

## DELIGNIFICATION OF SUGARCANE BAGASSE WITH ALKALI AND PERACETIC ACID AND CHARACTERIZATION OF THE PULP

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Sugarcane bagasse was delignified with alkali and peracetic acid in a two-stage process to obtain pulps with high yield and low kappa number. The experimental results indicated that alkali pretreatment prior to peracetic acid (PAA) delignification could significantly reduce PAA loading by partially removing lignin and swelling the fibers. An optimum condition for the two-stage delignification was obtained for pulping of sugarcane bagasse. The pulps were further characterized by chemical composition analysis, strength property tests, Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Thermal Gravimetric Analysis (TGA). It was found that the alkali-PAA process could be conducted under milder conditions with resulting higher pulping selectivity, higher degree of polymerization (DP), and superior mechanical properties of pulps, compared to the kraft pulping process. Both kraft pulps and alkali-PAA pulp had similar FTIR spectra, XRD spectra, and TGA (DTG) curves. However, further analysis indicated that the alkali-PAA pulp had higher infrared crystallization index and cellulose crystallinity.

*Keywords:* Sugarcane bagasse; Delignification; Alkali pretreatment; Peracetic acid; Characterization

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### INTRODUCTION

Lignocellulose is the most abundant biomass, representing nearly 70% of the total plant biomass. Classical uses of this raw material are for paper industries, building, and textiles, which are using only 2% of this type of biomass (Octave and Thomas 2009). For pulping of biomass, although many processes have been developed during the last decades, most of the world's chemical pulp is still produced by kraft processes. The main reasons for this dominance of the kraft process are its versatility in dealing with different raw materials coupled with superior pulp quality and a more matured recovery of cooking chemicals. In spite of these advantages this process displays certain serious drawbacks, such as air and water pollution and the high investment costs (Johansson et al. 1987; Muurinen 2000). Furthermore, the kraft pulping process is necessarily carried out at high temperature (165-175 °C) with resulting high pressure. This not only requires high equipment costs with associated maintenance, but, perhaps more significantly, it causes accelerated degradation of cellulose and hemicellulose. Therefore, the pulp yield of the kraft process is relatively low (typically lower than 50%).

One possibility for overcoming existing problems is the use of organic solvents for delignification, which is known as “organosolv pulping.” Several organosolv pulping processes have been developed, such as Acetosolv (Nimz et al. 1986), Kleinert (Aziz and Sarkanen 1989), Alcell (Pye and Lora 1991), ASAM (Black 1991), Organocell (Stockburger 1993), ASAE (Kirci et al. 1994), Milox (Sundquist 1996), and so on. However, these processes are also conducted at high temperatures under increased pressures, except for the Acetosolv and Milox processes, which can be operated at the boiling point of the solvents under atmospheric pressure. Therefore, most of the organosolv pulping processes have similar pulp yield compared with kraft process, while some even have lower ones. For increasing the pulp yield, the pulping temperature should be decreased in order to reduce the degradation of carbohydrates, which demands a delignification agent that functions under a mild condition.

Recently, peracids, such as Caro’s acid and peracetic acid (PAA), are being revisited as a potential complement to conventional non-chlorine bleaching agents (Ricketts 1995), because of their selective and effective delignification behavior under mild conditions (Springer 1997; Abou-Yousef 2001; Zhao et al. 2007). Actually, peracids do not possess high reactivity towards polysaccharides, and as a consequence the hollocellulose yields are high in delignification by peracids (Nada et al. 1999).

It has been reported that multi-stage delignification of bagasse by using alkali and Caro’s acid treatment at 40 °C could obtain pulp yield as high as 75% with kappa number values near 15 (Abou-Yousef et al. 2005). Such results imply that delignification of lignocellulose with peracids can achieve very high selectivity. Compared with Caro’s acid, PAA seems to be more promising because the corresponding acid, acetic acid, is much easier to recover than sulfuric acid.

Our previous study showed that single-stage PAA delignification of bagasse could yield similar selectivity compared with kraft pulping, however, the PAA consumption was much higher (50 % loading for single-stage PAA process compared with 15 % for the kraft process). Furthermore, high PAA concentration in the liquid phase also caused oxidative degradation of cellulose, leading to the decrease of pulp viscosity. The introduction of an alkali pretreatment for partially removing lignin before PAA delignification might reduce the PAA loading in the second stage and consequently decrease the degradation of carbohydrates. The objective of the present work is to investigate the effects of several factors on this two-stage delignification of sugarcane bagasse to obtain high pulp yield and pulp quality, and characterize the pulps by several chemical and instrumental methods, which would be helpful for further optimization of the delignification conditions and estimating the feasibility of this process.

## EXPERIMENTAL

### Materials and Analytical Methods

Sugarcane bagasse was purchased in Guangxi in South China. It was air-dried and screened for depithing. The fraction that could not pass 20-mesh sieve was used in all experiments. The compositions of sugarcane bagasse were determined according to the corresponding Chinese standards. The results and corresponding standards/methods were as follows: 3.42-6.07 wt% moisture (GB/T 2677.2-1993),

1.38 wt% ash (GB/T 2677.3-1993), 5.16 wt% hot water extractives (GB/T 2677.4-1993), 34.20 wt% 1% NaOH extractives (GB/T 2677.5-1993), 3.17 wt% benzene-ethanol extractives (GB/T 2677.6-1994), 44.98 wt% cellulose (Nitric acid-ethanol method) (Shi and He 2003), 76.76 wt% holocellulose (GB/T 2677.10-1995), 18.45 wt% Klason lignin (GB/T 2677.8-1994) and 1.80 wt% acid-soluble lignin (GB/T 747-2003). The total lignin content (*TLC*, %) was calculated by sum of Klason lignin plus acid-soluble lignin. The response variables determined in the delignification process were defined as follows: (1) Pulp yield (*PY*, %) is the ratio of the absolutely dry weight of materials after and before cooking; (2) Degree of delignification (*DD*, %) is the percentage of total lignin dissolved into the liquid phase; (2) Percentage of holocellulose dissolved (*PHD*, %) was defined as the percentage of holocellulose dissolved into the liquid phase.

