Improvement of Hardwood Pulp Yield in Continuous Kraft Cooking and Estimation of Pulp Yields Pulp yields of isothermal cooking with polysulfide and anthraquinone

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ABSTRACT

The pulp yield was improved by about 4.5-5% when polysulfide (PS) and anthraquinone (AQ) were added to the kraft cooking liquor (white liquor). The exchange of the black liquor with fresh white liquor further increased the yield. The highest pulp yield was obtained when the PS cooking liquor containing 70% of total active alkali (AA) and 100% of AQ was used from the beginning of the reaction and the black liquor was exchanged with fresh white liquor containing the residual 30% of AA just after temperature reached 135°C.

There was a good correlation between kraft pulp yields of a hardwood species and the ratios of the amount of xylose to glucose (X/G ratio), liberated by an acid hydrolysis of the pulps. However, the correlation was dependent on raw material wood species. Therefore, it is required in advance to establish a correlation between the yields and X/G ratios for raw material wood species of a target pulp in order to estimate pulp yield using X/G ratio. The X/G ratios of relatively high yield pulps showed higher values than those expected from the correlation.

In a mill trial, the superiority of the PS-AQ isothermal cooking (ITC) process over the kraft ITC process was confirmed by examining X/G ratio of pulps obtained. The pulp yield in the PS-AQ ITC process was estimated at about 57.0%. This yield is very high, which indicates that reaction conditions of the PS-AQ ITC process are optimal.

INTRODUCTION

The Law Concerning Special Measures Against Dioxins has been enforced in Japan since January 2000. Under enforcement of the Law, total amount of polychlorinated dibenzo-p-dioxins, dibenzofurans and co-planar biphenyls must be less than 10 pg-TEQ/L (TEQ: toxicity equivalency quantity) in effluent from a pulp mill and 1 pg-TEQ/L in environment water. This law has led Japanese pulp and paper mills to replace conventional chlorine bleaching with elemental chlorine free (ECF) bleaching. The chlorinated dioxins and chloroform are formed when molecular chlorine is used for pulp bleaching[1,2]. When ECF bleaching is introduced into a pulp mill, kraft cooking and oxygen delignification are required to further decrease kappa numbers of unbleached pulps. The decrease contributes to reduction of amounts of chlorine dioxide required and organic compounds in bleaching effluent. However, preparation of a pulp with a low kappa number during a cooking stage inevitably reduces pulp yield. Under these circumstances, improvement of pulp yield is currently a pressing issue for pulp mills.

Anthraquinone (AQ) additive cooking was developed and reported simultaneously by Nomura[3] and Holton[4] in 1977-1978. A mill trial with AQ to polysulfide (PS) cooking using the Moxy process was reported by

Kleppe[5] in 1981. The trial was made at M. Peterson & Søn A/S, Moss, Norway. A continuous digester system, which was called a dual vessel Kamyr digester, was used for producing PS-AQ softwood pulp with an estimated yield 56.2% at kappa number 60. The yield increase compared to kraft pulping was estimated 4.6% by analyzing mannose content of mill pulps. At the 1983 TAPPI Pulping Conference, Yamaguchi also reported on a mill trial and operation of PS (Moxy)-AQ cooking during 1979-1983 at Yuhutsu mill (currently, belongs to Nippon Paper Industries Co., LTD.) in Japan[6].

On the other hand, modified kraft processes for a continuous digester were studied and reported by Nordén and Teder[7] in 1979. This study has been advanced to the modified continuous cooking (MCC) and isothermal cooking (ITC) processes. MCC and ITC processes have been installed into many pulp mills[8]. Polysulfide (PS) and anthraquinone (AQ) have been added to a kraft cooking process to improve pulp yield[9-14]. Application of the ITC process with addition of both PS and AQ could currently be the best method for improvement of pulp yield. However, the best conditions for the application have not been optimized yet. It is possible to further improve pulp yield by the optimization of the process with PS and AQ.

Although the pulp yield during cooking stage is the most important factor in a pulp mill, it is very difficult to estimate the yield due to continuous operation of the mill. A gravimetric analysis cannot be used to examine the yield in continuous cooking because unbleached pulps produced are directly sent to subsequent bleaching stages. Therefore, it is necessary to develop a method for estimation of kraft pulp yield in continuous cooking. The method developed will also contribute to confirmation of yield improvement obtained by the optimization of the ITC process with PS and AQ.

In this paper, the optimal reaction conditions for the PS-AQ ITC process were established in a laboratory experiment to obtain a high yield pulp. A method for estimation of pulp yields during continuous cooking was also developed. It is evaluated whether or not ratios of xylose to glucose (X/G ratios), liberated from a pulp by an acid hydrolysis, can be applied as the method. Our attention is focused only on hardwood because hardwood is mainly used as a raw material in Japanese pulp mills. Secondly, the optimal conditions for the improvement of pulp yields were verified at a mill trial using a continuous digester with mixed hardwoods, PS, and AQ. Pulp yields at a mill trial were estimated by knowing X/G ratio of the mill pulps.

