Clean Bleaching Engineering Practice for Bagasse Pulp: Totally Chlorine-Free and Elemental Chlorine-Free Bleaching Realized with the Same Production Line

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The experimental research, process design principles, and engineering practice of a bagasse pulp production line that could run both totally chlorine-free (OP)Q(PO) and elemental chlorine-free (OP)D(EOP) bleaching sequences are discussed in this paper. Under specified process conditions, the oxygen delignification rate was up to 50% and the brightness of unbleached pulp increased. The (OP)Q(PO) sequence bleached pulp had a brightness of 83.1% ISO and an intrinsic viscosity of 888 mL/g, and the (OP)D(EOP) sequence bleached pulp had a brightness of 85.7% ISO and an intrinsic viscosity of 905 mL/g. Pulp quality produced from both bleaching sequences was better than pulp bleached by the chlorination, alkaline extraction, and hypochlorite (CEH) sequence. The wastewater was discharged only from the Q or D stage, and the chemical oxygen demand (COD) of Q or D stage was about 650 mg/L or 1100 mg/L, respectively. It was easy to alternate between these two bleaching sequences, and the bleached pulp quality from these sequences was stable.

Keywords: Sugarcane bagasse; Clean bleaching; Totally chlorine-free; Elemental chlorine-free; Oxygen delignification; Peroxide bleaching; Chlorine dioxide bleaching

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INTRODUCTION

New discharge standards for water pollutants for the pulp and paper industry (GB3544 2008) were enacted in China in October 2008 to promote the development of the economy while protecting the environment. The discharge limit of absorbable organic halides (AOX) has become a constraint indicator in the new standard. The AOX are organochlorine compounds that are generated during chlorine bleaching (Suntio *et al.* 1988). These compounds are usually biologically persistent, recalcitrant, and highly toxic to the environment (Thompson *et al*. 2001). Elemental chlorine bleaching with CEH (chlorination, alkaline extraction, and hypochlorite stage) was still commonly used in most of the bagasse pulp plants located in China in 2008. The emission targets, especially for AOX, were almost impossible to achieve relative to the new standard by using traditional CEH bleaching. Therefore clean production technology must be used to meet the requirements of the new GB3544 (2008) environmental discharge standard.

Bagasse is an abundant agro-industrial byproduct and is used in many different applications, such as animal feed and paper (Pandey *et al*. 2000; Hernández-Salas *et al*. 2009; Loh *et al*. 2013). Bagasse consists of approximately 50% cellulose and 25% each of hemicellulose and lignin; it represents an abundant, inexpensive, and readily available

source of renewable lignocellulosic biomass (Sun *et al*. 2004). Bagasse is easily pulped and bleached compared to wood chips, and it has very low ash content in comparison to other crop residues such as rice straw and wheat straw (Pandey *et al*. 2000).

Legislative and environmental pressures have been forcing the Chinese pulp and paper plants to use the new clean bleaching technology. The typical clean bleaching technologies are totally chlorine-free (TCF) bleaching and elemental chlorine-free (ECF) bleaching, which have been used for decades in the world and have been shown to be economical and environmentally friendly (Torres *et al*. 2000; Khristova *et al*. 2002; Andreas 2005). Many TCF and ECF studies for bagasse pulp have been reported. For instance, Mohta *et al*. (2001) found that ECF bleaching of oxygen-delignified pulps gave higher brightness as compared to the $D_0E_1D_1$ bleaching of soda and soda-AQ pulps. Hedjazi *et al.* (2008) used OQ(PO) bleaching sequence to delignify and bleach an alkaline sulfite-anthraquinone (ASAQ) bagasse pulp to a brightness of 80% ISO. Totally chlorine-free bleaching with the $Q_1(OP)Q_2P$ sequence of the unbleached ASAQ bagasse pulps yielded bleached pulps with 76.9% ISO brightness, which is suitable for producing writing and printing grades of paper (Khristova *et al*. 2006). Nie *et al.* (2014) studied the kinetics of AOX formation in chlorine dioxide bleaching of bagasse pulp. Studies by the authors (Wang *et al*. 2009; Liu *et al*. 2010; Zeng *et al*. 2012) also found that the alkaline bagasse pulp can be bleached to a brightness of over 80% ISO using the (OP)Q(PO) bleaching sequence.

