Oxygen Delignification of Wheat Straw Soda Pulp with Anthraquinone Addition

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Oxygen delignification of wheat straw soda pulp with the addition of anthraquinone (AQ) was conducted to evaluate the effects of AQ on pulp quality. The pulp yield, kappa number, intrinsic viscosity, and brightness were selected as the properties to optimize oxygen delignification. The optimal pulp was obtained via grey relational analysis with an alkali charge of 3%, oxygen pressure of 0.5 MPa at 120 °C for 85 min, and with 0.05% AQ. In contrast to conventional oxygen delignification, the addition of AQ produced pulp with a higher yield, and it did not generate other negative impacts on pulp kappa number, viscosity, and brightness. The reaction mechanism of AQ in oxygen delignification was different from that in alkali pulping.

Keywords: Anthraquinone; Wheat straw; Oxygen delignification; Grey-based Taguchi method

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INTRODUCTION

Agricultural crop residues are considered an enormous underutilized energy resource with great potential to be feed for ruminants. Crop residues are also considered a great alternative to wood as a raw material for making pulp, chemicals, fuels, and energy (Theander 1985; Kamm and Kamm 2004; Kabel *et al.* 2007). As an inexpensive and abundant annually harvested agricultural byproduct, wheat straw has been widely used in the pulp and papermaking industry in China, accounting for half of China's produced pulp (Chen *et al.* 2010; Singh *et al.* 2011; China Paper Association 2012). It contains 14 to 15% lignin, 35 to 40% cellulose, and 30 to 35% hemicelluloses (Sun *et al.* 1995; Sun *et al.* 1998; Sun and Tomkinson 2002). Most of the lignin is removed during pulping, but there is a 2 to 5% residual lignin content that needs to be removed by bleaching (Bajpai 1999; Minor 1996; Sjostrom 1993). Chlorine-containing chemicals are very effective at reacting with the residual lignin, and therefore most bleaching techniques are chlorine-based, such as Cl_2 or ClO_2. In addition to chlorine-based chemicals, oxygen and oxygen-based chemicals are other delignifying agents used in industrial processes, *e.g.*, H_2O_2, ozone, and peroxide acids. Because it is environmentally-friendly and low cost, oxygen delignification has been used in ECF and TCF bleaching (Rodriguez *et al*. 2007). However, oxidation with oxygen is based on a free radical reaction. The rapid and uncontrollable reaction results in very poor selectivity. The residual lignin and also the carbohydrates are degraded, in particular at high temperature, which leads to deterioration in pulp yield and quality. Therefore, many attempts have been made to improve the efficiency and selectivity of oxygen delignification, such as the installation of capital-intensive two-stage or multi-stage oxygen delignification systems, application of additives, and pretreatment before bleaching (Chen and Lucia 2002; Diaz *et al.* 2006;

Gamelas *et al.* 2005; Ruuttunen and Vuorinen 2005; Shatalov *et al.* 2000; Sahab *et al.* 2008; Tran 2000; Weinstock *et al.* 1998; Yokoyama *et al.* 2004).

Anthraquinone (AQ) is an additive widely used in alkaline pulping (Falk *et al.* 1984; Parthasarathy *et al.* 1995), but rarely used in bleaching. In pulp cooking, AQ is initially reduced to anthrahydroquinone (AHQ), and then it reacts with quinonemethide (QM) intermediates of lignin, ultimately leading to a reductive splitting of the β-O-4 linkages. Since the oxidized end-group of polysaccharides is not susceptible to alkaline peeling reactions, AQ thus accelerates delignification and protects the polysaccharides. Ng *et al*. (2011) studied the effect of AQ towards H_2O_2-reinforced oxygen delignification on oil palm empty fruit bunch soda-AQ-pulp and found that H_2O_2 and AQ addition during the O-stage appeared to enhance bleaching effectiveness, without substantially impairing cellulose degradation. But the effect of AQ on the oxygen delignification without other reinforcing additives has not been studied systematically. Therefore, to minimize carbohydrate deterioration in oxygen delignification of non-woody pulp, adding AQ to the oxygen delignification system was attempted in the present study. Additionally, a grey-based Taguchi orthogonal array ($L_9(3^4)$) was designed to evaluate the impacts of alkali charge, oxygen pressure, maximum temperature, and holding time at maximum temperature during oxygen delignification with AQ on pulp yield, kappa number, intrinsic viscosity, and brightness. Finally, to better demonstrate the effects of AQ on oxygen delignification, a series of oxygen-delignified pulps treated for different times were obtained throughout the delignification process under optimal conditions. The variation of pulp characteristics during the whole oxygen delignification with AQ was investigated.

