Two-step Delignification of Peracetic Acid and Alkali from Sugar Cane Bagasse

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Sugar cane bagasse was delignified in a two-step process with peracetic acid and alkali. Peracetic acid pre-treatment with concentration of 25% based on oven-dry fiber at 60 min, with a liquor to wood (L/W) ratio of 9:1 and a temperature of 50 °C improved the second stage delignification, compared with soda pulping. The second stage was carried out at three levels of temperatures, times, and 20% sodium hydroxide based on oven-dry fiber. Soda pulping at 165 °C, 120 min, 20% sodium hydroxide based on oven-dry fiber, and L/W 10:1 was selected to compare with two-step delignification. The two-step delignification reduces the severity of pulping conditions, including temperature and pressure, and subsequent imposes less risks compared with the soda pulping at 165 °C. The advantages of this method are high delignification and reduction of kappa number with respect to lower temperature and pressure compared with soda pulping. The total time in two-step was increased from soda pulping. Two optimum conditions for alkali step were obtained at 120 °C and 140 °C and 90 min for pretreated bagasse pulping, and similar properties were achieved with soda pulping at 165 °C and 120 min. The yield of fibers, Kappa number, and data analysis using Duncan method were measured and recorded.

Keywords: Peracetic acid; Bagasse; Soda pulping; Alkali; Two-step delignification; Kappa number

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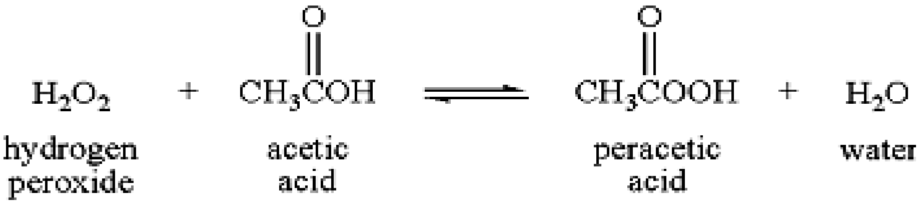
INTRODUCTION

Lignocellulose is the most abundant biomass, representing 70% of the total plant biomass. Classical uses of this material are paper making, building, and textiles, which use 2% of this biomass (Octave and Thomas 2009). One of the most important lignocellulosic substances in tropical countries is sugar cane bagasse, which is the fiber remaining after the extraction of sugar from stem (Martín *et al*. 2007). Chemical pulping processes including soda and kraft are carried out at 165 to 175 °C with high pressure, which requires high equipment costs and maintenance. Kraft pulping is commonly used to produce chemical paper pulp, which has the advantage of high strength characteristics and the disadvantages of air pollution through sulfur derivatives (Muurinen *et al*. 2000). The difficult recovery of black liquor is another disadvantage.

Peracetic acid (PAA) is a powerful oxidizing agent that is selective towards the lignin structure (Zhao *et al*. 2007). It oxidizes the aromatics in lignin, generating dicarboxylic acid and their lactones (Teixeira *et al*. 2000). Most existing pretreatment methods should be operated at high temperature, resulting in high pressure, which increases the energy consumption and costs of equipment. Furthermore, these processes leave most of the lignin in the material and limit the complete bioconversion of cellulose to sugar (Zhao *et al*. 2007). Delignification methods with peracetic acid cause less damage to the carbohydrate portion of the plant material and produce less harmful substances that could be released to the environment (Johnson 1975). Increasing swelling of the bagasse with PAA can improve delignification in the next step (Nimz *et al*. 1986). Water pollution results from colored and toxic effluents, in particular chlorinated lignin fragments from bleaching (Johansson *et al*. 1987). Thus, alternative pulping technologies, such as those based on the utilization of organic solvents (organosolv pulping), have been developed (Muurinen *et al*. 2000). Most organosolv pulping processes are conducted at high temperatures under increased pressures, and the organosolv pulp yield is similar or lower compared with kraft process.

Several peracids have been used for pulping or pulp bleaching, including peroxysulfuric acid (Caro's acid) (Abou-Yousef 2001; Abou-Yousef *et al*. 2005), performic acid (PFA), (Seisto *et al*. 1997; Perez *et al*. 1998), peracetic acid (PAA) (Nada *et al*. 2002), and peracids mixtures (Kham *et al*. 2005). Peroxysulfuric acid is the most common inorganic peracid used for delignification and bleaching. It has a higher oxidation potential than PAA (Brasileiro *et al*. 2001) and can selectively remove lignin at much lower temperature. PAA has been revisited for delignification and pulp bleaching. However, the reaction condition for pulping is always different from that for bleaching because more lignin should be removed in pulping process. (Zhao *et al*. 2011). The present work combined pre-treatment of peracetic acid with a one-step alkaline delignification. The pulp properties at low temperature and pressure were evaluated.

