DEVELOPMENT OF A NOVEL EMPIRICAL MODEL TO ESTIMATE THE KRAFT PULP YIELD OF FAST-GROWING *EUCALYPTUS*

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In this study, several kraft pulps were produced by kraft pulping of fast-growing *Eucalyptus* with a wide range of cooking conditions. The dependences between pulp yields and some pulp properties, namely, kappa number, HexA contents, and cellulose viscosities, were well investigated. It was found that kraft pulp yields linearly decreased with the reduction of HexA-free kappa number in two different stages, respectively, in which a transition point of measured pulp yield of 48.7% was observed. A similar relationship between pulp yield and HexA was also found, in which the resulting transition point of HexA content was 67 μmol/g. Moreover, the logarithm of pulp viscosity was linearly proportional to the reduction of lignin-free pulp yields. Then, a novel empirical model was successfully developed based on these findings. The parameters in this empirical model were calculated by least-squares estimation using the experimental data from active alkali values of 13.2, 14.7 and 17.8. Another data set was used to verify the effectiveness of this model in predicting the pulp yields. Finally, a good agreement (a linear regression coefficient of 90.59%) between experimental and fitting data was obtained, which indicated that the kraft pulp yield of fast-growing *Eucalyptus* could be accurately predicted by this novel empirical model.

Keywords: Novel empirical model; Estimation; kraft pulp yield; Fast-growing Eucalyptus; Transition point; Kappa number; Lignin content; HexA content

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INTRODUCTION

Pulp yield is one of most important determinants for application in a pulping mill to reduce the cost of production and enhance competitiveness. Therefore, it is essential to accurately and conveniently predict the pulp yield. However, up to the present, developed methods that have been previously reported all have had their own defects.

First, pulp yield normally has been measured by some direct methods. Initially, it was determined by installing a basket with a known quantity of chips in the digester, and then measuring the weight of resultant pulp after finishing the cooking (MacLeod et al. 1987). However, the operation for this method was troublesome and hard to control by operators. Also, such an approach could not be used in continuous process of cooking. Basically, for continuous pulping, pulp yields can be estimated by comparing the mass flow rates of chips input to and pulp streams output from the digester. Unfortunately,

accurate flow rates of these complex fluids have been really difficult to monitor when depending on existing sensors. Therefore, for an industrial mill, relatively reliable data of pulp yields can only be obtained by comparing the wood usage and pulp production from sale records over at least 3 to 6 months. However, the long evaluation time makes such an approach expensive for a mill to use for the development of an optimal pulping process.

Therefore, some indirect methods for estimating kraft pulp yield have been consequently developed (Vaaler et al. 2002; Juvekar et al. 1995; Genco et al. 1990; Britt et al. 1965; Çöpür et al. 2005; Luthe et al. 2003; Vaaler et al. 2005). In conventional kraft pulping, pulp yield could be estimated by residual effective alkali and H-factor (Juvekar et al. 1995), or total organic carbon of black liquor (Genco et al. 1990). However, both of these methods are dependent on the kinds of raw materials. Besides, since Britt et al. (1965) found that fiber coarseness was proportional to pulp yield, the predicted model of pulp yields related the fiber length and width had also been reported (Çöpür et al. 2005). Unfortunately, this procedure is hard to apply in commercial production due to the low precision of coarseness determination.

On the other hand, the contents of carbohydrate and lignin in the pulp are widely used as parameters to predict the pulp yield. For example, it was found that mannan (Luthe et al. 2003) and glucomannan (Vaaler et al. 2005) contents in softwood pulps had relationship to pulp yields. But, these results are not available for hardwoods. Afterwards, using pulp properties, such as kappa number, HexA content, and viscosity, etc., to predict pulp yield became promising methods because these properties could be accurately determined by standard methods. In 1970, Kleppe found that pulp yield was linearly proportional to kappa number, while alkaline pulp had a very low lignin content. But, to obtain a relatively high pulp yield, some mills are still cooking the wood chips to pulp with a high kappa number. Later, Easty and Malcolm (1982) estimated the pulp yield by comparing the percentages of cellulose in chips and resultant pulp. But this method ignored the effect of hemicellulose on the viscosity of cellulose based on a copper ammonia solution. Recently, Chai et al. (2003) predicted pulp yield with the measured contents of carboxyl and HexA groups. Although there was good agreement between measured and predicted pulp yields for some wood species in their studies, the assumption of no degradation for cellulose during the process of alkaline pulping is obviously not in agreement with the fact of that cellulose degrades by the peeling reaction. More recently, Van Heiningen et al. (2004) extended Easty and Malcolm's work and confirmed that the degree of polymerization in the fiber correlated well with pulp yields if considering the contribution of hemicellulose to viscosity of pulp. This method is reasonable and precise, but is complex due to requirement for measurement of all polysaccharides contents in pulps.