EXPERIMENTAL

Materials

Wheat straw soda pulp was provided by Quanlin Paper in Shandong, China. The kappa number, intrinsic viscosity, and brightness of the pulp were 23.1, 1081.0 mL/g, and 35.5% ISO, respectively. The pulp contained 59.6% glucan, 16.0% xylan, and 0.6% arabinan. The ash and silica contents of this wheat straw pulp were 11.1% and 8.0%, respectively.

Experimental Design

Based on the raw wheat straw soda pulp quality, which are the commonly used factors and levels in oxygen delignification of this kind of pulp, the oxygen delignification with AQ addition (O_{AQ}) of wheat straw soda pulp was conducted with four controllable 3-level factors and four performance characteristics. Optimization of process parameters is the key step in the Taguchi method, which is an efficient and systematic way for optimization so as to achieve high quality without increasing cost. It is a statistical method developed by Genichi Taguchi to improve the quality of manufactured goods. It is also applied in engineering, biotechnology (Rosa *et al.* 2009), marketing (Rao *et al.* 2008), and advertising (Selden 1997). A special design of orthogonal arrays was used to study the entire process parameter space with a small number of experiments. Therefore, nine experimental runs based on the orthogonal array $L_9(3^4)$ were required as shown in Table 1. Each run was conducted twice.

Oxygen Delignification

Twenty grams of wheat straw fibers (o. d. basis) were mixed with NaOH, H_2O, AQ, and $MgSO_4$ in sealed plastic bags and transferred to a 1.5 L stainless steel autoclave equipped with a gas inlet. Then the air was replaced in the autoclave by oxygen to a predetermined pressure. After that, the 1.5 L stainless steel autoclave was placed into a 15 L rotary electric digester containing water (as a water-bath) to heat the 1.5 L stainless steel autoclave to the target temperature. The maximum temperature was held for the appointed time. After delignification, the pulp was washed with tap water, dewatered in a centrifuge, homogenized, and placed in sealed plastic bags to balance water for further analysis. The conventional oxygen delignification (O) was also conducted as the same steps of O_{AQ} but without AQ addition.

Pulp Properties

The pulp samples were analyzed by the TAPPI method T-236 om-99, T-203 cm-99, T-211 om-93, and T-245 cm-98 to establish pulp kappa number, α-cellulose, ash, and silica content, respectively. Intrinsic viscosity was determined by SCAN-CM 15:88, and brightness was measured according to ISO 2470. Sugars content was calculated by Laboratory Analytical Procedures from National Renewable Energy Laboratory (NREL) (Sluiter *et al*. 2008).

Table 1. O_{AQ} – Stage of Wheat Straw Soda Pulp: Effect of Four 3-level Factors on Pulp Characteristics using Taguchi Experimental Design ($L_9(3^4)$)