### Preparation of PAA

Peracetic acid was prepared by reaction of anhydrous acetic acid and 30 wt% hydrogen peroxide at room temperature for more than 48h. The volume ratio of acetic acid and 30 wt% hydrogen peroxide was selected as 1.5:1 according to our previous optimized results (Zhao et al. 2008). 1.5% (w/w) sulfuric acid was added as catalyst. The determination of PAA concentration was in accordance with Chinese standard GB/T 19108-2003 with some modifications. In the standard, the iodometric determination of PAA after permanganometric titration of H<sub>2</sub>O<sub>2</sub> was conducted in one titration vessel, whereas in the present work the procedure was conducted in two separated vessels, a modification that provides more distinct conditions for the judgment of the titration end point. The equilibrium mixture prepared under the above conditions had PAA concentration of 14-18 wt%.

### Delignification Process

Two-stage delignification was carried out in a 1000 ml glass flask in a water bath. Mechanical stirring with a polytetrafluorethylene paddle was employed for intermittent stirring to keep the system as homogenous as possible. Bagasse was first treated with 1-9% NaOH (w/w, based on raw material) at 60-100 °C for 1-3 h with 3-6:1 (v/w, L/kg) liquor/solid ratios. The pretreated solid was washed with water until neutrality and filtered until the liquid content was about 75%. The solid was then further treated by an oxidative delignification stage with PAA loadings of 10 to 30% (based on raw material) at 70-75 °C for 1-3 h. The pulp was washed with water until neutrality and then dried for analysis. The reported data was the average of at least 2 duplicate tests, and the statistical data (*P* value) was calculated by Matlab 6.1 software in order to judge the significance of the effects of parameters on the response variables.

Kraft pulping was conducted with 11.25% NaOH and 3.75% Na<sub>2</sub>S in a 15L stainless steel digester at 170 °C for 2 h with 5:1 liquor/solid ratio according to Nada et al. (2002).

### Characterization of Pulps

#### *Chemical composition*

The compositions of the pulp samples were determined in accordance with the corresponding Chinese standards described previously. Kappa number was measured according to TAPPI method T236m, and limiting viscosity (Degree of Polymerization, *DP*) according to ISO 5351:2004. The optical property of the pulp was measured as

brightness according to Chinese standard GB/T 7974-2002, using a WSB-3A whiteness meter (Shanghai Xinrui Ltd, China). Each reported datum is the average of at least duplicate tests according to the standards.

#### *Strength properties of the pulp*

Pulps were beaten to 50-55 °SR in a Valley beater. Handsheets of about 60 g/m<sup>2</sup> were formed with a laboratory hand paper machine. The strength properties were tested according to corresponding Chinese standards as follows: folding endurance GB/T 475-1989, tear index GB/T 455.1-1989, and tensile strength and breaking length GB/T 453-1989.

#### *Fourier Transform Infrared Spectroscopy (FTIR)*

IR spectra of the pulps were recorded by using a NICOLET 560 FTIR spectrometer (Nicolet Company, the USA). The dried samples were ground and embedded in KBr pellets. The spectra were recorded in the absorption band mode in the range of 4000–400 cm<sup>-1</sup>.

#### *X-Ray Diffraction (XRD)*

Crystallinity of the pulp was determined by X-ray diffraction using a D8 ADVANCE diffractometer (Bruker AXS, Germany). The diffraction spectrum was taken by the  $\theta$ - $2\theta$  method. Samples were scanned at 1 °/min from  $2\theta=6$  to  $35^\circ$  with a step size of  $0.01^\circ$ . The pulp crystallinity was determined as the percentage of crystalline material in the sample and expressed as the crystallinity index (*CrI*),

$$CrI = [(I_{002} - I_{am}) / I_{002}] \times 100 \quad (1)$$

where  $I_{002}$  is the maximum intensity of the (002) lattice diffraction ( $2\theta \approx 22.5^\circ$ ) and  $I_{am}$  is the intensity at  $2\theta \approx 18.7^\circ$  (amorphous).

The average size of crystallites was calculated from the Scherrer equation, which was based on the width of the diffraction patterns obtained in the X-ray reflected crystalline region. In present study, the crystallite sizes were determined by using the diffraction pattern obtained from the 002 (*hkl*) lattice planes of cellulose samples,

$$D_{(hkl)} = \frac{K\lambda}{B_{(hkl)} \cos \theta} \quad (2)$$

where (*hkl*) is the lattice plane,  $D_{(hkl)}$  is the size of crystallite,  $K$  is the Scherrer constant (0.84),  $\lambda$  is the X-ray wavelength (0.154 nm),  $B_{(hkl)}$  is the FWHM (full width half maximum) of the measured *hkl* reflection, and  $2\theta$  is the corresponding Bragg angle (reflection angle) (Yang et al. 2008).

#### *Thermal Gravimetric Analysis (TGA)*

Thermal Gravimetric Analysis (TGA) of the pulp was performed with a thermal analyzer STA 409 C131F (NETZSCH-Gerätebau GmbH, Germany). The heating rate was 20 °C/min. High purity nitrogen was used as shielding gas at flow rate of 50 ml/min.