To alleviate the shortage of forest resources faced by the pulping and papermaking industry, some fast-growing wood species, such as fast-growing *Eucalyptus* (Xu 2006), have been widely used as feedstock to produce pulps in Chinese pulping mills. However, there has been no report on predicting kraft pulp yield of this fast-growing species. To overcome all above problems, this study is focused on developing a simple and accurate empirical model to predict kraft pulp yield of fast-growing *Eucalyptus* based on some pulp properties, which can be accurately determined.

EXPERIMENTAL

Materials

The fast-growing *Eucalyptus* was originated by hybridizing *Eucalyptus grandis* and *Eucalyptus urophylla*. It was about 6 years old, and generally provided by Stora Enso Guangxi Forest base, Guangxi, China. The harvested fast-growing *Eucalyptus* was firstly chipped and screened to the sizes of approximate 30×20×5mm. The resulting chips were collected and then stored in a cold room at 4 ^{o}C. The measurements of ash (GB/T2677.3-1993), hot-water (GB/T2677.4-1993) and benzene-alcohol (GB/T2677.6-1994) extractives, Klason (GB/T2677.8-1994) and acid-soluble (GB/T10337-1989) lignin, pentosans (GB/T2677.9-1994), and nitric acid-alcohol cellulose (Shi and He 2003) contents in wood chips were conducted according to National standards of People's Republic of China, respectively. The results are listed in Table 1.

Table 1. Chemical Composition of Wood Chips from Fast-growing Eucalyptus (%)

	Extractives		Nitric acid-alcohol cellulose	Pento-sans	Holo-Cellulose		Lignin	
Ash	Hot water	Benzene -alcohol				Klason	Acid-Soluble	Total
0.31	2.29	1.26	46.75	21.7	82.86	18.86	2.33	21.19

Kraft Pulping

Six 2.5-L stainless steel pressure vessels were mounted inside of a large digester and heated externally with steam. A 200 g of wood chips with a certain moisture content was put into a 2.5-L stainless steel pressure vessel, while the ratio of liquid to wood was kept at 4.0 (w/w). After impregnated at 90^{o}C for 30 min with the rotation speed of 2 rpm, the cooks were degassed and then heated to cooking temperature at the speed of 1^{o}C/min. Each variations was set at four levels: sulfidity at 25, 30, 35, and 45%, and active alkali (AA) at 13.2, 14.7, 15.5, and 17.8 % (as Na_2O on o.d. wood), temperature at 145, 150, 155, and 160℃, and durations on cooking temperatures at 45, 60, 90, and 135 min.

Pulp Properties Analysis

After cooking, the resultant pulps were disintegrated, washed, and then screened on a strainer with a 0.006 inch screen, respectively. Afterwards, a gravimetric method was used to measure pulp yield after equilibrating the moisture content overnight. Kappa number of these unbleached kraft pulps was measured according to TAPPI standard method T236 cm-85. Hexenuronic acid (HexA) contents were determined by a simple and rapid method developed by Chai et al. (2001a).

