連続クラフト蒸解における広葉樹材パルプの高収率化と その評価法 (第2報)

—工場の連続蒸解釜による検証—

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Improvement of Hardwood Pulp Yield in Continuous Kraft Cooking and Estimation of Pulp Yields (Part II)

—A Mill Trial at a Continuous Digester—

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The optimal conditions of isothermal cooking (ITC) for the improvement of pulp yields were applied to a mill trial using mixed hardwoods, polysulfide (PS), anthraquinone (AQ) and a continuous digester. 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 three circulation lines, i.e., top-cooking, bottom-cooking, and washing, where temperature reached about 130–145°C. Results from laboratory cooks of the mixed hardwoods showed that a linear correlation existed between pulp yields and ratios of xylose to glucose (X/G ratios), liberated from the pulps by an acid hydrolysis. Pulp yields at a mill trial could be estimated by knowing X/G ratios of the mill pulps. It was indicated that the PS-AQ ITC under the optimal conditions gave pulps with 0.235 X/G ratios at kappa number 18–19. It means that PS-AQ ITC shows about 7% higher pulp yields than laboratory kraft cooking and at least about 1.4% yield increases compared with the kraft ITC.

Keywords : kraft cooking, isothermal cooking, polysulfide, anthraquinone, carbohydrate, pulp yield

分類 : F₂KP 蒸解, W₁ 蒸解薬品, Y₄ セルロース化学

1. Introduction

Anthraquinone (AQ) additive cooking was developed and reported simultaneously by Nomura¹⁾ and Holton²⁾ in 1977–1978. A mill trial with AQ to polysulfide (PS) cooking using the Moxy process was reported by Kleppe³⁾ 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 Japan⁴⁾. On the other hand, modified kraft processes for a continuous digester were studied and reported by Nordin and Teder⁵⁾ 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 mills⁶⁾.

When ECF bleaching is introduced into a pulp mill, kraft cooking and oxygen delignification are required to further decrease kappa number of unbleached pulp. 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.

AQ has been added to a PS cooking process to improve pulp yield^{7–12)}. However, the best method for application of the ITC process with addition of both PS and AQ and reaction conditions for the application have not been known yet. It is possible to further improve pulp yield by the optimization of the process with PS and AQ.

Although 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. Therefore, it is necessary to develop a method for estimation of kraft pulp yield in continu-

ous 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 the previous paper (Part I)¹³⁾ on the research, the optimal reaction conditions for the ITC process have been established in laboratory experiments to increase pulp yield. It has been evaluated that ratios of xylose to glucose (X/G ratios), liberated from a pulp by an acid hydrolysis, can be applied as indexes for estimation of pulp yields during continuous cooking. In this paper (Part II) on the research, the optimal conditions of for the improvement of pulp yields were verified at a mill trial using mixed hardwoods, PS, AQ and a continuous digester. Pulp yield at a mill trial was estimated by knowing X/G ratio of the mill pulps.

2. Materials and Methods

2.1 Materials

Wood chips of *Acacia mearnsii* planted in Brazil, Thailand and Indonesia as well as *Eucalyptus globulus* or *Eucalyptus grandis* planted in Chile and West Australia were used as raw materials. Wood chips consist of six kinds named as A 1, A 2, A 3, E 1, E 2, and E 3. Lignin contents of those woods were determined according to the procedure described in the previous paper (Part I).

2.2 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 could suppress the peeling reactions of carbohydrates due to oxidation of their reducing end groups^{14,15)}. It is also recognized that PS is decomposed at an elevated temperature¹⁶⁾. 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 100 g 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.

2.3 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 T 236 cm-85), viscosity (TAPPI test method T 230 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.

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

Mixed wood chips of A 1, A 2, A 3, E 1, E 2, and E 3 were used. Each wood chip was 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 mixed 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 the autoclave was heated in a silicon oil bath under the following conditions; active alkali (AA) charge as Na₂O: 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 $\xrightarrow{25 \text{ min}}$ 100°C for 1 hr
 $\xrightarrow{20 \text{ min}}$ 135°C for 2 hr $\xrightarrow{15 \text{ min}}$ 145°C for 2 hr

The cooked chips were defiberized by a disintegrator, and the suspension obtained was filtrated. The disintegration and filtration were repeated twice to obtain a well-washed pulp. Hand sheets were prepared from the pulp, and the yield was determined by measuring a geometric weight of the sheets.

