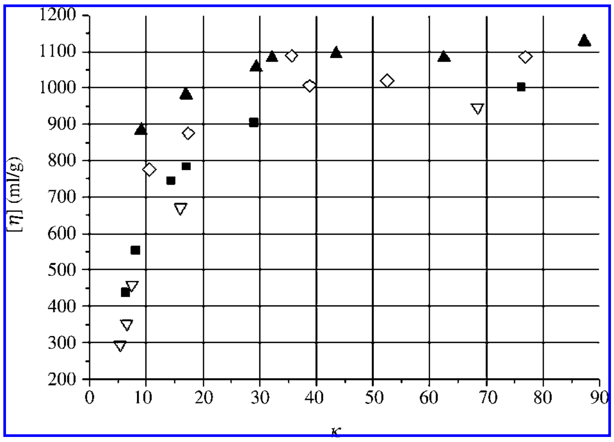

Figure 5 Intrinsic viscosity of pulp ([η]) versus kappa number (κ): ▲, 135°C; ◇, 145°C; ■, 155°C; ▽, 165°C.

$$-\frac{dn}{dt}=k'_{Cel}\,(T)n^{e}\,[H_3O^+]^{f}=k_{Cel}\,(T)n, \tag{5}$$

where n – the number of glycosidic bonds in all cellulose chains, k'_{Cel} and k_{Cel} – real and composite cellulose hydrolytic destruction rate constants; e and f – reaction orders.

The number of glycosidic bonds in one cellulose chain is equal to the number of glucose units in this chain minus one, so for M cellulose chains the number of glycosidic bonds, n, is (Emsley and Stevens 1994):

$$n=N-M=N\left(1-\frac{1}{DP}\right), \tag{6}$$

where N – total number of glucose units in cellulose; M – number of cellulose chains.

By inserting Eq. (6) in Eq. (5) and integration of Eq. (5) we obtain the following equation:

$$-\ln\left(1-\frac{1}{DP}\right)=k_{Cel}\,(T)t+const \tag{7}$$

Since DP»1, the cellulose degradation kinetics simplifies to a zero order expression:

$$\frac{1}{DP}=k_{Cel}\,(T)t+const \tag{8}$$

The cellulose DP can be calculated from the intrinsic viscosity of pulp solutions in CED by Eq. (9) (da Silva Perez and van Heiningen 2002):

$$DP=\left(\frac{1{,}65[\eta]-116[Hemi]_{pulp}}{[Cel]_{pulp}}\right)^{1.111}, \tag{9}$$

where $[\eta]$ – intrinsic viscosity of pulps in CED, ml/g; $[Hemi]_{pulp}$ – hemicelluloses content of pulp, unit fraction; $[Cel]_{pulp}$ – cellulose content of pulp, unit fraction.

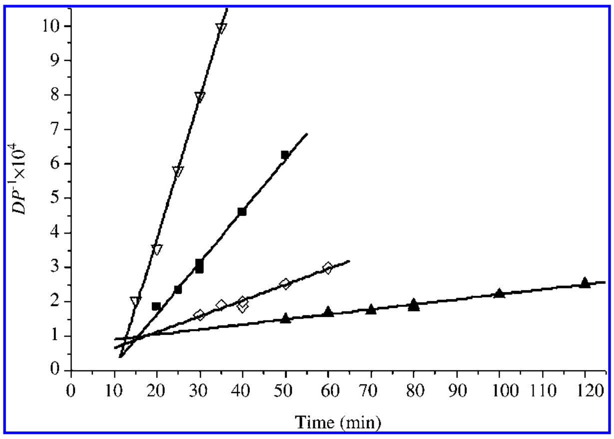

Figure 6 Inverse cellulose degree of polymerization (DP^{-1}) versus pulping duration (*t*): ▲, 135°C; ◇, 145°C; ■, 155°C; ▽, 165°C.

The inverse of the cellulose DP was plotted versus cooking time (Figure 6). The reaction rate constants were calculated from the slopes of the straight lines (Table 4). The intersection of the lines corresponds to the DP of cellulose in the native spruce (around 10 000).

According to the Arrhenius Eq. (3), the activation energy of cellulose hydrolytic cleavage was calculated to be 166 kJ mol^{-1}, which is within the known range of the activation energies for cellulose acid hydrolysis (160–180 kJ mol^{-1}) (Table 4). The selectivity of delignification relative to cellulose hydrolytic cleavage ($=k_{Lig}/k_{Cel}$) decreases with increasing temperature as a consequence of the high activation energy for the latter reaction: at 135°C $k_{Lig}/k_{Cel}=25\ 000$, while at 165°C $k_{Lig}/k_{Cel}=6000$.