RESULTS AND DISCUSSION

The Dependence of Pulp Yield on HexA-free Kappa Number

Kappa number is directly related to lignin content in pulp, and thereby, it indirectly affects the unbleached pulp yield. However, it is well known that, with the reaction between 4-*O*-methyl-D-glucuronic acid (MeGIcA) and alkali, hexenuronic acids (HexA) can be formed by β- elimination reaction of methanol during the process of kraft

cooking, especially under the conditions of high alkalinity and cooking temperature (Johansson et al. 1977). Based on current kappa number measurement method (TAPPI, SCAN or Chinese standard et al.), in addition to lignin, HexA also can be oxidized by potassium permanganate. Therefore, the value of measured pulp kappa number originates not only from lignin, but also from HexA (Li and Gellerstedt 1997). In other words, the relationship between pulp yield and kappa number does not really reflect the relationship between pulp yield and lignin content. To verify the dependence of pulp yield on lignin content, the contribution from HexA to kappa number should be deducted by following equation (Li and Gellerstedt 1997),

$$K_{Hf} = K - 0.086 * C_{HexA} \quad (1)$$

where K_{Hf} is the HexA-free kappa number; K and C_{HexA} represent the kappa number and content of HexA (μmol/g) in pulp, respectively.

Then, the relationship between HexA-free kappa number (lignin content) and pulp yield can be figured out based on Eq. 1. As shown in Fig. 1, in two stages (fast and slow), pulp yields from same AA charge decreased separately with the reduction of lignin contents. But the data of lignin contents from different AA charges did not fully fall onto same curve. Basically, pulps with same lignin content but from higher AA charge had lower pulp yields than that from lower AA charge, which was consistent with the result proposed by Santiago and Neto (2007). Therefore, it can be concluded that lignin removal affects the pulp yield, but it isn't the only factor.

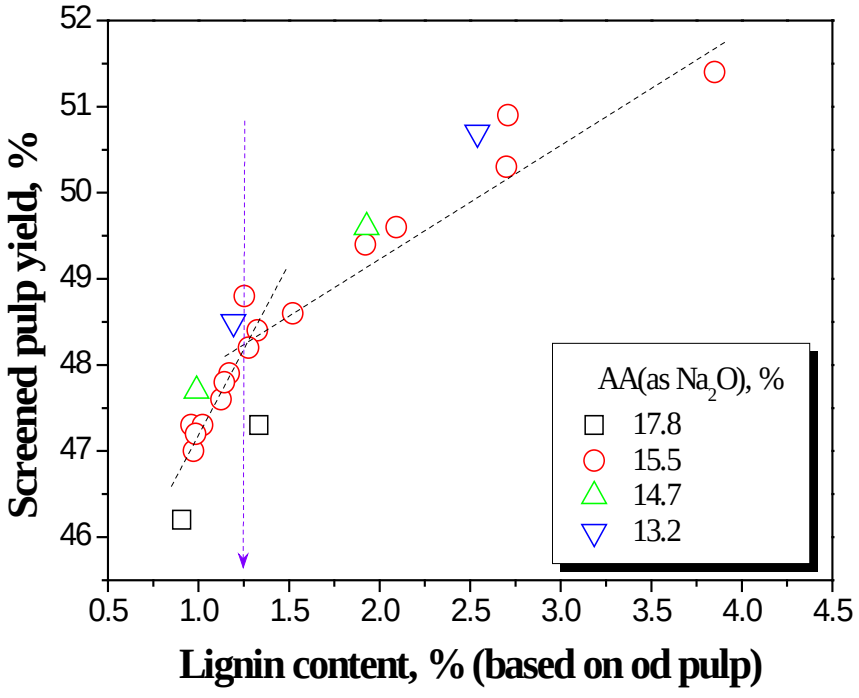

Fig. 1. The relationship between lignin content and screened pulp yield

Moreover, the ability to fit the data to two straight lines based on results from an AA change of 15.5% indicated that a transition existed from bulk to residual phase of delignification. Initially, pulp yields decreased slowly with the change of lignin content. Then, pulp yields decreased faster than they did in the first stage, which could be revealed by the slopes of two linear fitting functions in Fig. 1.