2.5 Analysis of X/G ratio of pulp

Analysis procedure of carbohydrate composition, which is also reported in the previous paper (Part I), is as follows:

About 330 mg (300 mg as oven-dried) of the pulp sheet was torn into small pieces. The torn pulp 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 9,000–10,000 rpm for 30 min. The products in a portion of 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 again concentrated. The addition of methanol and the concentration were repeated twice. This procedure removed most of the borates in the syrup as a volatile complex with methanol. The solu-

tion 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 chromatograph for the analysis of xylose ratio to glucose (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 BPX 70 (25 m × 0.22

mm × 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.

3. Results and Discussion

3.1 PS-AQ ITC operation under optimal conditions for improvement of pulp yield

Table 1 shows lignin contents and X/G ratios of raw materials. 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 (Fig. 1). 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.

Fig. 1 Cooking temperature profile during a mill trial

Table 1 Lignin content and xylose ratio to glucose of wood chips used at a mill trial

	<i>Acacia mearnsii</i>			<i>Eucalyptus globules or grandis</i>			Mixed
	A 1	A 2	A 3	E 1	E 2	E 3	
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

Fig.2 Xylose ratios to glucose of mill pulps by PS-AQ ITC and kraft ITC as well as PS-AQ and kraft laboratory pulps

Fig.3 Correlation between xylose ratios to glucose and pulp yields given by laboratory cooks of mill mixed wood chips.

Note : Pulp yield (%) = $141.4 \times \text{X/G ratio} + 25.19$ ($R = 0.9335$)

Kappa numbers during the kraft ITC operation were rather unstable and a little higher than those expected (Fig.2). The X/G ratios of pulps given by the PS-AQ ITC were larger than those by the kraft ITC, although an average kappa number of the PS-AQ ITC pulp was sufficiently lower than the other. If their X/G ratios are compared at a given kappa number, the kraft ITC pulp should show much smaller X/G ratios. Fig. 2 shows that extrapolated X/G ratios by

linear approximations are 0.225 for the kraft ITC pulp and 0.235 for the PS-AQ ITC pulp at kappa number 19.

3.2 Estimation of mill pulp yield using xylose and glucose ratio

It has been reported that the content of hemicelluloses in a pulp becomes high with an increase of the yield¹⁷⁻²⁰⁾. In the previous paper (Part I)¹³⁾, a linear correlation between pulp yields and X/G ratios was given by laboratory cooks of *Acacia mearnsii* wood.

Fig. 3 also shows a linear correlation given by laboratory pulps made from mill wood chips consisting of the six kinds of woods. The linear correlation was expressed as the following equation :

$$\begin{aligned} \text{Pulp yield (\%)} \\ = 141.4 \times \text{X/G ratio} + 25.19 \quad (R = 0.9335) \end{aligned}$$

The difference of pulp yields between the PS-AQ ITC and the kraft ITC was at least about 1.4 % according to the equation.

A more interesting result shown in Fig. 2 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.

One question might be put to the extrapolation of the equation. Therefore, further research is being undertaken to find conditions of laboratory cooking to give higher pulp yields or X/G ratios. Such conditions may be a high liquor ratio to wood, a low active alkali charge, a high temperature and/or a long cooking time and black liquor addition.

The small difference of yields between the PS-AQ ITC and the kraft ITC operation may be another future question to be examined. If the kraft ITC would operate under conditions of a much more active alkali charge, it should give a lower kappa number and a smaller X/G ratio. In fact, active alkali charge was kept constant or changed a little during the mill trial without PS and AQ. Therefore, it is considered that the kraft ITC showed a smaller yield decrease than speculated. Circulation of black liquor might have

some beneficial effects on yields of the kraft ITC, but it is not clear at present. In addition, black liquor may contain a part of AQ charged at preliminary mill trial, and then the AQ can beneficially affect the kraft ITC. Another mill trial will be examined under better conditions.

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

Fig.4 and Fig.5 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 present what the relation is.

Fig.4 Viscosity of mill pulps given by PS-AQ ITC and kraft ITC

Fig.5 ISO brightness of mill pulps given by PA-AQ ITC and kraft ITC

4. Conclusions

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 with average kappa number 18 were 0.23. It means that the pulp yield of the PS-AQ ITC was shown to be 57.7%. 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 at least about 1.4% yield increase, similar viscosity and high ISO brightness compared with the kraft ITC.

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