The aim of this work was to achieve a value of brightness around 80% ISO using the TCF bleaching sequence and around 85% ISO using the ECF bleaching sequence, while maintaining reasonable intrinsic viscosity values with the production line. So, a TCF sequence ((OP)Q(PO)) and an ECF sequence ((OP)D(EOP)) were investigated to bleach the bagasse pulp. Kappa number, brightness, intrinsic pulp viscosity, and yield were measured on these pulps to determine the appropriate bleaching conditions. Then, a new bagasse pulp plant combining (OP)Q(PO) bleaching and (OP)D(EOP) bleaching was built in 2010 based on our research and extensive engineering experience with TCF bleaching of wheat straw pulp (Li *et al*. 2009), which translated our conceptualized design into engineering practice. This dual bleaching sequence is suitable for bleaching various pulps, such as high or low brightness bagasse pulp, bamboo pulp, and eucalyptus slab pulp. This production line has been running for three years, and the total operating costs are lower than CEH bleaching and has shown good environmental benefit. These techniques will provide important information for designing new bleach plants and retrofitting old bleach plants.

RESULTS AND DISCUSSION: LABORATORY EXPERIMENTS

Materials

Unbleached bagasse pulp (soda pulping technology) was obtained from a pulp plant located in Guangxi Province, China. The pulp was dewatered to a consistency of about 30% and stored in sealed-plastic bag for at least 24 h. The unbleached pulp had a kappa number of 14.2, an intrinsic viscosity of 1065 mL/g, and a brightness of 44.4% ISO.

Methods

Two bleaching sequences were carried out with the above unbleached pulp. One was the TCF bleaching sequence (OP)Q(PO), which consists of a peroxide-reinforced oxygen delignification stage ((OP)), a chelating pretreatment stage (Q), and a pressurized peroxide bleaching stage ((PO)). The other one was the ECF bleaching sequence (OP)D(EOP), which consists of a peroxide-reinforced oxygen delignification stage (OP), a chlorine dioxide stage (D), and an extraction stage reinforced with peroxide and oxygen ((EOP)). The pressurized (OP), (PO) and (EOP) stages were performed in a FYXD-type steel autoclave equipped with a stirrer. The Q and D stages were performed in polyethylene bags submerged in an agitated water bath. After each bleaching treatment, the pulps were thoroughly washed with tap water.

Unbleached and bleached pulp properties were characterized by various TAPPI standards: brightness, T525 om-06 (2006); kappa number, T236 om-99 (1999); ash, T211 om-02 (2002); tear index, T414 om-04 (2004); burst index, T403 om-02 (2002); and tensile index, T494 om-01 (2001). Pulp viscosity in cupriethylene diamine (CED) solution was determined and expressed as intrinsic viscosity (mL/g). The AOX was determined according to Chinese standard GB/T15959 (1995) by using a Multi X® 2500 AOX/TOX analyzer (Analytik Jena AG, Eisfeld/Germany). The color of the wastewater was measured according to Chinese standard GB 11903 (1989) by the dilution method.

Orthogonal tests consisting of three factors at three levels were performed to determine the optimal bleaching conditions of chemical dosages, reaction times, and reaction temperatures as the main control parameters for the measured parameters of delignification rate, kappa number, brightness, and intrinsic viscosity. The final bleaching parameters are shown in Table 1.

Table 1. General Bleaching Conditions and Chemical Reagents Used in (OP)Q(PO) and (OP)D(EOP) Bleaching Conditions for Bagasse Pulp

Bleaching sequence	(OP)Q(PO)			(OP)D(EOP)		
	(OP)	Q	(PO)	(OP)	D	(EOP)
Consistency (%)	10	8	10	10	8	10
Temperature (°C)	95	65	100	95	65	95
Time (min)	60	60	120	60	60	120
NaOH (%)	2.5	-	1.0	2.5	-	2.0
$MgSO_4$ (%)	0.5	-	0.5	0.5	-	0.5
H_2SO_4 (%)	-[a]	1.5	-	-	0.5	-
H_2O_2 (%)	0.5	-	2.5	0.5	-	0.5
DTPA (%)[b]	-	0.1	0.1	-	-	0.1
$C_2N_4H_4$ (%)	-		0.3	-	-	-
ClO_2 (%)	-	-	-	-	1.0	-

a. "-" means that the chemical was not used in the corresponding bleaching stage.
b. DTPA is diethylene triamine pentacetate acid.