The Dependence of Lignin-free Pulp Yield on HexA Content

As we know, HexA is very stable once generated, even under the conditions of high alkalinity and cooking temperature, unless xylan is degraded and further dissolved into cooking liquor (Gilarranz et al. 2002). Also, approximately 60 to 80% hemicellulose in hardwoods were contributed by xylan. Thus, in this sense, the content of HexA in pulp could be used as an indicator to reflect hemicellulose degradation during kraft pulping. Therefore, the content of HexA will be regarded as another parameter to predict the pulp yield, especially the hardwood species.

Meanwhile, a relatively long process should be required for the complete formation of HexA during kraft pulping (Chai et al. 2001b and c). As shown in Fig. 2, HexA content first increased with the reduction of pulp yield; later, on the contrary, HexA content began to decrease with further reduction of pulp yield after the highest content (67 μmol/g) had been reached. Thus, similarly to the relationship between lignin content and pulp yield, it is of interest to find that there is also a transition from HexA formation to degradation. These results would definitely be helpful for the development of an empirical model for prediction of pulp yield based on the parameters of HexA (hemicellulose content) and HexA-free kappa number (lignin content).

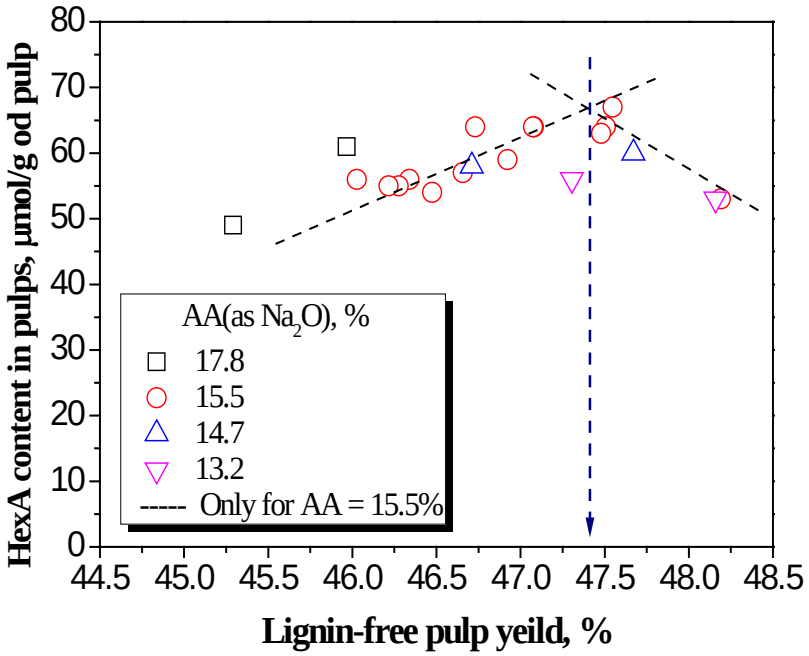

Fig. 2. The change of HexA content with lignin-free pulp yield

Based on the Eq.1 and the relationship between kappa number and lignin content in pulp (Chai et al. 2001a), the formula for calculating the lignin-free pulp yield is presented in Eq.2.

$$Y_{LF} = Y - 0.13 \times (K - 0.086 * C_{HexA}) \quad (2)$$

where Y_{LF} is the lignin-free pulp yield (%), and Y is the measured pulp yield (%); others parameters are the same as for Eq. 1. Unfortunately, although lignin-free pulp yield (calculated by Eq. 2) was linearly proportional to the content of HexA in pulps once it reached the highest value during kraft pulping, the result was not good enough (R^2=0.827 in Fig. 2), suggesting that hemicellulose and cellulose both affected the pulp yields.

The Change of Lignin-free Pulp Yield with the Logarithm of Pulp Viscosity

Actually, cellulose degradation contributed to the loss of pulp yield once the pulps had a relatively low kappa number. Earlier, Van Heiningen's group (Van Heiningen et al. 2004) extended Easty and Malcolm's work (1982) and developed a semi-empirical model to predict alkaline pulp yield by eliminating the effect of hemicellulose on the measurement of cellulose viscosity. It was found that the reciprocal of lignin-free pulp yield (based on o.d. wood) was linearly correlated to the reciprocal of cellulose DP (degree of polymerization). According to this finding, we simply check the relationship between lignin-free pulp yield and pulps' viscosities. Finally, for the data set of 15.5% AA, the results in Fig. 3 indicate that the logarithm of pulps' viscosities linearly decreased with the reduction of lignin-free pulp yields. But the data from AA of 17.8 significantly deviated from this curve, suggesting that cellulose degradation is also one of the important contributors to the carbohydrate loss.