MATERIALS AND METHODS
Materials
Acacia mearnsii planted in Brazil (BAC) as well as *Eucalyptus globulus* planted in Chile (CEG) and *Eucalyptus grandis* planted in South Africa was used as a raw material for laboratory experiments. All the chemicals used in this study were commercially available except soluble anthraquinone (AQ). The soluble AQ, 20% of 1,4-dihydro-9,10-dihydroxyanthracene sodium salt in alkaline solution, was provided by Kawasaki Kasei Chemicals Ltd. Distilled water was used in all the experiments except washing of cooked pulps.
Wood chips of *Acacia mearnsii* planted in Brazil (BAC) or *Acacia mangium* planted in Thailand (TAC) and Indonesia (IAC) as well as *Eucalyptus globulus* or *Eucalyptus grandis* planted in Chile (CEG or CEN) and West Australia (WEK) were used as raw materials of mill trials. Wood chips consist of six kinds named as BAC, TAC, IAC, CEG, WEK, and CEN.

Simulated cooks in laboratory for optimization of ITC parameters
Wood chips of *Acacia mearnsii* were screened, and a fraction consisting of about 25 mm × 10 mm × 3 mm sized chips was used. Knots and barks were removed by hand prior to cooking.
About 55 g of the chips (50 g as oven-dried) was soaked in distilled water and stood overnight. The chips were transferred into a stainless steel autoclave with cooking liquor and chemicals, and cooking was carried out in a silicon oil bath under the following conditions; active

alkali (AA) charge as Na_2O: 16-28%, sulfidity: 25%, sulfur charge: 0 or 1%, soluble AQ charge: 0 or 0.04%, liquor ratio: 5 L/kg. Total reaction time was 6 hr. Temperature profile was as follows:
Room temperature —(25min)→ 100°C for 1hr
　　　　　　　　 —(20min)→ 135°C for 2hr
　　　　　　　　 —(15min)→ 145°C for 2hr
An exchange of black liquor with fresh white liquor during reaction was performed as follows. White liquor containing a portion of total AA was used from the beginning of the cook. At a prescribed time, 40 mL of black liquor was withdrawn from a bulb of the autoclave, and consecutively, 40 mL of fresh white liquor containing the remaining AA was added through the bulb by help of pressure of 0.5 MPa nitrogen. The fresh white liquor was previously heated up to the same temperature as that of the cooking liquor, so that cooking temperature was kept constant during the liquor exchange. Concerning sulfur and soluble AQ, 100% of them were added at the beginning. For comparison, 100% of them were added during the reaction to the white liquor which was used for exchanging a part of black liquor in several runs.
After the cooking, the autoclave was cooled in cold water, and then, the cooked chips were thoroughly washed with tap water. The cooked chips were defibrillated by a disintegrator, and the suspension obtained was filtered. The disintegration and filtration were repeated twice to obtain a well-washed pulp. Hand sheets were carefully prepared from the pulp, and the yield was determined by measuring the geometric weight of the sheets. Kappa number of the pulp was measured according to a half scale method of the TAPPI standard method T236 cm-85.

Analysis of xylose and glucose contents of materials
About 330 mg (300 mg as oven-dried) of the pulp sheet was torn into small pieces. And also, about 330 mg (300 mg as oven-dried) of *Acacia mearnsii*, *Eucalyptus globulus* or *Eucalyptus grandis* wood chips were ground to pass a 60-mesh screen and extracted with ethanol/benzene (1/2). The torn pulp or the wood meal was hydrolyzed with 6 mL of a 72% sulfuric acid solution for 2.5 hr at room temperature being kneaded and stirred with a glass stick. The obtained solution containing materials was diluted with distilled water to be a 4% sulfuric acid solution. The 4% solution was kept at 120°C for 1 hr in a sterilization-autoclave.
The solution contained hydrolyzed compounds and residues. After cooling, a prescribed amount of the solution was neutralized to pH 6.5 with a saturated barium hydroxide solution. The precipitates were removed by a centrifuge at 9000-10000 rpm for 30 min, and a portion of the supernatant obtained was subjected to the following treatments. The products in the supernatant were reduced with a sufficient amount of sodium borohydride at room temperature for 1.5 hr.

To terminate the reduction, the solution was acidified with acetic acid, and then, concentrated by a rotary evaporator. The syrup obtained was dissolved in an aliquot of methanol and concentrated. The addition of methanol and concentration were repeated twice. This handling removed most of the borates in the syrup as a volatile complex with methanol. The solution was finally dried under vacuum. The crystals obtained were acetylated with an excess of acetic anhydride at 120°C for 3 hr to obtain xylitol pentaacetate, glucitol hexaacetate and others. The acetic anhydride solution containing the acetates was directly injected to a gas chromatography for the analysis of xylose and glucose ratio (X/G ratio). An area ratio of the xylitol pentaacetate peak to the glucitol hexaacetate peak observed was converted into a weight ratio of xylose to glucose (X/G ratio), liberated from a pulp by the above hydrolyses. The X/G ratio was based on a calibration line previously created for a correlation between the peak area ratio and the weight ratio.