A scheme for peracetic acid production is shown in Fig. 1. (Buschmann *et al*. 2012).



$$H_2O_2 + CH_3\overset{O}{\overset{\|}{C}}OH \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}OOH + H_2O$$

Fig. 1. Peracetic acid production

EXPERIMENTAL

Materials and Methods

Bagasse was taken from Pars factory in Khuzestan, Iran, and air dried so that moisture in the raw material became uniform. To determine the moisture content, a few samples were measured and then oven-dried at 103 ± 2 °C. Materials were kept in polyethylene bags to prevent moisture changes. The moisture content was determined according to TAPPI T-258 om-11(2011). The kappa number was measured using ISO 302 (2015). Data analysis was performed with IBM SPSS Statistics version 24 software. (Armonk. NY, USA). The peracetic acid was produced according to the Chinese standard method, GB/T 19108(2003).

Preparation of PAA

The PAA was prepared by the reaction of acetic acid and 30% hydrogen peroxide, with a volume ratio of 2 to 1 at room temperature for 72 h; 3% (w/w) sulfuric acid was added as catalyst. The peracetic acid concentration was determined in accordance with Chinese standard GB/T 19108(2003) (Zhao *et al*. 2011).

PAA Pretreatment

The pretreatment process was carried out in a polyethylene bag in a water bath. For each batch pretreatment, 50 g of bagasse was packed into a zipped polyethylene bag, and PAA solution was added to the dry material. To keep the bagasse and liquor homogeneous, the bag was shaken every 5 min. After pretreatment, the bagasse washed with water and sieved on a 200-mesh screen; the rest of the material was stored in a polyethylene bag. PAA pretreatment conditions shown in Table 1.

Table 1. PAA Pretreatment Conditions

PAA Concentration (%)	Temperature (°C)	Time (min)	Bagasse (g)	L/W
10	25	60	50	9:1
	50			
	75			
25	25			
	50			
	75			
40	25			
	50			
	75			

Alkaline Pulping

The prepared liquor was added to the digester. After completion of the process, the pulp was washed and screened on a 200-mesh screen. The pulp was refined with a PFI refiner to internally delaminate the fibers. The moisture content, yield, and kappa number were measured. The kappa number of each pulp was obtained with two replicates. Alkaline pulping conditions are shown in Table 2.

Soda Pulping

In the soda pulping process, sodium hydroxide was added to 20% concentration based on oven-dry fiber. The pulping temperature was 165 °C, and the time 120 min from the beginning of the heating. After completion of the process, the pulp was washed and screened on a 200-mesh screen. The pulp was refined with PFI refiner to internally delaminate the fibers. The moisture content, yield, and kappa number were measured. The kappa number of each pulp was obtained with two replicates. Soda pulping conditions are shown in Table 3, and pulping conditions for the second part of the two-step process are shown in Table 4.

Table 2. Alkaline Pulping Conditions

PAA concentration (%)	PAA temp. (°C)	Alkaline cooking temp. (°C)	Alkaline cooking time (min)	L/W	NaOH (%)
25	25	100	50	10:1	20
			70		
			90		
		120	50		
			70		
			90		
		140	50		
			70		
			90		
	50	100	50		
			70		
			90		
		120	50		
			70		
			90		
		140	50		
			70		
			90		
	75	100	50		
			70		
			90		
		120	50		
			70		
			90		
		140	50		
			70		
			90		

Table 3. Soda Pulping Conditions

Temp. (°C)	Time (min)	Bagasse (g)	L/W	NaOH (%)
165	120	50	10:1	20

Table 4. Pulping Conditions After the Pretreatment

Pulping Temp. (°C)	Time to Reach Temp. (min)	Time to Stay at Temp. (min)	Total Time (min)
100	25	25	50
		45	70
		65	90
120	35	15	50
		35	70
		55	90
140	45	5	50
		25	70
		45	90
165	60	60	120

RESULTS AND DISCUSSION

Effect of PAA Pretreatment

For treated bagasse, with increasing temperature and PAA charge, there was a decrease in fiber yield. The temperature is an important factor in the PAA reaction, as it can increase the acid permeability into the fiber and reaction with constituent components. Furthermore, the swelling of fiber and destruction of lignin and hemicellulose occurred. Increasing the PAA charge led to a decrease in fiber yield, an increase acid hydrolysis, and higher acid degradation. Therefore, increasing the temperature and consumption of peracetic acid reduced the fiber yield. Table 5 shows the consumption of PAA with temperature and yield variations. The reduction of the yield for treated bagasse for the second stage was equal to 5% on average.