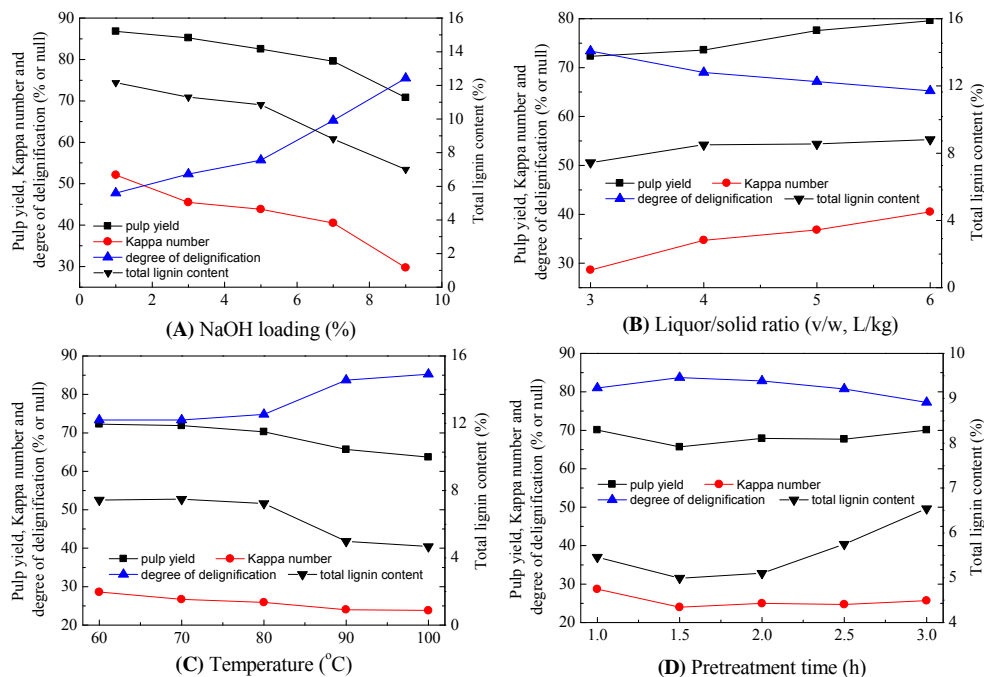
## RESULTS AND DISCUSSION

### NaOH Pretreatment

In kraft pulping, alkali (usually NaOH) plays the most important role for delignification. However, in order to obtain a sufficiently high degree of delignification (*DD*) to liberate cellulose fibers, kraft pulping needs a heat preservation process at 165-170 °C for about 2 hours. Nevertheless, NaOH pretreatments of lignocellulosic biomass are usually conducted under much milder conditions (Mosier et al. 2005). The effects of several factors in the NaOH pretreatment process were investigated in this section with the condition of the second stage being fixed as follows: 20% PAA loading (based on initial materials), temperature 70-75 °C, time 2 h and liquor/solid ratio 2.5:1 (L/kg). The experimental results are shown in Fig. 1.

#### *Effect of NaOH loading (based on initial raw materials)*

It was observed that NaOH loading had very significant influences on pulp yield (*PY*) ( $P < 0.0001$ ), kappa number (*KN*) ( $P < 0.0001$ ), *DD* ( $P < 0.0001$ ), and total lignin content (*TLC*) ( $P < 0.0001$ ). *DD* was dramatically increased with NaOH loading, while *KN*, *TLC*, and *PY* were decreased (Fig. 1 (A)). These findings imply that higher NaOH loading can remove more lignin but also dissolve more carbohydrates. However, it can be inferred from the high pulp yield that  $\alpha$ -cellulose was not affected under the above conditions. According to follow-up work, the NaOH loading used for pretreatment should be at least 7% in order to obtain a high degree of delignification.



**Fig. 1.** Effect of NaOH pretreatment on alkali-PAA delignification of sugarcane bagasse: (A) Effect of NaOH loading (other conditions: 6:1 liquor/solid ratio, 60 °C, 1.5 h); (B) Effect of liquor/solid ratio (other conditions: 7% NaOH loading, 60 °C, 1.5 h); (C) Effect of pretreatment temperature (other conditions: 7% NaOH loading, 3:1 liquor/solid ratio and 1.5 h); (D) Effect of pretreatment time (other conditions: 7% NaOH loading, 3:1 liquor/solid ratio and 90 °C)

### *Effect of liquor/solid ratio*

The results of delignification with different liquor/solid ratios in alkali pretreatment are shown in Fig. 1 (B). It can be seen that higher liquor/solid ratio led to higher *KN* and lower *DD* due to the lower concentration of hydroxyl anion ( $\text{OH}^-$ ) in the liquid phase when certain NaOH loading was used. It is obvious that *DD* at a liquor/solid ratio of 3:1 was higher than those at liquor/solid ratios of 4:1, 5:1, and 6:1. However, when the system was not well stirred, a small part of bagasse was overcooked at a liquor/solid ratio of 3:1. Therefore, a smaller liquor/solid ratio should not be selected for NaOH pretreatment, and a liquor/solid ratio of 3:1 was selected for the next experiments. Statistic analysis showed that liquor/solid ratio had very significant effects on *PY* ( $P=0.0037$ ), *KN* ( $P<0.0001$ ), and *DD* ( $P=0.0026$ ), while the effect on *TLC* was significant at 95% confidence ( $P=0.0317$ ).

### *Effect of temperature*

It was found that when temperature was increased from 80 °C to 90 °C, *DD* was increased from 74.81 % to 83.76%, and *KN* was decreased from 25.9 to 24.0 (Fig. 1 (C)). The experimental results indicated that temperature had very significant influences on *PY* ( $P=0.0006$ ), *DD* ( $P<0.0001$ ), and *TLC* ( $P<0.0001$ ), while it had significant influence on *KN* ( $P=0.0143$ ). However, there was no obvious difference for the response variables when temperatures were 90 °C and 100 °C. Therefore, 90 °C was selected for further investigation.

### *Effect of pretreatment time*

The effects of pretreatment time are shown in Fig. 1 (D). It was observed that the optimum time for alkali pretreatment at 90 °C was 1.5 h. Prolonging pretreatment time led to a little increase of *KN* and decrease of *DD*. Therefore, pretreatment for 1.5 hours was preferred in our latter experiments. The statistic analysis of experimental data indicated that time had no significant effect on all the response variables ( $P>>0.05$ ).

According to the above experimental results, favorable conditions for alkali pretreatment can be stated as follows: >7% NaOH loading, 3:1 liquor/solid ratio, 90 °C, and 1.5 hours. The next session will focus on the screening of PAA delignification conditions.

## **PAA Delignification in the Second Stage**

After NaOH pretreatment, the solid was further delignified with PAA. Our previous study showed that PAA loading (based on initial raw materials), liquor/solid ratio, temperature, and time all had very significant effects on single-stage delignification of bagasse. The optimum temperature for PAA delignification was 70 to 75 °C. Significant dissolution of carbohydrates was observed when the temperature was higher than 80 °C. Therefore, in the second stage delignification, temperature was controlled at 70-75°C.

### *Effect of PAA loading (based on initial untreated bagasse) on delignification*

In order to obtain pulp with low *KN*, several PAA loadings were used for further delignification. The results are shown in Table 1. It can be seen that NaOH loading in the first stage had significant influence on PAA loading required in the second stage. When 7% NaOH was used in the first stage, 30 % PAA was needed in order to obtain pulp with low *KN*. However, when NaOH loading was increased to

10%, PAA loading could be reduced to 15 % and *KN* was decreased to 3.6. It can be found that increasing PAA loading resulted in enhancement of pulp brightness but a little decrease of *PY*. Nevertheless, when NaOH loading was increased to 11% in the first stage, the corresponding *PY* was decreased compared with those of 10% NaOH pretreatment. Therefore, with integrated consideration of all the response variables, 10% NaOH was selected for further experiments.