Results

The experimental laboratory results of final optimized (OP)Q(PO) bleaching and (OP)D(EOP) bleaching are shown in Table 2. The single-stage (OP) delignification rate could be as high as 50%, with an accompanying increase in pulp brightness. The final bleached pulp brightness levels were 82.5% ISO and 87.5% ISO, respectively. The bleached pulps had intrinsic viscosities that were greater than 800 mL/g, and final yields that were greater than 90%. According to the above tests results, bleached bagasse pulp can be produced to targeted specifications by using optimized bleaching processes.

Table 2. Characteristics of (OP)Q(PO) and (OP)D(EOP) Bleached Bagasse Pulp

Treatment	Kappa Number	Delignification Rate (%)	Yield[a] (%)	Brightness (% ISO)	Viscosity (mL/g)
Unbleached	14.2±0.1	-	-	44.4±0.3	1065±23
(OP)	7.1±0.1	50	95.4±0.1	56.4±0.2	967±17
(OP)Q(PO)	-[b]	-	92.5±0.1	82.5±0.3	873±20
(OP)D(EOP)	-	-	92.3±0.1	87.5±0.3	897±25

a. yield is based on unbleached pulp
b. "-" means that the chemical was not used in the corresponding bleaching stage.

DESIGN PRINCIPLES OF TCF AND ECF DUAL BLEACHING SEQUENCE

Both the TCF (OP)Q(PO) sequence and the ECF (OP)D(EOP) sequence can be employed in the production-scale bleach plant, where the Q stage can be switched to a D stage and the (PO) stage can be operated as an (EOP) stage; the only difference is the chemicals added into the system. Reasons for this bleach plant design include: (1) The (OP) delignification stage can lower the kappa number of the brownstock from the digester. This lowers the bleach chemical demand needed in either (PO) for TCF or D(EOP) for ECF. Besides, recycling the effluents from (OP) back to chemical recovery can also reduce the effluent discharge from the bleach plant; (2) It is difficult to produce economical high brightness pulp (>85% ISO) using the TCF (OP)Q(PO) sequence since the chemical costs are greatly influenced by the market price of hydrogen peroxide; (3) If the supply of bagasse is not enough, the bamboo or eucalyptus slab fiber, which are suitable to horizontal tube digester cooking, can be used as backup materials. However, these unbleached pulps from these alternative raw materials may have higher kappa numbers, which makes using the TCF (OP)Q(PO) sequence difficult to reach high brightness targets when economical chemical costs are constraining; and (4) The ECF (OP)D(EOP) bleaching can meet the requirement of higher brightness of the final bleached pulp and higher kappa number of the unbleached pulp. The required dosage of chlorine dioxide is small because the use of oxygen delignification has lowered the kappa number entering the D stage. Thus, COD emission load and wastewater emission amount can be kept to within the new standard.

The bleach plant flow diagram is shown in Fig. 1. The oxygen delignification stage reinforced with peroxide (OP) was placed prior to a closed screen room in order to reduce the amount of steam needed to reach the high operating temperature of the (OP) stage. Screened pulps were washed and thickened by two vacuum filter washers, and then they were treated by Q(PO) or D(EOP). The final bleached pulp were thickened to a consistency of 30 to 40% prior to being sold to the surrounding paper plants. The detail design principles are presented in Fig. 1.