Table 5. Consumption of PAA with Temperature and Yield Variations

No.	PAA Concentration (%)	Temp. (°C)	Mean of yield (%)
1	10	25	96.44
2	25	25	95.35
3	40	25	94.98
4	10	50	97.18
5	25	50	95.43
6	40	50	93.51
7	10	75	94.82
8	25	75	93.3
9	40	75	92.34

Analysis of PAA pretreatment

Based on PAA pretreatment analysis, the peracetic acid was found to be effective in changing the yield of treated bagasse. The increased charge of PAA was effective in reducing fiber yield. Furthermore, increasing the temperature was effective in reducing fibers yield. For optimum alkaline pulping, the PAA charge of 25% was selected. It should be noted that the combination of temperature and acid charge both effective on fibers yield reduction.

Effect of alkaline cooking on pretreated bagasse

Compared with soda pulping, two-step delignification has lower temperature and pressure, as well as higher pulping. However, the yield of two-step and soda in some places was the same, and in some places, two-step had a lower yield and kappa number. One of the reasons of this event is destruction of hemicellulose, cellulose, and lignin of fibers during PAA pretreatment, which prepares the bagasse for better pulping in the alkaline step. The lowest kappa number for soda was 23.04, but in two-step, the lowest kappa number of 14.98 was recorded. To achieve soda pulp yield and kappa number, the intensity of two-step delignification, including temperature, time, and chemicals, can be reduced. PAA loading and temperature are also important parameters. When the liquor ratio is fixed, increasing the PAA loading can enhance the delignification rate, but too high PAA loading can also cause greater loss of carbohydrates due to oxidative degradation. It is clear the pulp yield was continually decreased with the increase of PAA loading (Nada *et al.* 2002). The decrease of pulp yield was mostly due to two aspects: removal of lignin and loss of carbohydrates. In pulping processes, lignin should be removed but it is impossible to avoid the degradation of carbohydrates, especially for hemicellulose (Zhao *et al.* 2011).

Analysis of two-step delignification compared to soda pulping

The result indicate that the temperature of pretreatment and also temperature and time (duration) of alkaline cooking influenced the yield of cooks. Regarding the effect of peracetic acid pretreatment temperature, the average yield was lowest at 75 °C compared to 50 °C and 25 °C. The effect of temperature of pretreatment and cooking temperature on lowering the yield was greater than the effect of cooking time. The results shown in Figs. 2 and 3 indicate that a temperature of 50 °C in the pretreatment stag, may result in yield similar to or more than normal soda cooking.