The analysis was performed on an instrument of GC-14 (Shimadzu Co., Ltd., Kyoto, Japan) equipped with a flame ionization detector using helium as a carrier gas. Temperature of an injector and detector was 245°C and 280°C, respectively. The separations were achieved on a capillary column of BPX70 (25 m X 0.22 mm X film thickness 0.25 μm, SGE Japan Inc.). The temperature program was from 215°C to 225°C at a rate of 0.5°C/min with an initial time delay of 1 min.

When the wood meals of three wood species were analyzed, acid insoluble lignin was quantified by the geometric weight of the residue formed during the above hydrolyses, and acid soluble lignin was determined by the UV-absorbance of the filtrate at 205 nm using 110 $(L \cdot g^{-1} \cdot cm^{-1})$ as an absorptivity.

Pulp plant description and operation for optimization of ITC

A pulp line is running with hardwood bleached kraft pulp. Cooking digestion consists of a vapor-phase single vessel. A washing zone in the digester is also used for the prolonged cooking operation. Cooking liquor can be charged into a chip-feeding circulation and also charged separately into three points, such as a top-cooking circulation, a bottom-cooking circulation, and a washing-circulation of the digester. The temperature of the cooking and washing circulation is about 130-145°C. In general, the ITC has a longer cooking time, and the cooking temperature can then be lowered by 10°C compared with conventional cooking.

It is known that AQ and/or PS can suppress the peeling reactions of carbohydrates due to oxidation of their reducing end groups[17]. It is also recognized that PS is decomposed at an elevated temperature[15,16]. In operation for optimization of the ITC with PS and AQ, PS cooking liquor containing about 70% of total alkali was charged into a chip-feeding circulation line, and AQ

solution containing about 0.024% AQ on wood was charged into the same circulation line. Then, kraft cooking liquor containing about 30% of total alkali was mainly introduced into the circulation lines for top-cooking, bottom-cooking and washing originally designed. For comparison, the kraft ITC without any PS and AQ was operated. This means that the PS cooking liquor is changed to kraft cooking liquor and that AQ stops. The cooking temperature was increased and adjusted to keep a target kappa number. Sulfidity of cooking liquor was 27%. About 55% of sulfide was oxidized for polysulfide cooking.

A preliminary mill trial was done during 7:00-22:00 on April 8, 2003. The kraft ITC without PS and AQ was operated from 22:00 on April 8 to 16:00 on April 10. The optimized ITC operation was started from 16:00 on April 10. Retention time of wood chips in the digester was about five and a half hours.

Control pulp samples from kraft ITC operation were taken out during 9:00-13:30 on April 10. For the optimized ITC, pulp samples were taken out during 18:00-22:30 on April 11. Every thirty minutes, about 100g of pulp was taken out from a sampling line connected with a blow line between a digester and a pressure diffuser, and washed with tap water.

Analysis of pulp qualities

Visible shives in the pulp suspension were removed by decantation. Hand sheets were made from the pulp samples for analyses of kappa number (TAPPI test method T236 cm-85), viscosity (TAPPI test method T230 om-94), brightness, and carbohydrate composition. Brightness was measured using a digital color meter Model TC-3600 (0°-d method, JIS Z 8722) provided by Tokyo Denshoku Co., Ltd., and ISO brightness was calibrated.

Laboratory cooks for making calibration between pulp yields and X/G ratios

Mixed wood chips of BAC(A1), TAC(A2), IAC(A3), CEG(E1), WEK(E2), and CEN(E3) were used. Each wood chip was screened, and a fraction consisting of about 25 mm X 10 mm X 3 mm sized chips was used. Knots and barks were removed by hand prior to cooking. The mixed chips (50 g as oven-dried) were cooked under the following conditions; active alkali (AA) charge as Na_2O: 20-24%, sulfidity: 25%, sulfur charge: 0 or 1%, soluble AQ charge: 0 or 0.04%, liquor ratio to wood: 5 L/kg. Total reaction time was 6 hr. Kappa numbers were varied by changes of active alkali and AQ charge. Black liquor was not exchanged with fresh white liquor. Temperature profile was as follows:

Room temperature —(25min)→ 100°C for 1hr
　　　　　　　　　—(20min)→ 135°C for 2hr
　　　　　　　　　—(15min)→ 145°C for 2hr