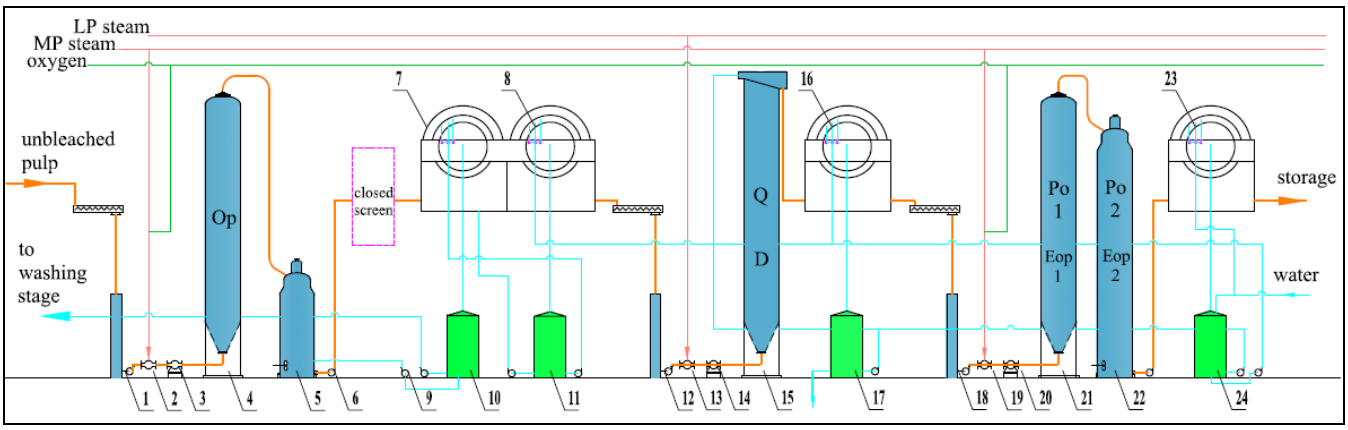

Fig. 1. Process flow diagram of (OP)Q(PO) and (OP)D(EOP) dual bleaching sequence:
1. #1 medium consistency pump; 2. #1 steam heater; 3. #1 medium consistency mixer;
4. pressurized reactor; 5. blow tank; 6. pump; 7. #1 washer; 8. #2 washer; 9. filtrate pump;
10. #1 filtrate tank; 11. #2 filtrate tank; 12. #2 medium consistency pump; 13. #2 steam heater;
14. #2 medium consistency mixer; 15. upflow tower; 16. #3 washer; 17. #3 filtrate tank;
18. #3 medium consistency pump; 19. #3 steam heater; 20. #3 medium consistency mixer;
21. upflow tower; 22. downflow tower; 23. #4 washer; 24. #4 filtrate tank.

Oxygen Delignification with Peroxide Reinforcement Stage

Oxygen delignification with peroxide reinforcement is the most important stage in the dual (OP)Q(PO) and (OP)D(EOP) bleach plant line. Bleaching was not obtainable with the same production line without adopting the (OP) stage into the bleaching sequence. The (OP) stage can be successfully used to delignify various pulp and has become a major unit operation in the clean production process. The use of oxygen delignification systems is widespread in the world, but few oxygen delignification systems for bagasse pulp are used in China because of the restriction in technology and economy.

Oxygen delignification reduces the lignin content of the brownstock by using oxygen under alkaline conditions. It can effectively reduce the kappa number of unbleached pulp, simplify the follow-up bleaching sequence, and reduce the dosage of subsequent bleaching chemicals (Mân Vu *et al*. 2004; Thomas *et al*. 2007; Liu *et al*. 2013). Furthermore, effluents generated from the oxygen delignification stage can be recycled to brownstock washing and combined with the recovered black liquor that is sent to the recovery boiler. Compared with typical oxygen delignification (O), the pulp brightness after peroxide-reinforced oxygen delignification ((OP)) increases sharply while delignification rate and viscosity are nearly identical to O stage; the brightness stability of high brightness pulp can also be increased with peroxide reinforcement (Parthasarathy *et al*. 1990; Wang *et al*. 2009). Therefore, peroxide-reinforced oxygen delignification was adopted and the optimal process conditions were explored. As shown in Table 2, after the (OP) stage, the pulp kappa number was below 7 and brightness exceeded 55% ISO, which provided advantages in subsequent bleaching stages. Therefore, short sequence TCF bleaching is feasible for producing bleached bagasse pulp.