**Table 1.** Effect of PAA Loading in the Second Stage on Delignification

NaOH loading in the first stage (%)	Second stage (75 °C, 2h)				
7	PAA loading (%) <sup>a</sup>	15	20	25	30
	Unscreened pulp yield (%)	66.0	62.2	63.2	61.6
	Kappa number, <i>KN</i>	31.2	18.5	19.0	15.3
	Total lignin content, <i>TLC</i> (%) <sup>b</sup>	7.24	5.17	4.02	3.00
	Degree of delignification, <i>DD</i> (%)	76.34	83.55	87.43	90.86
9	PAA loading (%) <sup>a</sup>	15	20	25	30
	Unscreened pulp yield (%)	58.2	58.0	58.1	57.8
	Kappa number, <i>KN</i>	12.2	8.1	7.1	5.0
	Total lignin content, <i>TLC</i> (%) <sup>b</sup>	1.97	0.66	0.58	1.08
	Degree of delignification, <i>DD</i> (%)	94.31	98.10	98.34	96.91
	Degree of polymerization, <i>DP</i>	1130	1270	1240	1280
10	ISO brightness (%)	63.70	64.25	67.49	69.22
	PAA loading (%) <sup>a</sup>	15	20	25	30
	Unscreened pulp yield (%)	59.4	57.7	57.7	58.3
	Kappa number, <i>KN</i>	3.6	2.4	2.7	2.3
	Total lignin content, <i>TLC</i> (%) <sup>b</sup>	1.49	1.38	1.20	0.29
	Degree of delignification, <i>DD</i> (%)	96.91	96.05	96.58	99.17
11	Degree of polymerization, <i>DP</i>	1400	1280	1390	1310
	ISO brightness (%)	62.68	69.07	71.73	72.33
	PAA loading (%) <sup>a</sup>	5	10	15	20
	Unscreened pulp yield (%)	61.0	57.2	56.1	55.7
	Kappa number, <i>KN</i>	21.2	4.9	2.6	1.5
	Total lignin content, <i>TLC</i> (%) <sup>b</sup>	3.91	1.83	1.13	1.02
11	Degree of delignification, <i>DD</i> (%)	88.20	94.81	96.86	97.19
	Degree of polymerization, <i>DP</i>	1030	1170	1270	1340
	ISO brightness (%)	42.06	55.96	68.15	73.78

<sup>a</sup> PAA loading was based on initial dry bagasse; <sup>b</sup> Total lignin content was on dry pulp basis.

#### *Effect of time in PAA stage on delignification*

PAA loading affects the kinetics of delignification. In order to study whether prolonging reaction time in PAA stage could reduce the PAA loading, several experiments were done to compare the effects of reaction time on delignification. The results are shown in Table 2. It was found that when PAA loading was fixed, increasing reaction time resulted in a little decrease of unscreened pulp yield but an increase of screened pulp yield and ISO brightness. However, the screened pulp yields obtained by 10% and 12% PAA loading were lower than those obtained by 15% PAA, which demonstrated that more cellulose fibers were separated when PAA loading was increased. It was also found that increasing reaction time had no significant influences on pulp viscosity, indicating that PAA did not cause degradation of cellulose under mild conditions. Therefore, according to the experimental results, the optimum reaction time and PAA loading in the second stage can be selected as 3.0 h and 15%.

**Table 2.** Effect of Time in PAA Stage on Pulping

PAA loading (%)	PAA Stage					
10	Time (h)	1.0	1.5	2.0	2.5	3.0
	Unscreened pulp yield (%)	63.8	59.8	59.4	58.3	58.6
	Screened pulp yield (%)	51.2	52.6	54.7	54.1	52.8
	Kappa number, <i>KN</i>	18	9.5	7.8	6.4	7.5
	Degree of polymerization, <i>DP</i>	1200	1170	1210	1330	1440
	ISO brightness (%)	41.55	53.95	55.28	55.46	56.01
12	Time (h)	1.0	1.5	2.0	2.5	3.0
	Unscreened pulp yield (%)	61.9	60.4	59.2	58.8	59.9
	Screened pulp yield (%)	53.7	56.7	55.5	56.2	56.2
	Kappa number, <i>KN</i>	11.1	10.4	9.1	5.4	5.1
	Degree of polymerization, <i>DP</i>	1290	1220	1340	1310	1380
	ISO brightness (%)	47.26	53.83	56.31	58.50	58.92
15	Time (h)	1.0	1.5	2.0	2.5	3.0
	Unscreened pulp yield (%)	61.5	60.3	59.4	59.5	60.0
	Screened pulp yield (%)	54.3	56.7	56.9	58.1	58.7
	Kappa number, <i>KN</i>	9.1	3.8	3.5	3.6	3.6
	Degree of polymerization, <i>DP</i>	1510	1360	1380	1490	1500
	ISO brightness (%)	50.66	57.96	61.17	63.94	63.74

### Comparison of Alkali-stage and PAA-stage

A comparison of the alkali stage and PAA stage was undertaken to study the “contributions” of the two stages to delignification, as shown in Table 3. After the first stage, 27.6 % of the raw materials were dissolved into the liquid phase. 48.56 % of the origin lignin and 19.12% of holocellulose were dissolved in alkali stage, but the pulp still had a *KN* as high as 53.4 and *TLC* of 14.39%. Furthermore, after the first-stage, the solid matter had a very low brightness due to the formation of some chromophores. Comparatively, after the PAA stage, *DD* was increased to 96.90% and the Kappa number was decreased to 3.6, but the loss ratio of holocellulose was only increased by 4.3%. These results indicated that PAA was a very selective delignification agent with little degradation of carbohydrates. The brightness of pulp obtained after the second stage was enhanced to 63.74%, which demonstrated that PAA also played a role for pre-bleaching. Therefore, the PAA stage can be considered as a combination of further delignification and primary bleaching. However, the alkali stage partially removed lignin and swelled the fibers, resulting in the increase of interface for the reaction of PAA molecules towards lignin. Therefore, PAA loading was significantly decreased compared with single-stage PAA pulping, in which 50% PAA was consumed in order to obtain a kappa number below 15. It can be known that both of the two stages played important roles for delignification. Since the alkali pretreatment process achieved delignification by reaction of  $\text{OH}^-$  and lignin, some other alkalis (bases), such as KOH, lime, and ammonia also can be employed for pretreatment.

### Characterization of the Pulps and Comparison of Alkali-PAA Pulping with Kraft Pulping

#### *Chemical compositions and pulp properties*

For further investigating the pulping effectiveness of the alkali-PAA process, detailed comparisons of alkali-PAA pulping with kraft pulping are given in Table 4.