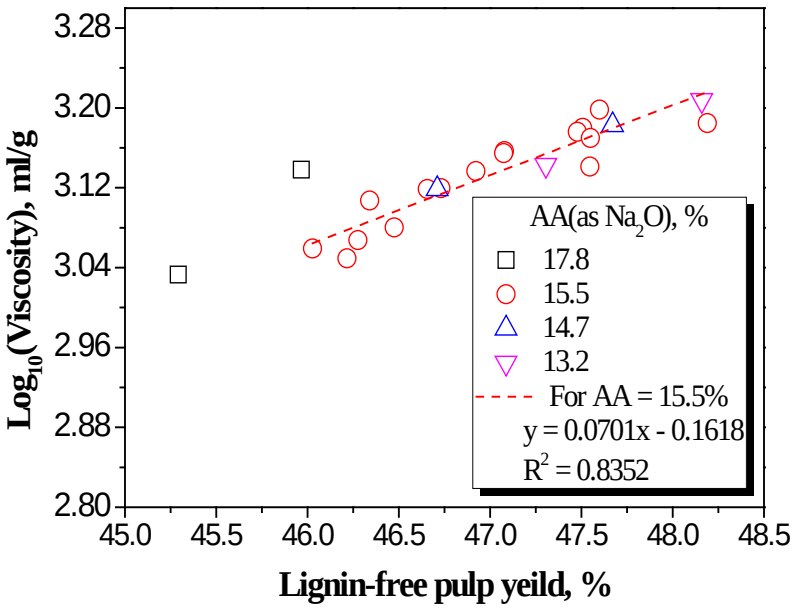

Fig. 3. The change of lignin-free pulp yields with the logarithm of pulps viscosities

In fact, the reduction of cellulose DP has no effect on the pulp yield unless significant degradation occurred. But, with DP decreasing and with oligosaccharides being hydrolyzed to monosaccharides, monomeric sugars can be released to the surrounding liquid medium and therefore involved partial loss of pulp yield. Thus, the present relationship between lignin-free pulp yield and cellulose DP might be effective for us to predict the cellulose degradation during kraft pulping of this fast-growing eucalyptus. Their mathematic relationship can be expressed as follows,

$$Y_{LF} = a\mathrm{Log}_{10}(Vis) + b \quad (3)$$

where *Vis* is the viscosity of pulp (ml/g); a and b are constants; others are the same as in the previous descriptions related to Eqs. 1 and 2.

Transition Point among Pulp Yield, HexA Content, and Kappa Number

Although HexA content in pulp has no direct relationship with kappa number, they can't be completely independent from each other because the removal of lignin from wood is accompanied by the formation and further dissolving of HexA on xylan. The relationships between these two parameters from pine and some hardwood species had also been fully investigated and reported by Dr. Zhu's group (Chai et al. 2001 b and c). In the above discussion (Figs. 1 and 2), a measured pulp yield of approximately 48.7 percent was observed as a transition point, for which the corresponding kappa number and HexA content were approximately 15.7 and 67μmol/g o.d. pulp, respectively. But we also don't know whether these later two parameters can match to each other or not.