Chelating Pretreatment Stage

In TCF (OP)Q(PO) sequence, transition metal ions in the pulp are deleterious to high-temperature peroxide bleaching. Hydrogen peroxide and the hydroperoxide anion

are very sensitive to the presence of certain metal ions, the presence of which leads to their catalytic decomposition. Manganese ion will reduce the pulp brightness, although copper ions have little influence on pulp brightness, but it will cause the pulp viscosity to decrease due to catalytic peroxide decomposition (Zhang *et al*. 2000). Abrantes *et al.* (2007) found that when the chelating pretreatment was applied prior to (PO), the treated pulps had higher viscosities, consumed less peroxide, and had higher brightness levels. Carbohydrate degradation might occur during hydrogen peroxide bleaching because of the decomposition of hydrogen peroxide into hydroxyl radicals, catalysed by metal ions. The addition of chelants for the control of metals and applying peroxide stabilizers into the peroxide stage can minimize the loss of carbohydrates. The purpose of chelating pretreatment is thus to remove the transition ions such as iron, manganese, and copper ions. It promotes the utilization of peroxide, protecting carbohydrates and improving pulp brightness.

Chlorine Dioxide Bleaching Stage

Chlorine dioxide is an efficient bleaching agent, with less environmental impact, and is also a strong oxidant. It can oxidize lignin selectively without causing cellulose and hemicellulose degradation. In addition, the bleached pulp brightness is high, physical strength is high, and brightness stability is good (Jahan *et al*. 2010; Bajpai 2012). Replacing chlorine with chlorine dioxide is an effective measure to reduce bleaching pollution load. The reaction between chlorine and lignin is mainly a substitution reaction. Chlorophenol is easily generated during the reaction process, but the reaction between chlorine dioxide and lignin is mainly an oxidation reaction; thus, the AOX content in the D stage effluent is very low. Gellerstedt *et al*. (1995) found that a chlorine dioxide stage should be carried out at a pH around or above three in order to minimize chlorination of the lignin. Because the dosage of chlorine dioxide was low and there was residual alkali in the (OP)-treated pulp, H_2SO_4 was added prior to D stage to adjust the pH of the entering pulp.

Although some bagasse bleach plants use the $D_0E_1D_1$ sequence in China, the dosage of chlorine dioxide is about or more than 20 kg/tons and significant amounts of halogenated hydrocarbons are still generated. As mentioned before, the use of oxygen delignification can reduce kappa number effectively, so if oxygen delignification is used prior to the $D_0E_1D_1$ sequence, the use of chlorine dioxide can be reduced. Therefore, the present work combined the advantage of oxygen delignification and chlorine dioxide bleaching, which are incorporated into the (OP)D(EOP) bleaching sequence.

Pressurized Peroxide Bleaching Stage

The peroxide bleaching stage is the core component of the TCF (OP)Q(PO) sequence; this stage makes possible to achieve a high final brightness in TCF bleaching. As mentioned before, bagasse is easily bleached, and the kappa number can be reduced by using the (OP) stage. Thus, the short sequence (OP)Q(PO) is practical for bleaching bagasse pulp.

Peroxide has mainly a brightening effect as it eliminates coloured structures under moderate temperature (70 °C and below) and alkaline conditions; it also reacts rather slowly in comparison to other bleaching chemicals. The higher the temperature of the hydrogen peroxide stage, the greater will be the occurrence of radicals. The phenolate anion in lignin is attacked by the hydroxyl radical, giving a phenoxy radical, which can then react with the superoxide radical. The final result is the opening of the aromatic ring

and the formation of muconic acid derivatives, which makes the lignin soluble (Gierer 1997). Increasing the pressure and temperature enables reaching higher brightness in a much shorter time, and higher pressure makes it possible to run the process at high temperature and avoid boiling (Stromberg *et al*. 1994; Bajpai 2012). By the kinetics of peroxide bleaching, the reaction rate of chromophore destruction proceeds *via* a very fast phase initially, followed by a second phase, which is much slower and approaches asymptotically a "floor level" of chromophore concentration (Ni *et al* 1997; Wang *et al*. 2008). In addition, to prevent undesired peroxide decomposition in the initial reaction, static pressurization is needed to mitigate peroxide decomposition reactions (Chen 2007).

Therefore, according to the above principles, a peroxide bleaching tower that combined a pressurized upflow tube and an atmospheric downflow tower was designed, where the initial 60 min of reaction is in the pressurized upflow tube and the last 60 min is in the downflow atmospheric tower. This bleaching stage design helps to utilize the peroxide more effectively and to improve the overall bleaching effect.