**Table 3.** Comparison of Alkali Stage and PAA-Stage

	After/In Alkali-stage	After/In PAA-stage
Loading of chemicals (based on raw materials)	10%	15%
Liquor/solid ratio (based on initial raw materials)	3:1	1:1
Temperature (°C)	90	70 ~ 75
Time (h)	1.5	2.5~3.0
pH	>12	<1.5
Total pulp yield (%)	72.4	60.0
Kappa number, <i>KN</i>	53.4	3.6
Total lignin content (%)	14.39	1.04
Acid-soluble lignin content, <i>ASLC</i> (%)	1.05	0.56
Klason lignin content, <i>KLC</i> (%)	13.34	0.48
Degree of delignification, <i>DD</i> (%)	48.56	96.90
Holocellulose content, <i>HC</i> (%)	85.75	98.01
Percentage of holocellulose dissolved, <i>PHD</i> (%)	19.12	23.40
Cellulose content, <i>CC</i> (%)	68.65	78.50
ISO brightness (%)	26.65	63.74

**Table 4.** Comparison of Alkali-PAA Pulping and Kraft Pulping of Sugarcane Bagasse

	Kraft pulping	Alkali-PAA pulping
Loading of chemicals (based on raw materials, %)	NaOH: 11.25 ; Na <sub>2</sub> S: 3.75	NaOH: 10 ; PAA: 15
Liquor/solid ratio (based on raw materials)	5:1	3:1/1:1
Temperature (°C)	165 ~ 170	90/70~75
Pressure (MPa)	0.75 ~ 0.8	atmospheric pressure
Time (h)	3.5	1.5/2.5~3
pH	>12	>12/<1.5
Total pulp yield, <i>PY</i> (%)	51.5	60.0
Kappa Number, <i>KN</i>	12.7	3.6
Total lignin (%)	2.05	1.04
Acid-soluble lignin (%)	0.44	0.56
Klason lignin (%)	1.61	0.48
Degree of delignification, <i>DD</i> (%)	94.77	96.90
Holocellulose (%)	95.56	98.01
Percentage of holocellulose dissolved, <i>PHD</i> (%)	35.89	23.40
Cellulose content, <i>CC</i> (%)	86.01	78.50
Degree of polymerization, <i>DP</i>	1100	1500
ISO Brightness (%)	30.22	63.74
Beating degree (°SR)	55	55
Grammage (g/m <sup>2</sup> )	60.35	56.2
Tear index (mN.m <sup>2</sup> /g)	2.05	5.41
Folding endurance	9	23
Tensile strength (N.m/g)	72.41	71.15
Breaking length (km)	7.34	7.26

It can be seen that the conventional kraft pulping needed higher temperature with resulting higher pressure, but alkali-PAA pulping could be operated at below 100 °C under atmospheric pressure. Kraft pulping was conducted under a single alkaline condition, but for alkali-PAA pulping, the conditions should be changed from an alkaline one to an acidic one. Therefore, a washing step was required between the two

stages. In terms of the recovery of lignin, the PAA lignin could be easily precipitated by addition of water to the concentrated spent liquor. Nevertheless, in the kraft process and alkali pretreatment, the recovery of NaOH should be conducted by a complicated recovery system, and acid, usually sulfuric acid, was used to adjust the pH value of the black liquor to precipitate the dissolved lignin. Another important aspect was that the alkali-PAA pulping process did not consume sulfur compounds, which would significantly decrease the environment pollution.

Table 4 also shows that alkali-PAA pulping could achieve much higher *PY* and lower *KN*, and significantly decrease of *PHD*, which illustrated that the process had higher selectivity in delignification. This can be explained by the mild delignification conditions and the selective reaction of PAA towards lignin rather than carbohydrates under optimum conditions.

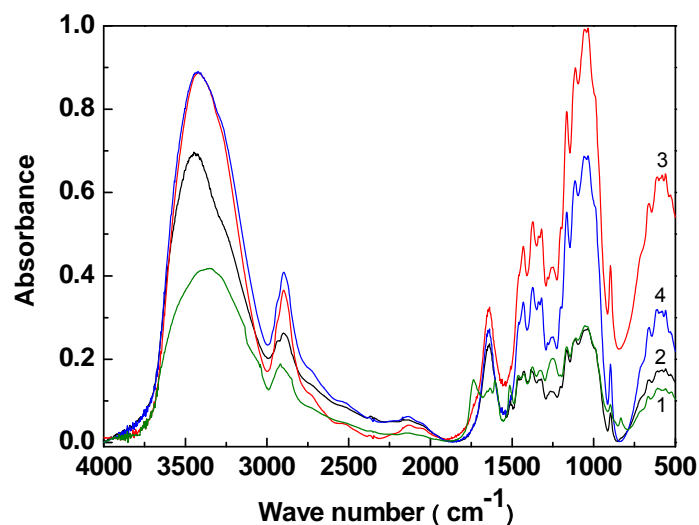
The comparisons of physical and mechanical properties of the two pulping processes showed that alkali-PAA pulping obtained higher *DP*. *DP* is an important index for pulp. Generally, pulp with higher *DP* gives higher mechanical strength of the paper sheet. The experimental results illustrated that alkali-PAA pulp was superior to kraft pulp in tear index and folding endurance, and the tensile strength of the two pulps was similar. It also can be seen that alkali-PAA pulp has a much higher ISO brightness, indicating that less bleaching agent would be used in bleaching of alkali-PAA pulp.

One important aspect that should be noted was that the alkali-PAA process consumed much more of the expensive chemical – PAA, which might increase the production cost. However, as mentioned above, the PAA stage functioned also a pre-bleaching process. The obtained pulps had much higher brightness, demonstrating that less bleaching agent would be consumed in subsequent bleaching process. On the other hand, the process was environmentally friendly. Therefore, an economic evaluation of the process should be conducted for further comparison in future. This work thus can serve as a step for further optimization and development of the process.