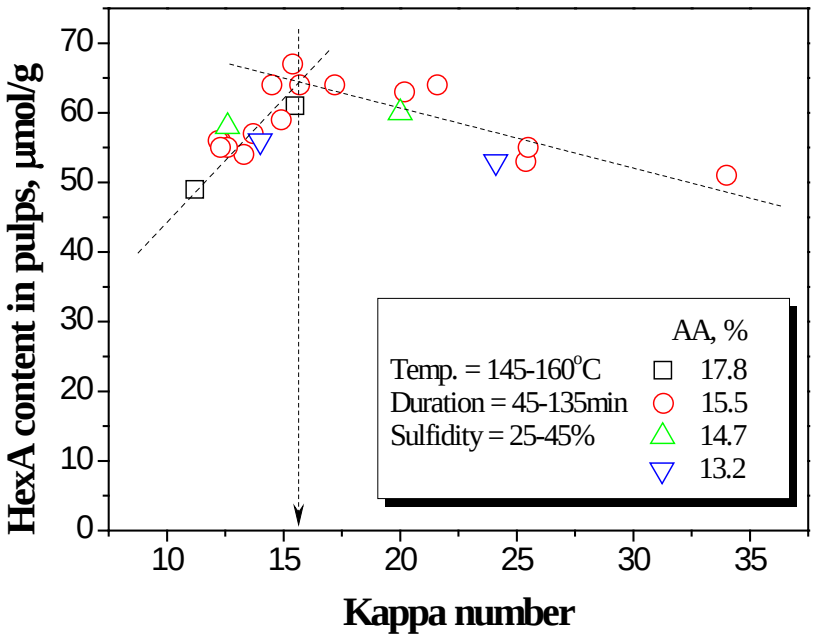

Fig. 4. The formation and dissolving of HexA with kappa number change of pulps

As shown in Fig. 4, it was interesting to find that the HexA content at the transition point of pulp yield (approximately 48.7% in Figs. 1 and 2) corresponded to a kappa number of 15.7. Therefore, we can absolutely make sure that a general transition point of pulp yield (48.7%) and the corresponding HexA content and kappa numbers of 67μmol/g and 15.7 could be used as related constants at same time to develop a reasonable model for pulp yield prediction.

Empirical Model Development and Evaluation

It is well known that both wood and pulp are mainly composed of cellulose, hemicelluloses, and lignin. From above discussions, we found that the cellulose, hemicelluloses, and lignin contents can be separately related to DP (Fig. 3), HexA content (Fig. 2), and kappa number (Fig. 1). Therefore, the contributions of cellulose, hemicelluloses, and lignin to pulp yields can be calculated directly by these three parameters based on the relationships found previously. The general formula can be written as,

$$Y = Y_t \pm \Delta C \pm \Delta X \pm \Delta L \quad (4)$$

where the quantities $\triangle C$, $\triangle X$ and $\triangle L$ are the respective changes of cellulose, hemicelluloses, and lignin before and after the transition point of pulp yield (%), and Y is the measured pulp yield (%).

In two stages of delignification, a linear relationship between pulp yield and HexA-free kappa number can be approximately observed, as shown in Fig. 1. Thus, the contribution of lignin content to pulp yield can be presented as follows,

$$\Delta L = 0.13 \times [(K_t - 0.086 * C^t_{HexA}) - (K - 0.086 * C_{HexA})] \quad (5)$$

where K_t and K are the measured kappa numbers at the transition point and any other cooking conditions used in this study. C^t_{HexA} and C_{HexA} are HexA contents in pulp at the transition point and any other cooking conditions.

From Fig. 2, it had been established that the degradation of hemicellulose was also linearly proportional to the reduction of HexA content in pulp. Therefore, the change of hemicelluloses in pulp can be summarized as,

$$\Delta X = X - X^t = \pm k(C^t_{HexA} - C_{HexA}) \quad (6)$$

where k is constant; C^t_{HexA} is the HexA content at the transition point (67 μmol/g).

For cellulose degradation, the relationship between pulp yield and cellulose DP was given out as,

$$\Delta C = C - C^t = \pm[a\mathrm{Log}_{10}(Vis) + b] \quad (7)$$

where a and b are constant; Vis respects cellulose viscosity in pulp.

When the value of measured pulp yield is larger than 48.7, we take the positive sign in Eq. 4; otherwise the negative sign should be selected. Considering the relationships between the pulp yield and HexA content, the measured kappa number, and the content of HexA in pulp in Figs. 1 and 2, a unified expression for Eq. 4 can be realized if the rounding function INT is used,

$$\psi = [1 + 2 \cdot INT(\frac{K_t - K}{K})] \quad (8)$$

where k is a constant; INT is a rounding function in Microsoft Excel, and other parameters are as previously defined. For details of INT (number), we can take some examples, as follows: if the number is 1.5, then the value of INT (number) equals 1; if the number is -0.25, the value of it is -1.