Oxidative Alkaline Extraction with Pressurized Peroxide

Alkaline extraction is an important stage in multistage ECF bleaching process; it is often used after chlorine dioxide delignification stage (Shackford *et al*. 2009). The role of alkaline extraction is to remove soluble lignin in the former oxidation treatment or to reactivate the residual lignin for the next oxidation process. After chlorine dioxide oxidation treatment, a large part of oxidized lignin still remains in the pulp; therefore, alternating acid and alkaline bleaching treatments can improve the solubility of the oxidized lignin (Shackford *et al*. 2009). Alkaline extraction efficiency can be improved by increasing the dosage of caustic, but high caustic charges will also increase the overall bleaching cost. In order to improve the efficiency of alkaline extraction, oxidizing agents are often used (Suess and Davies 2007). Oxygen and peroxide are often used to enhance the effect of alkaline extraction. Adding hydrogen peroxide in an existing extraction stage is a simple way to further reduce the kappa number and improve the brightness. In an (EO) or (EOP) stage, this can be partially or totally pressurized during the extraction reaction. Various studies have noticed that the bleachability of pulp various in an order of (EOP) > (EP) > (EO) >E_1 (Brogdon and Lucia (2005); Zhao *et al*. 2010).

According to the above principles and combined with the equipment in the (PO) stage of TCF ((OP)Q(PO)) bleaching sequence, oxidative alkaline extraction with pressurized peroxide (EOP) was selected as the final bleaching stage in ECF ((OP)D(EOP)) bleaching sequence.

RESULTS AND DISCUSSION: PRODUCTION-SCALE TESTS

The described dual production line for bleached bagasse pulp has been running for nearly three years for both (OP)Q(PO) and (OP)D(EOP) sequences as well as for the (OP)D(EOP) sequence for eucalyptus slab pulp, which was successfully realized in October 2014. The final brightness was able to reach 85% ISO, and the consumption of chlorine dioxide was at most 10 kg /tons. This is the first implementation of engineering practices that allow a pulp plant to easily switch between TCF and ECF bleaching sequences while utilizing the same bleach plant equipment. This dual process design decreased the operation costs and increased production competitiveness. The quality of

the bleached pulp from this production has been good, and its demand for papermaking has exceeded the production line output.

Production Process

In the (OP) delignification stage, NaOH and $MgSO_4$ were added into the 14% consistency brownstock in the spiral conveyor from the last washer of washing stage; then the brownstock was diluted to 10% consistency using recycled wastewater from (PO) stage of TCF or (EOP) stage of ECF sequence. Medium pressure steam and O_2 were then added to the pulp slurry in the #1 steam mixer (2), where the pulp was heated to about 95 °C; afterwards, H_2O_2 was added into pulp before the #1 medium consistency mixer (3). After fully mixing, the pulp slurry reacted as it passed through the pressurized reactor (4) for about 60 min; the pressure at the top of the reactor was controlled at 0.3 to 0.4 MPa. After reacting in the pressure reactor, the pulp was discharged into a blow tank (5). The wastewater effluent from (OP) stage was alkaline and highly colored. The (OP) effluent was similar to that of the weak black liquor from brownstock washing. Thus, the effluent was recycled to the brownstock washers as washing water, and its spent alkali was recover with that of the black liquor in chemical recovery system.

In the Q (or D) stage, chemicals were added into 8% consistency pulp in the spiral conveyor of the #2 washer (8) of bleaching stage; afterwards, the pulp was then mixed and heated by the #2 medium consistency pump (12), #2 steam heater (13), and #2 mixer (14). The mixed slurry reacted in an atmospheric upflow tower (15) for about 60 min at 65 °C. The treated pulp was diluted at the top of tower and overflowed into the #3 washer (16) after the Q (or D) stage. This overflow method can save a pulp tank and a medium consistency pump system between Q (or D) tower and #3 washer. Both in the (OP)Q(PO) and (OP)D(EOP) bleaching process, the reuse of the washing wastewater from Q (or D) stage is limited because of acidity. About 50% of the washing liquid from Q (or D) stage was discharged into wastewater treatment system, and Q (or D) stage was the only emission point of the middle stage wastewater in the whole bleaching process.