#### *FTIR spectra of the pulps*

Infrared spectroscopy is frequently used for investigating the structure of constituents and the chemical changes in lignocellulosic materials during delignification. The FTIR spectra of raw bagasse, alkali treated solid, alkali-PAA pulp, and kraft pulp are shown in Fig. 2. It can be observed that the intensities of the bands at 3400 and 2910  $\text{cm}^{-1}$ , which are assigned to O–H stretching and C–H stretching, respectively, became strengthened for alkali-PAA pulp and kraft pulp. This could be attributed to the increase of cellulose content in the pulps compared with raw bagasse and alkali-treated solid. The bands at 1430, 1375, 1155, 1108, 1030, and 895  $\text{cm}^{-1}$  are assigned to C–H asymmetric deformation, C–H symmetric deformation, C–O–C asymmetric vibration, glucose ring asymmetric stretching, C–O stretching, and C–O–C stretching at  $\beta$ -glycosidic linkages between glucose, which were associated with the typical absorption of cellulose (Yang et al. 2008; Li 2003). These bands became more intense compared with those of raw bagasse and alkali-treated solid. The band at 1640  $\text{cm}^{-1}$  was assigned to O–H bending of adsorbed water (Yang et al. 2008). Moreover, the conjugated C=O stretching of lignin also appeared at this wavenumber (Zhao et al. 2008b). The lignin-associated bands at 1600 and 1510  $\text{cm}^{-1}$ , which were assigned to aromatic skeletal vibrations, were absent for alkali-PAA pulp and kraft pulp, but obvious for raw bagasse. However, a weak signal was observed for alkali-treated solid at 1510  $\text{cm}^{-1}$ , indicating that there was some residue lignin in the

solid. Raw bagasse also showed strong signal at  $1732\text{ cm}^{-1}$ , which was assigned to unconjugated C=O stretching in acetyl group of hemicellulose. No such absorption peak was observed for the other three samples, indicating that deacetylation happened during alkali pretreatment and pulping.

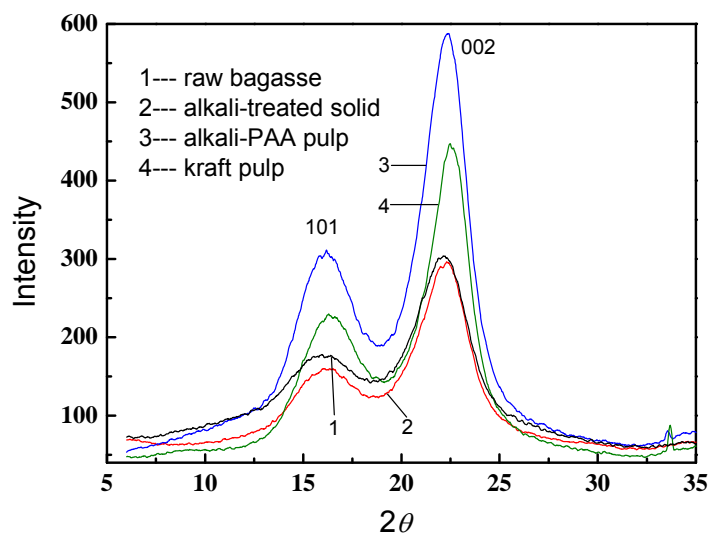


**Fig. 2.** FTIR spectra of raw bagasse, alkali-treated solid, alkali-PAA pulp and kraft pulp: 1- raw bagasse; 2- alkali-treated solid; 3- alkali-PAA pulp; 4- kraft pulp.

Infrared spectra in the  $850\text{--}1500\text{ cm}^{-1}$  region have been used to characterize the polymorphs of highly crystalline cellulose. The absorption band at  $1430\text{ cm}^{-1}$  assigned to the  $\text{CH}_2$  scissoring motion is strong in type I crystalline (cellulose I); it is very weak and shifts to  $1420\text{ cm}^{-1}$  in type II crystalline (cellulose II) and amorphous cellulose. The absorption band at  $897\text{ cm}^{-1}$  assigned as C–O–C stretching at the  $\beta$ -(1→4)-glycosidic linkage is weak and broad in cellulose I, whereas it is strong and sharp in cellulose II and amorphous cellulose (He et al. 2008). Therefore, the lateral order index (LOI), evaluated with the intensity ratio of the bands at  $1430$  and  $897\text{ cm}^{-1}$ , has been used to reflect the cellulose I fraction in the cellulose structure (Kuo and Lee 2009; Yang et al. 2007). It can be calculated that the LOIs for alkali-treated solid, alkali-PAA pulp, and kraft pulp were 2.39, 1.11, and 1.79, respectively. Alkali-treated bagasse had the highest LOI, indicating that it had the highest cellulose I content. Alkali-PAA pulp had lower LOI than kraft pulp, which demonstrated that less cellulose I was present. In other words, more cellulose I was converted to cellulose II during alkali-PAA delignification. Cellulose II contains anti-parallel arrangement of the strands and some inter-sheet hydrogen-bonding, so it is more thermodynamically stable than cellulose I. Alkali-PAA pulp had higher cellulose II content than kraft pulp, which demonstrated that it would be more stable during storage. The infrared crystallization index ( $\text{N.O'KI}$ ,  $A_{-1372}/A_{-2900}$ ) for raw bagasse, alkali-treated solid, alkali-PAA pulp, and kraft pulp were 0.97, 0.670, 1.45, and 0.91, respectively. Alkali-PAA pulp had the highest N.O'KI, indicating that the pulp had the highest cellulose crystallinity. However, more information on the crystallinity of the pulps should be obtained by X-ray diffraction (XRD) analysis, which will be presented in the next section.

### XRD of the pulps

X-ray diffraction spectra of the pulps were performed as shown in Fig. 3. It can be seen that the intensity of 101 and 002 peaks for alkali-PAA pulp and kraft pulp were dramatically increased. The pulp *CrI* calculated based on equation (1) were 53.3%, 58.5%, 67.9%, and 68.2% for raw bagasse, alkali-treated solid, alkali-PAA pulp, and kraft pulp, respectively. Nevertheless, pulp *CrI* (not cellulose crystallinity) was strongly influenced by the compositions of samples. For lignocellulosic biomass (bagasse), pulp *CrI* measures the relative amount of crystalline cellulose in the total solid. Therefore, when lignin and hemicellulose, both of which are amorphous, were partially removed, *CrI* would be increased after delignification. This interpretation could be proved by the fact that alkali-treated solid had higher *CrI* than raw bagasse. It has been known that alkali pretreatment of lignocellulosic biomass causes significant swelling of cellulose, with resulting decrease of crystallinity. However, the *CrI* of alkali-treated solid was higher than that of raw bagasse, which could be explained by the fact that lignin and hemicellulose was partially removed and the proportion of cellulose was increased. The *CrI* of alkali-PAA pulp was similar to that of kraft pulp. Nevertheless, alkali-PAA pulp had lower cellulose content than kraft pulp, which demonstrated that the former had higher cellulose crystallinity. In our previous work we found that the crystallinity of cotton fiber (cellulose content > 99%) was increased from 67.38 % to 79.77% when it was treated with 10% (w/v) PAA (Zhao et al. 2008b). It can be inferred that PAA treatment could convert part of the disordered regions in the cellulose chains to crystalline regions. Therefore, the higher cellulose crystallinity of alkali-PAA pulp might also contribute to its superior mechanical properties.