RESULTS AND DISCUSSION
Optimization of ITC parameters for improvement of pulp yield
Effects of polysulfide and anthraquione
Under the conditions of alkaline cooking including kraft cooking, carbohydrates decompose by the peeling reactions from their reducing end groups, and therefore the pulp yield decreases[18-21]. In simulating the ITC process, cooking temperature was raised up by several steps and kept at relatively low degrees. It is known that addition of PS and/or AQ increases pulp yields. This effect could result from suppression of the peeling reactions due to oxidation of reducing end groups in carbohydrates[17]. It is also recognized that PS is decomposed at an elevated temperature[15,16]. In this study, cooking temperature was kept at 100°C for the initial 1 hr, in which the oxidation of reducing end groups in carbohydrates would be enhanced without a considerable decomposition of PS.
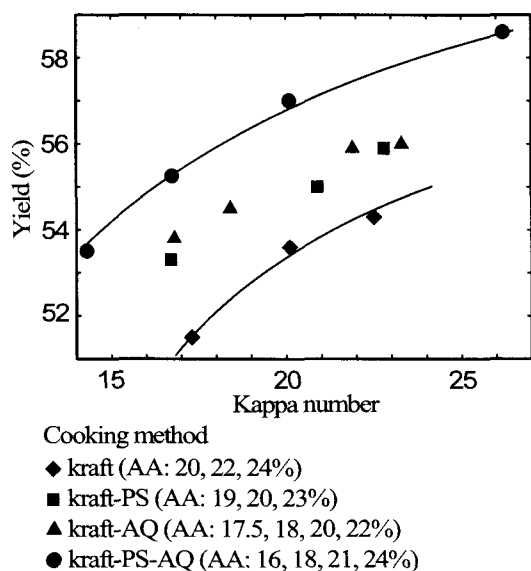
Fig. 1 shows effects of PS and/or AQ addition on pulp yields and kappa numbers. When the yields of pulps are compared between the kraft, kraft-PS, kraft-AQ and kraft-PS-AQ cooks at a kappa number of about 17, the kraft-PS and kraft-AQ improve the yield by about 2 and 2.5%, respectively, while an about 4.5-5% yield increase is obtained by the kraft-PS-AQ. It seems that the increase gained by the kraft-PS-AQ is equal or greater than the sum of the yield increases obtained by the kraft-PS and kraft-AQ. This result suggests that catalytic oxidation-reduction cycles of PS and AQ operate well and that oxidation of reducing end groups in carbohydrates is efficiently enhanced when both PS and AQ are co-existed. It has been reported in several papers that addition of PS and AQ to a kraft cooking process has a synergistic effect on pulp yields[10-12].

Effects of exchanging black liquor with white liquor during cooking
Fig. 2 shows effects of exchanging black liquor with fresh white liquor and timing of the exchange. In all the experiments shown in Fig. 2, 100% of both PS and AQ were added at the beginning of cooking. Data points with the Arabic numerals describe results obtained when total AA charge was 20%. Those with the alphabetical letters refer to the cases when total AA charge was 23%. Black circles show results obtained by the cooks without the liquor exchange. White circles represent exchanges at various reaction times when 70% of total AA was added at the beginning. The exchange had a significant influence on pulp yields. Referring to the cooks with total AA charge being 20% (data points: 1-4), the best result was achieved when fresh white liquor containing the remaining 30% of total AA was added just after temperature reached 135°C (data point: 1). The yield in this case was 2% higher than that gained when the liquors were exchanged after 2 hr of the reaction at 135°C (data point: 3). The phenomena observed when total AA charge was 23% (data points:

A-D) were similar to those occurred when total AA charge was 20%.
Fig. 3 shows effects of varying amount of total AA added at the beginning. White diamonds describe exchanges with varying amount of AA added at the beginning when the liquors were exchanged just after temperature reached 135°C. The best result was obtained when 70% of total AA was added at the beginning (data point: 7). The addition of 80% (data point: 8) of total AA at the beginning gave a higher kappa number than that of 70% (data point: 7). The phenomena observed when total AA charge was 23% (data points: E-F) were similar to those occurred when total AA charge was 20%.
Only the data point 1 in Fig. 2 (7 in Fig.3) is located at a better position than those obtained by the cooks without the liquor exchange. It is confirmed that exchanging black liquor with fresh white liquor can increase pulp yield when the liquors are exchanged in an optimal way although the increase is small.

Effects of exchanging black liquor with orange liquor during cooking
The comparison of the white square data point G and H in Fig. 4 indicates that 100% of both PS and AQ should be added at the beginning. This is reasonable because PS is decomposed if it is added with fresh white liquor during the reaction due to an elevated temperature.