No.			1	2	3	4	5	6	7	8	9
Four controllable 3-level factors*	A (%)		2	2	2	3	3	3	4	4	4
	B (MPa)		0.3	0.5	0.7	0.3	0.5	0.7	0.3	0.5	0.7
	C (°C)		90	105	120	105	120	90	120	90	105
	D (min)		60	85	110	110	60	85	85	110	60
Experimental Results	Yield (%)	1	83.0	85.9	88.0	85.9	87.8	85.9	81.3	87.3	83.8
		2	83.5	85.6	87.4	86.2	88.1	86.3	81.4	86.9	84.1
	Kappa number	1	17.3	12.7	11.0	11.1	9.4	12.5	7.6	12.4	9.5
		2	17.9	13.1	9.7	9.9	9.0	13.3	6.2	11.5	8.6
	Intrinsic viscosity (ml/g)	1	769.3	954.3	869.0	892.9	895.9	958.0	844.3	895.5	825.1
		2	745.2	941.2	888.2	918.1	909.7	937.0	828.3	911.6	914.8
	Brightness (% ISO)	1	37.3	45.0	48.8	47.1	49.0	42.8	54.0	43.7	48.6
		2	37.7	43.9	49.8	46.0	49.7	43.9	54.9	44.6	49.0
	Residual pH	1	11.8	10.6	9.3	11.2	10.7	12.6	10.7	12.9	12.4
		2	11.9	10.5	9.4	11.2	10.7	12.4	10.6	12.7	12.2
S/N ratio[a]	Yield		38.40	38.66	38.86	38.70	38.89	38.70	38.21	38.80	38.48
	Kappa number		-24.91	-22.22	-20.32	-20.45	-19.30	-22.18	-16.81	-21.56	-19.11
	Intrinsic viscosity		57.58	59.53	58.87	59.14	59.11	59.53	58.45	59.12	59.28
	Brightness		31.48	32.95	33.85	33.35	33.86	32.73	34.72	32.89	33.77

* The four controller factors of this O_{AQ} – stage of wheat straw soda pulp were A (alkali charge (odp, based on NaOH)),B (oxygen pressure), C (the maximum temperature), and D (holding time at the maximum temperature). The AQ and $MgSO_4$ amounts both were constant with 0.05% (odp), and the pulp concentration was maintained at 20%.

[a] S/N ratio was the signal to noise ratio. In this experiment, the S/N ratio of pulp yield, intrinsic viscosity and brightness were all the higher the better, but the S/N ratio of kappa number is the lower the better.

RESULTS AND DISCUSSION

Determination of Optimal O_{AQ} Parameters

In this section, the use of the orthogonal array with the grey relational analysis for determining the optimal O_{AQ} parameters is reported step-by-step. Optimal parameters with considerations of multiple performance characteristics (pulp yield, kappa number, intrinsic viscosity, and brightness) were obtained and verified.

Orthogonal array experiment and grey relational analysis

The orthogonal experiment $L_9(3^4)$ was conducted, and the results are shown in Table 1. A loss function was defined to calculate the deviation between the experimental value and the desired value. Taguchi recommends the use of the loss function to measure the performance characteristic deviation if further transformed into a signal-to-noise (S/N) ratio. Usually, there are three categories of performance characteristics in the analysis of the S/N ratio. That is, the lower the better (LB), the higher the better (HB), and the more nominal the better (NB) (Kuo and Su 2006; Kuo *et al.* 2007; Mavruz and Ogulata 2010). In this experiment, the S/N ratio of the pulp yield, intrinsic viscosity, and brightness were all calculated by the higher the better (HB) characteristic. However, a minimal kappa number was required, so that the S/N ratio of kappa number was calculated by the lower the better (LB) characteristic. The S/N ratio of these four quality characteristics and the mean S/N ratio of the i^{th} level of factor F can be calculated by Eq. (1) and Eq. (2), where y refers to the measurement value, n refers to the total number of measurements (n = 2), m is the number of level i in the orthogonal array factor column, and y_i is the S/N ratio produced on each i level row.

$$\begin{aligned} &\mathrm{HB}: \eta = -10\log(1/n\textstyle\sum y^{-2}) \\ &\mathrm{LB}: \eta = -10\log(1/n\textstyle\sum y^{2}) \end{aligned} \tag{1}$$