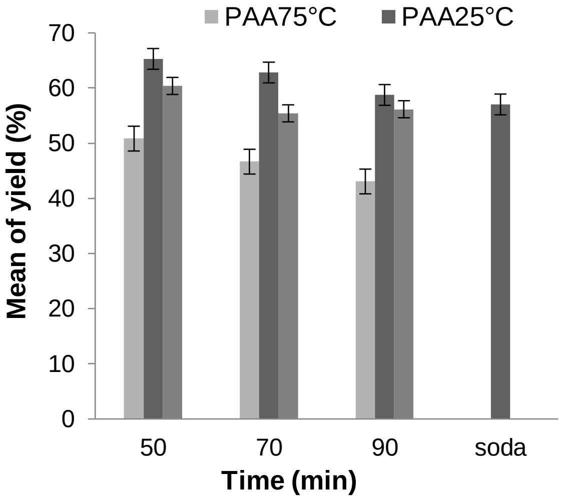


Fig. 2. Effect of alkaline time and PAA on yield

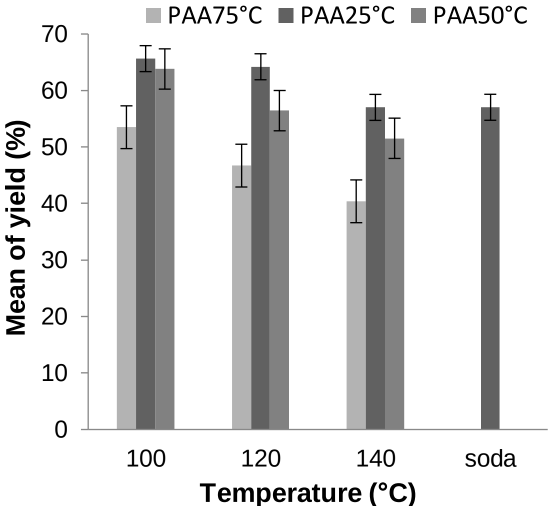


Fig. 3. Effect of alkaline temperature and PAA on yield

Regarding the effect of temperature at alkaline cooking on the yield, the results showed that the yield was lowest at 140 °C and highest at 100 °C. But the yield values at 120 °C cooks were close enough to usual soda cooks. Comparing to soda cooks, alkaline cooking at two-step cooks were performed at lower times, pressure, and temperature and therefore, consuming lower energies and applying lower pressure, while pulp yield achieved were quite similar to soda cooks. However the total times of two-step cooks were approximately 30 min longer than the usual soda cooking. Figures 2, 3, and 4 indicate that the effect of total variable (shown by a) was meaningful, but the effect of each variable (shown by b) was not meaningful.

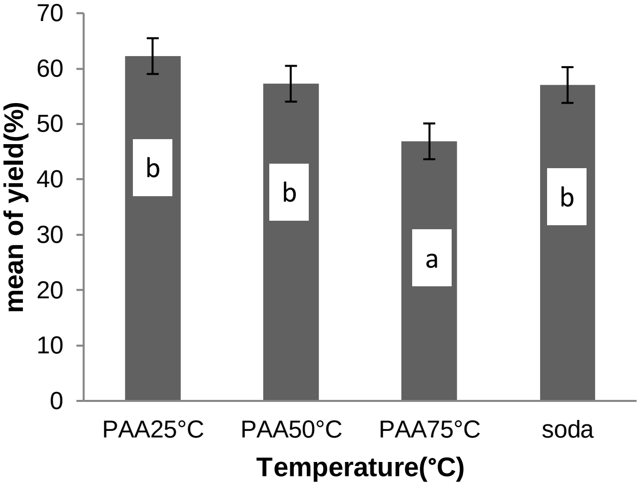


Fig. 4. Effect of total variable on alkaline yield

Kappa number analysis

The experimental results in two-step cooking indicate that the combination of peracetic acid pretreatment, and temperature and time of cooking, together all affected the kappa number. The maximum kappa number was observed at 25 °C peracetic acid pretreatment temperature. On the other hand, the lowest kappa number was observed at 140 °C cooking temperature. This means that high cooking time will tend to result in high delignification and therefore lower kappa numbers. The effect of peracetic acid pretreatment and time and temperature of alkaline cooking stage, and comparison of these results with soda cooking are shown in Figs. 5, 6, and 7.

The residual lignin content of pulp is usually characterized by kappa number, which is established by measuring the amount of a standard potassium permanganate solution that is consumed by the pulp being considered. It relatively reflects the degree of delignification and can be used for appraisal of cooking effectiveness and pulp bleachability. The data indicate a decrease of kappa number with increased PAA loading, illustrating that more lignin was dissolved with higher PAA loading. It was found that kappa number decreased quickly when PAA loading was less than 40%. With increased temperature, the decomposition rate of PAA was increased and the concentration of OH+ produced by PAA treatment, which reacts with both lignin and carbohydrates, was also increased. This resulted in removal of more lignin (Zhao *et al.* 2011).