Estimation of pulp yield using xylose and glucose ratio
Pulps from Acacia mearnsii planted in Brazil
The main components in hardwood kraft pulp are cellulose and hemicelluloses. Cellulose has a crystalline nature and high molecular weights while hemicelluloses have amorphous characteristics and relatively low molecular weights. These facts result in a difference in behavior toward alkali between cellulose and hemicelluloses. Cellulose is much more resistant toward alkali than hemicelluloses. Based on these facts, it is speculated that there would be a correlation between pulp yield and proportion of hemicelluloses to cellulose in the pulp because severer alkaline conditions, in addition to severer temperature conditions, bring a lower yield pulp, and hence, hemicelluloses should have further been decomposed or dissolved. It has been reported that the content of hemicelluloses in a pulp becomes higher with an increase of the yield[22]. Several methods for estimating mill pulp yields have been proposed[23-25]. Vaaler and Moe[25] have proposed a method based on the analysis of mannan or glucomannan contents of pulp. Luthe and others[26] have reported that softwood pulp yields can be estimated by this method. However, hardwood pulp contains less glucomannan, and then its yield can not be estimated.
Since a backbone of hardwood hemicelluloses mainly consists of xylan, it is evaluated whether or not ratio of xylose to glucose (X/G ratio), which are liberated from

pulp by an acid hydrolysis, can be applied as a method for estimation of pulp yield at continuous cooking. To evaluate X/G ratio, *Acacia mearnsii* was primarily used. The wood was cooked to produce pulps with various yields and kappa numbers, and it was examined whether or not the X/G ratios obtained from these pulps have a correlation with the yields. First, the relationship between pulp yield and kappa number is discussed. Figs. 1-4 are interpreted as figures showing relationships between various yields and kappa numbers. It is possible to produce pulps with the same kappa number but different yields. This fact indicates that no good correlation exists between these two factors although there is a correlation when cooking method is the same.
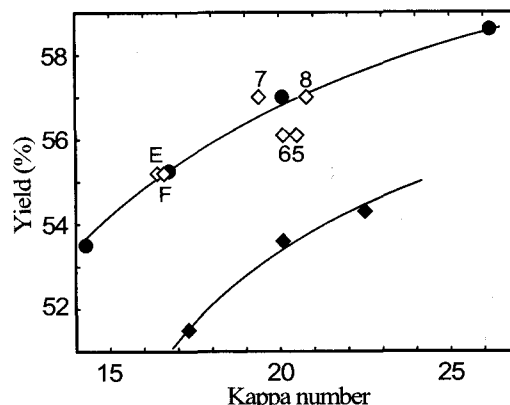
amount of total AA used from the beginning; 5: 30%, 6: 50%, 7: 70%, 8: 80%, E: 70%, F: 80%

total AA charge; 5-7: 20%, E-F: 23%

Fig. 3 Effect of percentage of total AA charge added at the beginning of cook on pulp yield when the liquors were exchanged just after temperature reached 135°C

Cooking method

◆ kraft (AA: 20, 22, 24%)
■ kraft-PS (AA: 19, 20, 23%)
▲ kraft-AQ (AA: 17.5, 18, 20, 22%)
● kraft-PS-AQ (AA: 16, 18, 21, 24%)

Fig. 1 Effect of PS and/or AQ addition on pulp yield and kappa number

remainning 30% of AA was added at 135°C-0min with; G: 0%, H: 100% of PS and AQ,
G: 100% of PS and AQ was added at the beginning

total AA charge; G-H: 23%

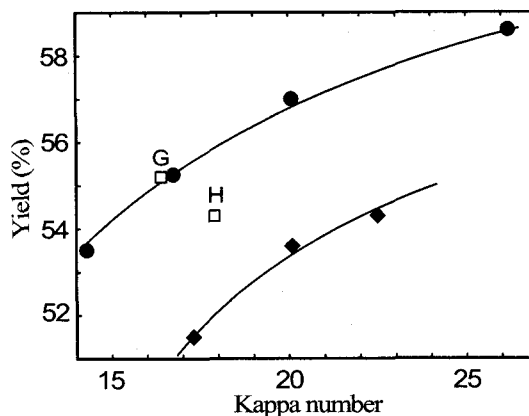**Fig. 4** Effect of adding PS and AQ in the middle stage of cook on pulp yield

exchanged at; 1: 135°C-0min, 2: 135°C-80min,
3: 135°C-120min, 4: 145°C-40min, A: 135°C-0min,
B: 135°C-60min, C: 135°C-120min, D: 145°C-60min
total AA charge; 1-4: 20%, A-D: 23%

Fig. 2 Effect of black liquor being exchanged with fresh white liquor on pulp yield

Fig. 5 shows that a linear correlation between pulp yield and the X/G ratio with the square of the correlation factor (R^2) to be 0.969 exists. A formula showing the correlation is: (yield) = 65.5 x (X/G ratio) + 39.8. The correlation is independent of cooking methods. When an X/G ratio is obtained by the hydrolysis of a pulp produced from *Acacia mearnsii*, the yield is calculated following to the above formula. The result indicates that X/G ratio can be applied as a method for estimation of pulp yield at continuous cooking.
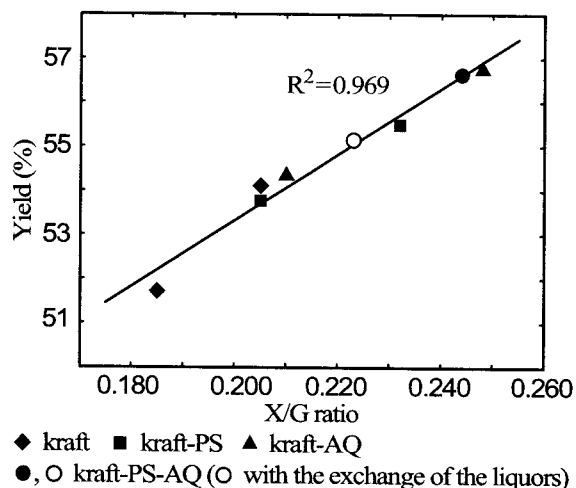
◆ kraft   ■ kraft-PS   ▲ kraft-AQ