Conclusions

1. The presence of ethanol allows fast impregnation of SO_2 into the chips irrespective of chip thickness over the range of 2–8 mm.
2. SEW pulping enables the production of pulp in a very short time (starting from 15–20 min including heat-up time). At 135°C, the delignification rate is close to that of conventional kraft pulping at 170°C.
3. The pulps have a higher yield compared to kraft pulps of the same kappa number due to higher hemicellulose retention. The average DP of cellulose remains high down to a kappa number of around 30.
4. The rate constants of the main pulping reactions – delignification, hemicelluloses removal, and cellulose hydrolytic destruction – were calculated at different temperatures. The activation energies for these reactions were obtained. Based on these values one can conclude that higher yield and higher cellulose DP pulps are obtained at lower cooking temperatures.

Acknowledgements

The support of Dr. Sergey Malkov for this research project and the help of Rory Jara with the Klason lignin determination are acknowledged. Financial support by TEKES (Finnish Funding Agency for Technology and Innovation) through the FiDiPro program is greatly appreciated.

References

Browning, B.L. Methods of Wood Chemistry. John Wiley & Sons, New York, 1967.

Eliashberg, M.G., Parfenova, A.I., Primakov, S.F. (1960) The delignification of wood with SO_2 solutions not containing bisulfite. Trudy Leningrad. Lesotekh. Akad. S.M. Kirova 91: 235–245.

Emsley, A.M., Stevens, G.C. (1994) Kinetics and mechanisms of the low-temperature degradation of cellulose. Cellulose 1: 26–56.

Kushko, M.S., Primakov, S.F. (1984) Characteristics of lignosulfonic acids after wood pulping using water-alcohol solutions of sulfur dioxide. Vestn. Kiev. Politekh. Instit. Khimich. Mashinostr. Tekhnol. 21:29–30.

Primakov, S.F. (1961) Delignification of various wood species with aqueous-alcoholic solutions. Nauchn. Tr. Vses. Nauchn.-Issled. Inst. Tsellyulozn.-Bumazhn. Prom. 47:69–75.

Primakov, S.F., Barbash, V.A. (1989) Wood delignification by aqueous alcohol solutions of sulfur dioxide. Bumazhnaya Promyshlennost 1:6–7.

Primakov, S.F., Tsarenko, I.M., Zaplatin, V.P. (1979) Delignification of wood by aqueous-alcohol solutions of sulfur dioxide. Kiev. Politekh. Inst., Kiev, USSR. Koksnes Kimija 6:39–42.

Pye, E.K., Lora, J.H. (1991) The Alcell process – a proven alternative to kraft pulping. Tappi J. 74:113–118.

Richards, T., van Heiningen, A. (2004) Development of a fundamental expression of the delignification rate for acid sulphite pulping. J. Pulp Pap. Sci. 30:263–268.

Scandinavian Standard (2000) SCAN-C 1:00. Chemical Pulp: Kappa number.

Scandinavian Standard (1999) SCAN-CM 15:99 Pulps: Viscosity in cupriethylenediamine solution.

Schorning, P. (1957) Base-free sulfite pulping of wood. Faserforsch. Textiltech. 8:487–494.

da Silva Perez, D., van Heiningen, A.R.P. (2002) Determination of cellulose degree of polymerization in chemical pulps by viscosimetry. In: The Seventh European Workshop on Lignocellulosics and Pulp (EWLP, Proceedings), Turku, Finland. Ed. Sixta, H. Wiley-VCH, Weinheim, Germany. pp. 393–396.

Sixta, H., Potthast, A., Krotschek, A.W. (2006) Chemical pulping processes. In: Handbook of Pulp, Vol. 1. pp. 109–509.

Tappi standard (1966) T 230. Om-66, Viscosity of pulp (capillary viscometer method).

Tsypkina, M.N., Vishnevskaya, S.S., Boyarskaya, R.K., Grunchak, V.G., Khvorostin, Ya.S., Rodichev, A.G. (1981) Sulfonation and dissolution of lignin in sulfite pulping. 1. Sulfonating agents. Vses. Nauchno-Proizvod. Ob'edin. Tsellyul. Bum. Prom., Leningrad, USSR. Koksnes Kimija 1:19–22.

van Heiningen, A. (2006) Converting a Kraft pulp mill into an integrated forest biorefinery. Pulp Paper Canada 107:38–43.

Vishnevskaya, S.S., Boyarskaya, R.K., Tsypkina, M.N. (1981) Sulfonation and dissolution of lignin in sulfite pulping. 2. Factors determining the dissolution of lignin. Vses. Nauchno-Proizvod. Ob'edin. Tsellyul. Bum. Prom., Leningrad, USSR. Koksnes Kimija 1:23–28.

Vroom, K.E. (1957) The 'H' factor: a means of expressing cooking times and temperatures as a single variable. Pulp Paper Mag. Can. 58C:228–231.

Westmoreland, R.A., Jefcoat, I.A. (1991) Sulfur dioxide-ethanol-water pulping of hardwoods. Chem. Eng. Comm. 104:101–115.

Received October 15, 2008. Accepted May 11, 2009.