Finally, by combining equations (5), (6), (7), and (8), the pulp yield can be described by Eq. 9:

$$Y = Y_t - 0.13 * [(K_t - 0.086 * C^t_{HexA}) - (K - 0.086 * C_{HexA})] - \psi * [k * (C^t_{HexA} - C_{HexA}) + (\mathrm{aLog}_{10}(Vis) + b)] \quad (9)$$

To calculate the parameters in Eq. 9, the least-square estimation was conducted by Solver in Microsoft Excel based on the experimental data from AAs of 13.2, 14.7, and 17.8.

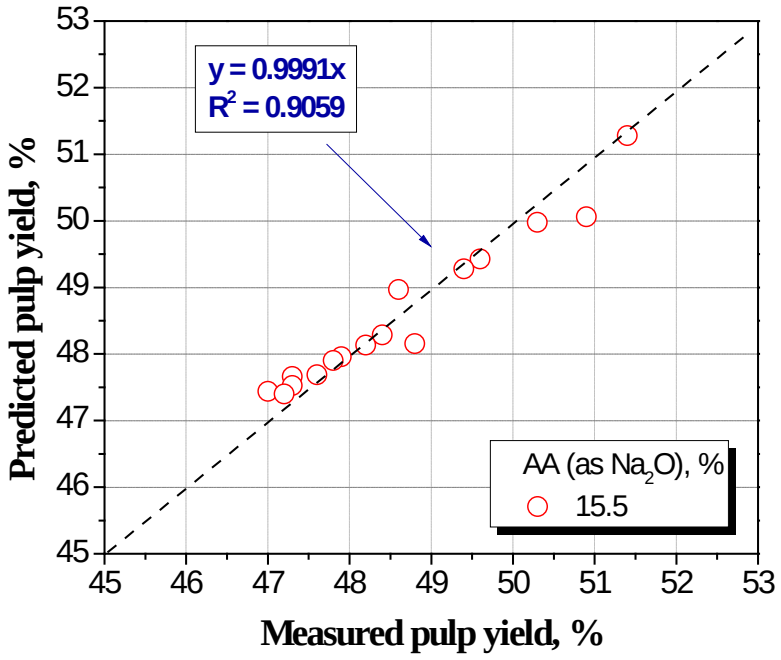

Fig. 5. Comparison the experimentally measured and predicted pulp yields of fast-growing *Eucalyptus* with the AA charge of 15.5%

Finally, the values of *k*, *a*, and *b* in Eq. 9 are -0.0466, -4.8738, and 15.6137, respectively. To test whether Eq. 9 and these parameters are effective or not to predict the pulp yield, the data of predicted pulp yield from AA of 15.5 was directly plotted against to the corresponding experimental data (Fig. 5). The plot shows a linear regression coefficient of 90.59% by forcing the intercept to 0, which suggests that kraft pulp yield from kraft pulping of fast-growing eucalyptus could be accurately predicted by this empirical model.

CONCLUSIONS

The relationships among measured kappa number/lignin content, HexA content, cellulose DP, and kraft pulp yield of fast-growing *Eucalyptus* under a wide range of kraft pulping conditions were fully investigated in this study. The results indicated that pulp yield decreased linearly with kappa number and HexA content in two different stages, respectively, in which a transition point for a pulp yield of 48.7% (corresponding kappa number and HexA content were 15.7 and 67μmol/g o.d. pulp) was observed. Moreover, it was also found that the logarithm of pulp viscosities was linearly proportional to the reduction of lignin-free pulp yields. Then, a novel empirical model based on these relationships among kappa number, HexA content, cellulose DP, and pulp yield was developed. After calculating the parameters based on the experimental data from AAs of 13.2, 14.7 and 17.8, a high linear regression coefficient of 90.59% was also obtained based on another data set, suggesting that this empirical model would be definitely effective to predict pulp yield from kraft pulping of fast-growing eucalyptus.

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