●, O kraft-PS-AQ (O with the exchange of the liquors)

Fig. 5   Correlation between pulp yield and X/G ratio for *Acacia mearnsii* pulp

Comparison of various hardwoods species

Although the calibration line for the yield estimation of *Acacia mearnsii* pulp has been created, the line is not necessarily applied to pulps produced from other wood species. Each wood species has its particular carbohydrate composition and this particularity will be reflected in pulps produced from each wood species. Therefore, it is speculated that an X/G ratio of a pulp prepared from *Acacia mearnsii* could be different from that of a pulp produced from another wood species even when these pulps have the same yield. Based on this speculation, the X/G ratios of pulps prepared from *Eucalyptus globulus* and *Eucalyptus grandis* were determined, and correlations observed between the yields and the X/G ratios were compared with those for *Acacia mearnsii* pulps. The X/G ratios obtained from *Acacia mearnsii*, *Eucalyptus globulus* and *Eucalyptus grandis* woods were also determined to confirm a difference in X/G ratio between the original woods.

Table 1 lists lignin contents and X/G ratios obtained from *Acacia mearnsii*, *Eucalyptus globulus* and *Eucalyptus grandis* woods. As expected, the X/G ratios of three woods are varied. The lignin contents of the woods are also different.

Table 2 shows yields, kappa numbers and X/G ratios of pulps obtained when *Eucalyptus globulus* and *Eucalyptus grandis* were kraft cooked. The X/G ratios of the pulps were much smaller than those of the woods. This fact indicates that xylan is much more easily removed during kraft cooking than cellulose. As expected, the X/G ratios of pulps produced from *Eucalyptus globulus* and *Eucalyptus grandis* are different from *Acacia mearnsii* even when their yields or kappa numbers are similar to those. It should be observed that the pulps produced from each wood species have a particular (ΔX/G ratio)/(Δyield). This speculation will be confirmed by a study where more cooking data are gathered. The result indicates that the calibration line for *Acacia mearnsii* in Fig. 5 cannot be applied to any

other wood species. A particular calibration line for each wood species has to be created to estimate pulp yield using X/G ratio when mixed wood chips of various species are used in continuous cooking at a mill.

Application for mill hardwoods chips

Table 3 shows lignin contents and X/G ratios of raw materials. Then, the calibration was made from the results of laboratory cooks of the mill mixed wood chips. The mixed ratio was 27:16:12:23:12:10 for A1:A2:A3:E1:E2:E3.

Fig. 6 shows a linear correlation expressed as the following equation:

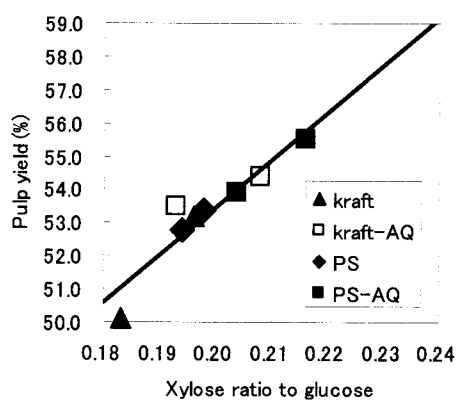Pulp yield (%) = 141.4 × X/G ratio + 25.19 (R=0.9335)

Fig. 6   Correlation between xylose ratios to glucose and pulp yields given by laboratory cooks of mill mixed wood chips

Note: Pulp yield (%) = 141.4 × X/G ratio + 25.19 (R=0.9335)

Pulp yields of kraft and polysulfide ITC with anthraquinone

Mill trials

Compositions of raw materials were changing during the preliminary trial and the first half of the kraft ITC operation, and temperature profile was unfortunately fluctuating. The composition was fixed by a start of the latter half of the kraft ITC operation. However, temperature profile was still fluctuating. A target temperature of cooking circulation was 146°C at a start of the preliminary trial, and then it was increased by 0.5°C at a stop of AQ charge and a change of polysulfide liquor to kraft liquor. It was finally 149°C.