In the (PO) or (EOP) stage, required chemicals except for H_2O_2 and O_2 were added to the 10% consistency pulp in the spiral conveyor of the #3 washer (16) of the bleaching stage. The pulp was further mixed and heated consecutively using the #3 medium consistency pump (18), #3 steam heater (19), and #3 mixer (20). Medium pressure steam and O_2 were added in the steam heater to elevate the pulp temperature to about 100 °C. Then H_2O_2 was added in the front of the mixer, and the pulp pump into the upflow tower (21). The pulp had a residence time of 60 min in the upflow tower, with the remaining 60 min of reaction time being conducted in the atmospheric downflow tower (22). After the end of the bleaching reaction, the pulp was diluted in the bottom of the downflow tower and then pumped into the #4 washer of bleaching stage. The bleaching effluent from the (PO) stage and the (EOP) stage was alkaline and was low in color. Thus, it could be recycled to (OP) and Q stage as washing water and dilution water in (PO) or (EOP) stage, so that there is no wastewater discharged from this terminal stage.

Characteristic of Bleached Bagasse Pulp

According to production records, the kappa number of the unbleached pulp was maintained between 14.0 and 15.0; after the (OP) stage, the kappa number decreased to 7.0 to 7.3, which equated to a delignification rate of about 50%. Pulp brightness increased from about 43% ISO to about 59% ISO. It seemed that (OP) delignification not only can degrade lignin effectively, but can also improve pulp brightness, which is beneficial for subsequent bleaching stages.

Bleached bagasse pulp from different production line that used various bleaching sequence (*i.e.*, (OP)Q(PO), (OP)D(EOP), D_0ED_1, and CEH) were sampled and were analyzed; the results are shown in Table 3.

Table 3. Bleached Pulp Characteristics of Different Bleaching Sequences

Pulp Characteristic	(OP)Q(PO)	(OP)D(EOP)	D0ED1	CEH
Brightness (% ISO)	83.1±0.3	85.7±0.5	86.0±0.4	79.5±0.4
Ash (%)	0.513±0.015	0.553±0.024	0.542±0.021	0.912±0.028
Viscosity (mL/g)	888±28	905±18	928±31	531±24
Tear Index (mN·m2/g)	4.59±0.21	5.29±0.23	4.48±0.17	4.13±0.16
Burst Index (kPa·m2/g)	5.14±0.10	5.16±0.08	5.19±0.12	5.08±0.08
Tensile Index (N·m/g)	76.71±1.07	76.90±1.23	77.12±1.00	71.52±1.31
Elongation (%)	3.98±0.18	3.81±0.15	3.24±0.20	3.18±0.12
The drainage of the four pulps for strength measurement were all controlled at 45 ± 2 °SR				

As shown in Table 3, the final bleached brightness could reach 83.1% ISO for the (OP)Q(PO) sequence and 85.7% ISO for the (OP)D(EOP) sequence; both sequences achieved the targeted brightness requirements. Brightness of (OP)Q(PO) and (OP)D(EOP) pulps were higher than the CEH pulp, but lower than the D_0ED_1 pulp. This demonstrated that the bleaching ability of chlorine dioxide performed better than peroxide. From the point of ash content, the (OP)Q(PO) pulp had the lowest ash content (0.513%), whereas the (OP)D(EOP) and D_0ED_1 pulps had similar ash levels and the CEH pulp had the highest ash content (0.912%). In addition, judging from the color of the ash residue, (OP)Q(PO) had the lightest color of white, and (OP)D(EOP) and D_0ED_1 pulps had a light color of yellow. Most ash consists of minerals that remain after high temperature combustion; this ash contains significant levels of metal ions such as Fe, Cu and Mn, which can result in colored inorganic salts. Some of these metal ions were removed during the chelating pretreatment (Q) stage, which reduced the content of these colored salts in the (OP)Q(PO) bleached pulp.

Intrinsic pulp viscosity is mainly used for the determination of the average degree of polymerization of the cellulose chains, and it also reflects on how much cellulose degradation has occurred during the bleaching process. As can be seen from Table 3, the viscosity of the (OP)Q(PO) pulp was slightly lower than the (OP)D(EOP) and D_0ED_1 pulps and was higher than CEH pulp. This is mainly because the bleaching selectivity of chlorine and hypochlorite can be low, and it is very easy to cause the intrinsic pulp viscosity to decrease. Although the selectivity of (PO) bleaching is enhanced, it is still lower than with chlorine dioxide bleaching. Thus, D_0ED_1 pulp had the highest viscosity of the four bleached pulps.