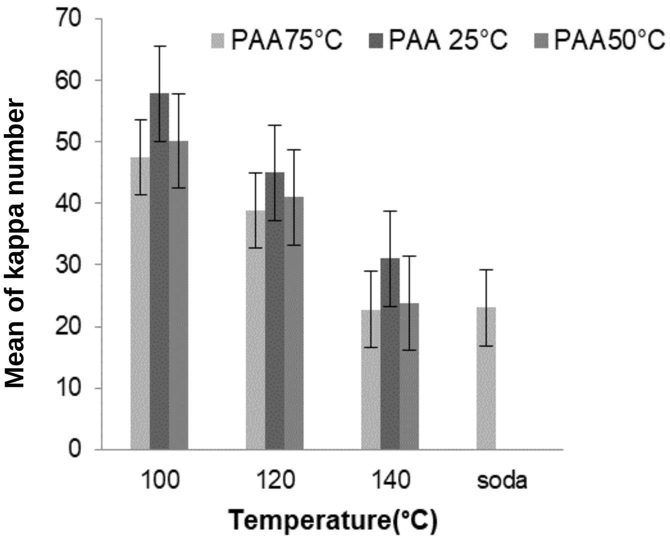


Fig. 5. Effect of alkaline temperature and PAA on kappa number

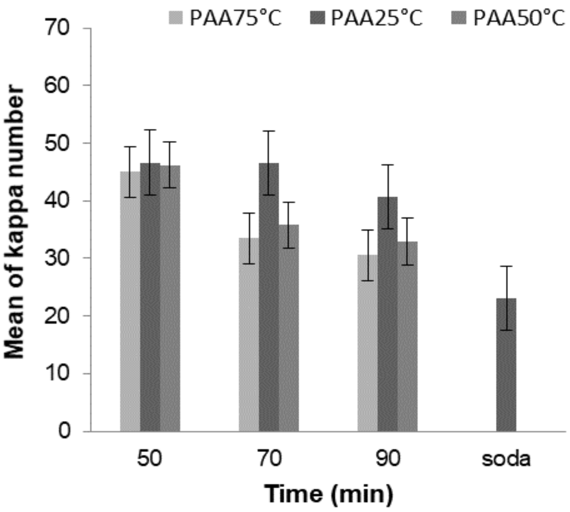


Fig. 6. Effect of alkaline time and PAA on kappa number

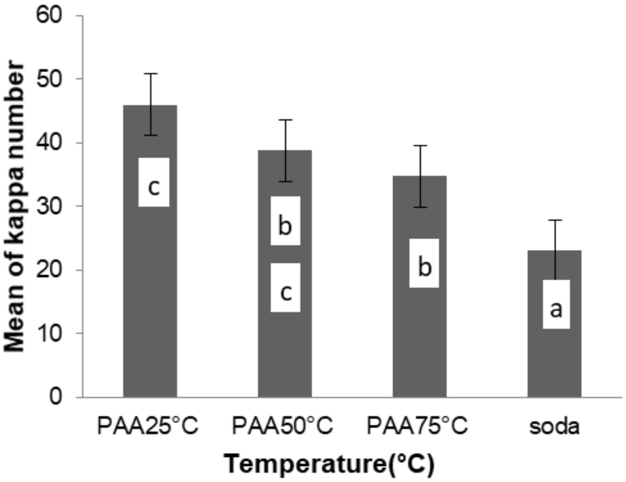


Fig. 7. Effect of total variable on alkaline kappa number

The total results and effect of per acetic acid pretreatment and two-step cooking, and comparison of these results with soda cooking are shown in Table 6.

Table 6. Total Comparison at 50 °C PAA Temperature with Two-Step and Soda

Process name	Temp. (°C)	Pressure (bar)	Pretreatment time (min)	Alkaline cooking time (min)	Mean of yield (%)	Mean of kappa	Alkaline cooking temp. (%)	Alkaline cooking time (%)	Total pulping time (%)	Pulping Pressure (%)
Soda pulping	165	9	0	120	57.03	23.03	Reference	Reference	Reference	Reference
two-step pulping	140	6	60	90	48.9	17.65	-15	-25	+20	-33
two-step pulping	120	3	60	90	58.34	37.82	-27	-25	+20	-66

CONCLUSIONS

1. Two-step delignification was able to reduce the severity of pulping conditions, including temperature and pressure while achieving similar delignification and yield results in the case of sugar cane bagasse.

2. Peracetic acid (PAA) pretreatment at 50 °C could be the optimum point. Alkaline pulping at 120 °C and 90 min without pretreatment gave similar yield and higher kappa number, whereas soda pulping at a temperature of 140 °C for 90 min resulted in a lower yield and kappa number compared to soda.

3. The two-step process can lead to high delignification, and all of factors could be help to improve pulping conditions. If a two-step process is selected as an alternative to soda pulping, it can be reduce energy consumption, as well as allowing for the optimization to achieve high delignification and produce pulp with appropriate properties.

4. One of the main challenges in the pulp and paper industry is high temperature and pressure, and the two-step can relax these requirements. Temperature and pressure reduction in the pulp and paper factory avoids the need for expensive and advanced machinery to be utilized, which can translate into lower costs to produce bagasse pulp.

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