Although the mill trial controlled the cooking parameters to give pulps with a given kappa number, kappa numbers of kraft ITC pulps were unintentionally higher than those of PS-AQ ITC pulps. (Fig. 7) However, the X/G ratios of PS-AQ ITC pulps were expectedly higher than those of the other. When we compare the pulp yields between the two cooking methods, we should compare the X/G ratios of the two at the same kappa number. Fig. 7 shows that

300

extrapolated X/G ratios by linear approximations are 0.225 for the kraft ITC pulp and 0.237 for the PS-AQ ITC pulp at kappa number 19. The difference of those is 0.012.
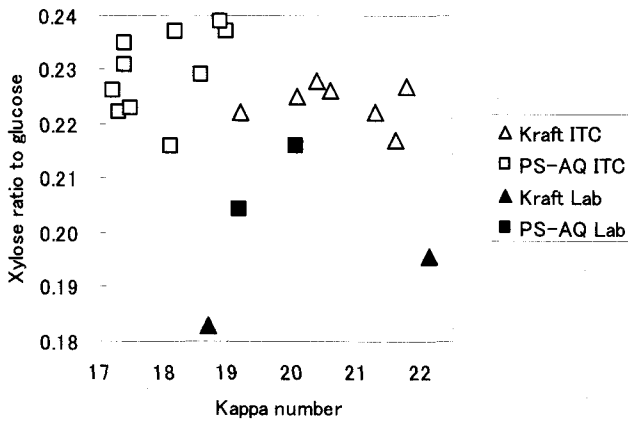

Fig. 7 Xylose ratios to glucose of mill pulps by PS-AQ ITC and kraft ITC as well as PS-AQ and kraft laboratory pulps

Estimation of mill pulp yield using X/G ratio

The difference of pulp yields between the PS-AQ ITC and the kraft ITC might at least about 1.7% according to the above equation.

A more interesting result shown in Fig. 7 is that the X/G ratios of mill pulps are in the range of 0.215 and 0.240, which are much larger than those of laboratory pulps. When the PS-AQ ITC is compared with laboratory kraft cooking, the pulp yield is calculated to be about 7% higher than the laboratory kraft pulp yield. The average X/G ratio of the PS-AQ ITC pulp was 0.23 at the average kappa number 18. It means that the pulp yield is 57.7% on the basis of the estimation method by the above equation.

Table 1 Lignin content and X/G ratio obtained from three wood species

Wood species	Acid insoluble lignin	Acid soluble lignin*	Total lignin	X/G ratio
Acacia mearnsii	20.6%	3.6%	24.2%	0.400
Eucalyptus globulus	20.6%	6.3%	26.9%	0.353
Eucalyptus grandis	24.1%	5.1%	29.2%	0.301

* These values are too large when compared with those that are generally accepted. This could be due to the difference in the reaction conditions of acid hydrolyses.

Table 2 Kappa number, yield and X/G ratio of pulps produced from three wood species*

Raw material wood	AA	Kappa number	Yield	X/G ratio
Acacia mearnsii	22%	20.1	53.6%	0.205
	24%	17.3	51.5%	0.185
Eucalyptus globulus	20%	16.5	52.6%	0.218
	24%	13.7	49.4%	0.196
Eucalyptus grandis	24%	17.3	51.7%	0.201
	28%	14.1	49.8%	0.156

* Neither PS nor AQ was added when *Eucalyptus globulus* and *Eucalyptus grandis* were cooked.

Table 3 Lignin content and xylose ratio to glucose of wood chips used at a mill trial

	Acacia mearnsii or *Acacia mangium*			*Eucalyptus globulus* or *Eucalyptus grandis*			Mixed
	A1	A2	A3	E1	E2	E3	
Acid insoluble lignin, %	20.6	27.7	26.7	22.9	27.6	23.6	24.1
Xylose ratio to glucose, g/g	0.434	0.358	0.281	0.354	0.388	0.426	0.379

Table 4 Kappa number, yield and X/G ratio of pulps with high yields

Pulp ID	Kappa number	Yield	X/G ratio
1	28.4	58.1%	0.250
2	30.9	57.9%	0.251
3	30.2	57.0%	0.243
4	24.2	56.9%	0.247

Modification of the calibration line for mill pulps

As mentioned before, the X/G ratios of the mill pulps are 0.225 for the kraft ITC and 0.237 for the PS-AQ ITC at kappa number 19. The results might show the pulp yields could be 57.1% and 58.8%, respectively. Those values on yields are those of the extrapolation of the above equation, because it is derived from the laboratory data in the range of 50.1% and 55.5%. One question might be put to the extrapolation of the equation. Therefore, a further research was undertaken to find conditions of laboratory cooking to give higher pulp yields or X/G ratios. Table 4 shows that kappa numbers, yields and X/G ratios of those pulps.
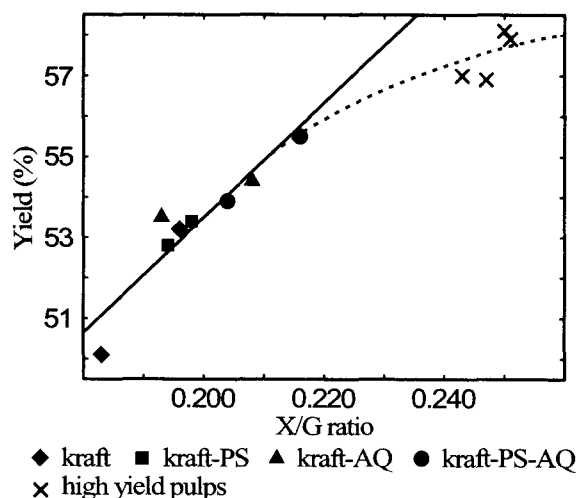