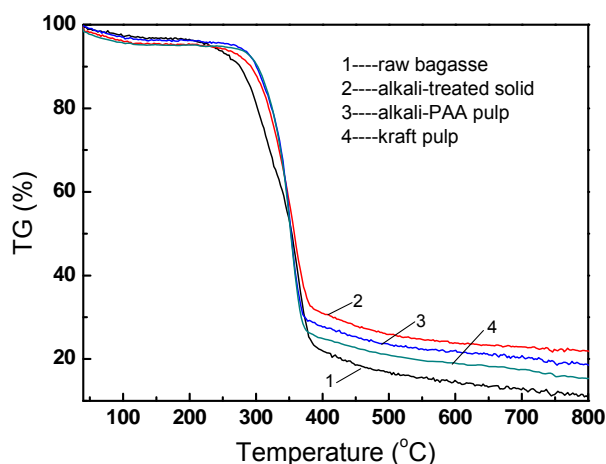


**Fig. 3.** XRD spectra of raw bagasse, alkali-pretreated bagasse, alkali-PAA pulp and kraft pulp

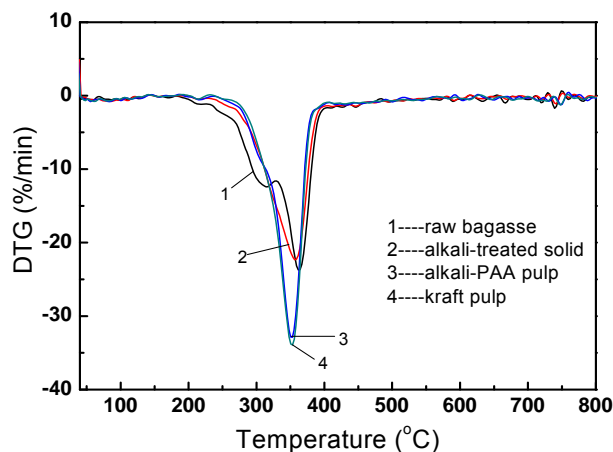
According to the Scherrer equation, the average sizes of crystallite for raw bagasse, alkali-treated solid, alkali-PAA pulp, and kraft pulp were 3.14, 3.76, 4.78, and 5.18 nm, respectively. The experimental data showed that during delignification, the size of crystallite was increased.

*TGA of the pulps*

The TGA and DTG curves of raw bagasse, alkali-treated solid, alkali-PAA pulp and kraft pulp are shown in Figs. 4 and 5, respectively. It can be seen that the TGA and DTG curves of alkali-PAA pulp and kraft pulp were very similar, both of which showed the maximum rate of weight loss at around 352 °C.



**Fig. 4.** TGA curves of raw bagasse, alkali-pretreated bagasse, alkali-PAA pulp and kraft pulp



**Fig. 5** DTG curves of raw bagasse, alkali-pretreated bagasse, alkali-PAA pulp and kraft pulp

The thermal decomposition of the samples can be divided into several stages:

1. 30-230 °C, in which water vaporized and the weight losses for the samples were less than 8%;
2. 230-390 °C, in which weight loss became significant.
3. 390-800 °C, in which the decomposition happened slowly, with weight loss being less than 15%. During this stage, the cellulose decomposed into monomer of D-glucopyranose, and finally transformed into thermo-stable graphite (Kuo and Lee 2009).

In the second stage the weight losses for raw bagasse, alkali-treated solid, alkali-PAA pulp, and kraft pulp were 72.87, 63.82, 68.13, and 69.94%, with the maximum rate of weight loss being at 362.9, 357.2, 351.8, and 352.3, respectively. Raw bagasse showed somewhat different thermal behavior. Its weight loss was higher than those of other three samples in the temperature range of 250-350 °C. Raw bagasse had the highest hemicellulose content, and the pyrolysis of hemicellulose started at the lowest temperature compared with cellulose and lignin (Yang et al. 2007; Wang et al. 2008). Therefore, two obvious peaks were observed in the DTG curve of raw bagasse. The TGA and DTG curves of alkali-PAA pulp and kraft pulp were found to be very similar to that of pure cellulose reported by Yang et al. (2007), Wang et al. (2008) and Stenseng et al. (2001). For pulps, it is believed that in this pyrolysis stage, the crystalline region of cellulose starts to destruct and the polymer simultaneously decomposes, which evidently results in an increase of the amorphous structure and decrease of DP (Yang et al. 2008);

It also can be seen that alkali-PAA pulp had somewhat more solid residue at 800 °C, which probably can be explained by the fact that alkali-PAA pulp had higher cellulose crystallinity.

Therefore, according to the above analysis of alkali-PAA pulp and kraft pulp by FTIR, XRD, TGA, and DTG, it can be concluded that the reason why alkali-PAA pulp had superior mechanical properties relative to kraft pulp can be explained by the fact that alkali-PAA pulp had a higher degree of polymerization and cellulose crystallinity, which increased the cellulose intercrossing and fiber strength during paper-sheet formation.

## CONCLUSIONS

Two-stage delignification of sugarcane bagasse with alkali and PAA could obtain pulps with high pulp yield and low kappa number. Alkali pretreatment prior to PAA delignification could significantly reduce PAA loading in the second stage by partially removing lignin and swelling the fibers. The effects of several factors in NaOH pretreatment and PAA treatment were investigated. The experimental results indicated that NaOH loading, liquor/solid ratio, and pulping temperature all had very significant effects on degree of delignification for alkali pretreatment. PAA loading in the second stage was dramatically affected by NaOH loading. The relative optimum condition for the two-stage pulping was obtained as follows: 10% NaOH loading, 3:1 liquor/solid ratio, 90 °C, 1.5 h for the first stage, and 15% PAA loading, 70-75 °C, 2.5-3.0 h for the second stage. Comparison of alkali-stage and PAA-stage showed that both of the stages played importantly for obtaining a high degree of delignification and pulp yield. PAA stage could be considered as a combination of delignification and pulp prebleaching. Compared with kraft pulping, alkali-PAA pulping could be carried out under much milder conditions with higher pulp yield and degree of polymerization, but without sulfur-contained effluents. The pulp obtained by the two-stage process had superior mechanical properties and pulp brightness relative to kraft pulp.