From the aspect of physical pulp properties, tear index, burst index, tensile index, and breaking length of (OP)Q(PO), (OP)D(EOP), and D_0ED_1 pulp showed little

difference. All three pulps exhibited higher strength properties than the CEH pulp. These results were mirrored with the intrinsic viscosity values. Viscosity decreases indicated damage to the cellulose chains during CEH bleaching, which translated to lower pulp strength. The results also imply that modern medium-consistency clean bleaching technology can improve pulp quality. Moreover, the elongation of the (OP)Q(PO) pulp was 3.98%, which was higher than the D_0ED_1 and the CEH pulp. It was indicated that that pulp fibers obtained from (OP)Q(PO) were soft and were beneficial to the production of tissue paper.

Environment Benefits of (OP)Q(PO) and (OP)D(EOP) Bleaching

In this production line, only one stage (Q or D) had a sewered effluent that amounted to about 30 m^3/tons, which was lower than the 60 to 100 m^3 of sewered effluents from traditional CEH bleaching. The AOX content generated during (OP)Q(PO) bleaching was very small and could meet the requirement of Chinese standard GB 3544 (2008) without any special treatment. In (OP)D(EOP) bleaching sequence, the amount of AOX generated was only about 0.3 kg/tons because of the small dosage of chlorine dioxide used. In addition, the high concentration of dissolved organics in the (OP) effluent was recycled to the chemical recovery system, which reduced the pollution load of this production line compared to CEH bleaching. According to the bleach plant data, the COD of the second stage effluent of (OP)Q(PO) bleaching was about 650 mg/L, whereas it was 1100 mg/L for the (OP)D(EOP) bleaching. This indicated that the second stage wastewater from these short sequences was easily handled with the aerobic treatment method.

There is not an economically effective method to get rid of the AOX in the wastewater at present. Therefore, the most effective method is not to use any elemental chlorine bleaching agents or to use little elemental chlorine-free bleaching agents. In this production line, bleach plant effluents could meet the emission limits set by the Chinese environmental regulations by using wastewater physicochemical, anaerobic, and aerobic treatments. This is because of the use of the (OP) delignification stage, which effectively decreased the COD emanating from the sewered effluent of the second stage. The online monitoring indicated that the COD of final discharged wastewater was between 50 and 70 mg/L for the (OP)Q(PO) sequence, and between 60 and 80 mg/L for the (OP)D(EOP) sequence. Furthermore, the suspended solids (SS) of the final discharged wastewater from two bleaching sequences was between 0 mg/L and 30 mg/L, the color intensity of the final discharged wastewater was about 30 times of optically pure water, and the pH was between 7.0 and 8.0. All the measured effluent indicators were lower than those in the standard GB3544 (2008).

CONCLUSIONS

1. This production line is the first bagasse clean bleaching line that can run both TCF and ECF bleach sequences in China. It has been demonstrated that the process design is reasonable, and equipment operation is stable and reliable.
2. Compared with the CEH bleach sequence, modern clean bleaching can improve pulp quality and meet environmental effluent discharge limits. The (OP)Q(PO) and (OP)D(EOP) bleached pulps have good physical strength and low ash content. The

(OP)Q(PO) pulps were bleached to >80% ISO brightness and (OP)D(EOP) pulps were bleached to >85% ISO brightness; both processes yielded pulps with intrinsic viscosity >800 mL/g.

3. Water consumption, wastewater emission load, and pollution load decreased sharply by using this TCF/ECF dual bleaching sequence. Wastewater could meet the emission limits set by the Chinese environmental regulations by using wastewater physicochemical, anaerobic, and aerobic treatments. The TCF/ECF dual bleaching sequence has better environmental benefits.

ACKNOWLEDGMENTS

The authors are grateful for the support of the China Major Science and Technology Program for Water Pollution Control and Treatment, Grant No. 2014ZX07213001.

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Article submitted: November 4, 2014; Peer review completed: March 1, 2015; Revised version received and accepted: March 5, 2015; Published: March 16, 2015.
DOI: 10.15376/biores.10.2.2667-2680