Fig. 8 Correlation between pulp yield and X/G ratio for pulps produced from the mixture of 6 wood species

As shown in Fig. 8, the data are in a lower area than the calibration line by the above equation. It means that higher-yield pulps show higher X/G ratios than the extrapolation. According to the modified calibration curve, the yields of the kraft ITC and the PS-AQ ITC at kappa number 19 were 56.0% and 57.0%, respectively. The yield gain is about 1.0%.

The small difference of yields between the PS-AQ ITC and the kraft ITC operation may be another further question to be examined. Black liquor may contain a part of AQ charged at preliminary mill trial, and then the AQ can beneficially affect the kraft ITC.

Comparison of pulp properties between PS-AQ ITC and kraft ITC

Fig. 9 and Fig. 10 show pulp viscosities and brightness, respectively. Viscosity level of the mill pulps was around 54, which was good enough for following bleaching processes. Difference in viscosity was not clear between the PS-AQ ITC and the kraft ITC. The average ISO brightness of the PS-AQ ITC pulps was better than that of the kraft ITC. The brightness probably depends on kappa numbers, but it is not clear at presence what the relation is.
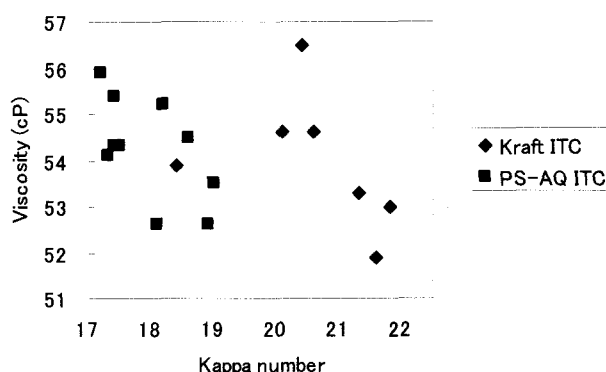

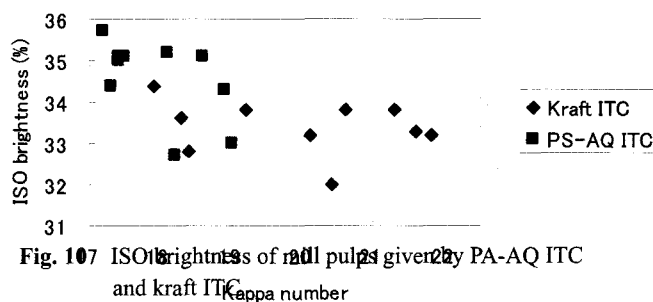**Fig. 9** Viscosity of mill pulps given by PS-AQ ITC and kraft ITC

Fig. 10 ISO brightness of mill pulps given by PA-AQ ITC and kraft ITC

CONCLUSIONS

It was observed that the highest pulp yield is obtained when 70% of total AA and 100% of PS and AQ are added at the beginning of cook, and successively, black liquor is exchanged with fresh white liquor containing

the remaining 30% of total AA just after the cooking temperature reaches 135°C.

A linearly calibrated correlation was observed between pulp yields and xylose/ glucose (X/G) ratios obtained from the *Acacia mearnsii* pulps by acid hydrolyses. This result indicates that X/G ratio of a pulp can be applied as a method for estimation of the yield at continuous cooking. Because the X/G ratios of pulps produced from various wood species are different even when the pulps have the same yield, a particular calibration line for various raw material woods has to be created to estimate pulp yield using X/G ratio.

The ITC was operated with PS-AQ at a mill trial under the optimal conditions which have been simulated in the laboratory cooks. PS cooking liquor containing 70% of total alkali and AQ (0.02% on wood) were charged into a chip-feeding circulation line, and then kraft cooking liquor containing 30% of total alkali was introduced into circulation lines of 130-145°C.

A mill pulp yield could be estimated by knowing X/G ratios of the mill pulps. The X/G ratios of pulps (kappa number 18-19) were in the range of 0.225 and 0.237. It means that the pulp yield of the PS-AQ ITC was shown to be 57.0%. It was about 7% higher than laboratory kraft pulps. The PS-AQ ITC gave a lower average kappa number than the kraft ITC at this mill trial. It achieved about 1.0% yield increase, similar viscosity and high ISO brightness compared with the kraft ITC.

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