Alkali-PAA pulp and kraft pulp had similar FTIR spectra. However, further analysis indicated that alkali-PAA pulp had lower LOI than kraft pulp, which demonstrated that less cellulose I was present in the former. Alkali-PAA pulp had the

highest infrared crystallization index (N.O'KI), indicating that the pulp had the highest cellulose crystallinity. XRD spectra showed that the intensity of 101 and 002 peaks for alkali-PAA pulp and kraft pulp were dramatically increased compared with those of raw bagasse and alkali-treated solid, but the two pulps had similar pulp *CrIs*. Since alkali-PAA pulp had lower cellulose content, it can be inferred that it had higher cellulose crystallinity than kraft pulp, which was also reflected from N.O'KI comparison. Both of alkali-PAA pulp and kraft pulp had similar thermal behavior, with the maximum rate of weight loss being at around 352 °C. However, alkali-PAA pulp had a little more solid residue at 800 °C.

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## REFERENCES CITED

- Abou-Yousef, H. (2001). "Bagasse pulping by using Caro's acid," *J. Korea Techni. Assoc. Pulp Pap. Ind.* 33(5), 30-36.
- Abou-Yousef, H., El-Sakhawy, M., and Kamel, S. (2005). "Multi-stage bagasse pulping by using alkali/Caro's acid treatment," *Ind. Crop. Prod.* 21(3), 337-341.
- Aziz, S., and Sarkanen, K. (1989). "Organosolv pulping – A review," *Tappi J.* 72(3), 169-175.
- Black, N. P. (1991). "ASAM alkaline sulfite pulping process shows potential for large-scale application," *Tappi J.* 74(4), 87-93.
- He, J. X., Cui, S. Z., and Wang, S.Y. (2008). "Preparation and crystalline analysis of high-grade bamboo dissolving pulp for cellulose acetate," *J. Appl. Polym. Sci.* 107(2), 1029-1038.
- Johansson, A., Aaltonen, O., and Ylinen, P. (1987) "Organosolv pulping: Methods and pulp properties," *Biomass* 13(11), 45-65.
- Kirci, H., Bostanci, S., and Yalinkilic, M. K. (1994). "A new modified pulping process alternative to sulfate method 'alkaline-sulfiteantranquinone-ethanol (ASAE)'," *Wood Sci. Technol.* 28(2), 88-89
- Kuo, C. H., and Lee, C. K. (2009). "Enhancement of enzymatic saccharification of cellulose by cellulose dissolution pretreatments," *Carbohydr. Polym.* 77(1), 41-46.
- Li, J. (2003). *Spectroscopy of Wood*, Science Press, Beijing.
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., and Ladisch, M. (2005). "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresour Technol.* 96(6), 673-686.
- Muurinen, E. (2000) *Organosolv Pulping – A Review and Stillation Study Related to Peroxyacid Pulping*, Department of Process Engineering, University of Oulu, FIN-90014 University of Oulu, Finland.
- Nada, A. A. M. A., Ibrahim, A. A., Fahmy, Y., and Abou-Yousef, H. E. (1999). "Peroxyacetic acid pulping of bagasse and characterization of the lignin and pulp," *J. Sci. Ind. Res.* 58(8), 620-628.
- Nada, A. A. M. A., Ibrahim, A. A., Fahmy, Y., and Abou-Yousef, H. E. (2002).

- “Peroxyacetic acid pulping of bagasse. I. Two-stage pulping,” *Cellul. Chem. Technol.* 36(1-2), 123-136.
- Nimz, H. H., Granzow, C., and Berg, A. (1986). “Acetosolv pulping,” *Holz. Roh. Werkstoff.* 44(9), 362.
- Octave, S. and Thomas, D. (2009). “Biorefinery: Toward an industrial metabolism,” *Biochimie* 91(6), 659-664.
- Pye, E. K., and Lora, J. H. (1991). “The Alcell process. A proven alternative to kraft pulping,” *Tappi J.* 74(3), 113-118.
- Ricketts, J. D. (1995). “Role of peracids revisited for delignification, bleaching,” *Pulp. Pap.* 69(3), 89-94.
- Shi, S. L., and He, F. W. (2003). *Analysis and Detection of Pulping and Papermaking*. Chinese Light Industry Press, Beijing.
- Springer, E. L. (1997). “Delignification of wood and kraft pulp with peroxymonophosphoric acid,” *J. Pulp Pap. Sci.* 23(12), 582-584.
- Stenseng, M., Jensen, A., and Dam-Johansen, K. (2001). “Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry,” *J. Anal. Appl. Pyrolysis* 58-59(1), 765-780.
- Stockburger, P. (1993). “An overview of near-commercial and commercial solvent-based pulping process,” *Tappi J.* 76(6), 71-74.
- Sundquist, J. (1996). “Chemical pulping based on formic acid. Summary of Milox research,” *Paperi ja Puu* 78(3), 92-95.
- Wang, G., Li, W., Li, B., and Chen, H. (2008). “TG study on pyrolysis of biomass and its three components under syngas,” *Fuel* 87(4-5), 552-558.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). “Characteristics of hemicellulose, cellulose and lignin pyrolysis,” *Fuel* 86(12-13), 1781-1788.
- Yang, Z. P., Xu, S. W., Ma, X. L., and Wang, S. Y. (2008). “Characterization and acetylation behavior of bamboo pulp,” *Wood Sci. Technol.* 42(8), 621-632.
- Zhao, X., Wang, L., and Liu, D. (2008b). “Peracetic acid pretreatment of sugarcane bagasse for enzymatic hydrolysis: A continued work,” *J. Chem. Technol. Biotechnol.* 83(6), 950-956.
- Zhao, X., Zhang, T., Zhou, Y., and Liu, D. (2007). “Preparation of peracetic acid from hydrogen peroxide - Part 1: Kinetics for peracetic acid synthesis and hydrolysis,” *J. Mol. Catal. A-Chem.* 271(1-2), 246-252.
- Zhao, X., Zhang, T., Zhou, Y., and Liu, D. (2008a). “Preparation of peracetic acid from acetic acid and hydrogen peroxide: Experimentation and modeling,” *Chinese J. Process Eng.* 8(1), 35-41.

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