$$\bar{F}_i = \frac{1}{m}\sum_{j=1}^{m} y_{ij} \tag{2}$$

The S/N ratios of O_{AQ} for each performance characteristic are also shown in Table 1. The average S/N values obtained for each experiment are presented in Table 2 for pulp yield, kappa number, intrinsic viscosity, and brightness. Regardless of the category of the performance characteristic, a larger S/N ratio corresponded to better performance, and ΔF was the main effect of each factor on each characteristic. As indicated in Table 2, among these four factors, ΔF_Y of B (oxygen pressure) on pulp yield was 0.34, which was higher than that of A (alkali charge), C (maximum temperature), and D (holding time). Those values were 0.27, 0.04, and 0.25, respectively, indicating that B was the most important factor affecting pulp yield. The increase of B improved the dissolution of oxygen in alkali liquor, and then generated more hydroperoxy and hydroxyl radicals. These radicals not only reacted with lignin, but also degraded cellulose and hemicelluloses, resulting in a decline in pulp yield. The ΔF_{Kn} of A, B, C, and D were 3.32, 0.49, 4.07, and 0.70, respectively. Thus, C and A had a much greater effect on the kappa number of delignified pulp after O_{AQ}, and B had little impact on the pulp kappa number. As is well known, high temperature and the presence of alkali result in ionization of lignin-free phenolic hydroxyl groups and promote a reaction with oxygen, forming soluble acidic degradation lignin products (Duarte *et al.* 2001). Therefore, a high temperature and sufficient alkali should be employed in the O_{AQ} process. The ΔF_V of B was 0.86, in contrast to A, C, and D (0.60, 0.52, and 0.51, respectively), which revealed that B affected pulp intrinsic viscosity significantly. As mentioned above, an increase of B, A, C, and D could lead to more extensive degradation of lignin, which could increase the proportion of cellulose, improving the intrinsic viscosity. If these parameters increased excessively, the carbohydrates would degrade rapidly. In addition, C was of greater significance to the pulp brightness than the other three characteristics. Its ΔF_B was 1.77. A, D, and B followed with values of 1.03, 0.43, and 0.27. D and B showed relatively insignificant effects on pulp brightness.

Table 2. Average Signal to Noise Ratio (S/N) of $L_9(3^4)$ for Each Pulp Characteristic after O_{AQ}

		Average S/N[b]			
		Alkali charge	Oxygen pressure	Maximum temperature	Holding time
		A	B	C	D
Yield	Level 1	38.64	38.44	38.63	38.59
	Level 2	38.76	38.78	38.61	38.53
	Level 3	38.49	38.68	38.65	38.78
	ΔF_Y[a]	0.27	0.34	0.04	0.25
Kappa number	Level 1	-22.48	-20.72	-22.88	-21.10
	Level 2	-20.64	-21.03	-20.59	-20.40
	Level 3	-19.16	-20.54	-18.81	-20.78
	ΔF_{Kn}[a]	3.32	0.49	4.07	0.70
Intrinsic viscosity	Level 1	58.66	58.39	58.80	58.66
	Level 2	59.26	59.25	59.32	59.17
	Level 3	58.95	59.23	58.81	59.04
	ΔF_V[a]	0.60	0.86	0.52	0.51
Brightness	Level 1	32.76	33.18	32.37	33.04
	Level 2	33.32	33.24	33.36	33.47
	Level 3	33.79	33.45	34.14	33.37
	ΔF_B[a]	1.03	0.27	1.77	0.43

[a] ΔF was the subtraction of the maximum and the minimum average S/N of the corresponding pulp characteristic. The higher the ΔF, the greater the impact of the factor on this pulp characteristic.
[b] Average S/N ratio was the mean signal to noise ratio of the i^{th} level of factor A, B, C or D. And a larger average S/N ratio corresponded to better performance.

As previously stated, a larger S/N ratio corresponds to a better performance characteristic. Therefore, optimal levels of the process parameters were the levels with the highest S/N ratio. However, optimization of the four oxygen-delignified pulp characteristics was not straightforward, like optimization of a single performance characteristic. A higher S/N ratio for one performance characteristic might correspond to a lower S/N ratio for another performance characteristic. As a result, the overall evaluation of the S/N ratio was required for the optimization of multiple performance characteristics. To solve this problem, the grey relational analysis was adopted.

In the grey relational analysis, data preprocessing was first performed in order to normalize the raw data for analysis. The linear normalization of the experimental results for O_{AQ} pulp yield, kappa number, intrinsic viscosity, and brightness, shown in Table 1, was performed in the range between 0 and 1, which was also called the grey relational generating. The normalized experimental results x_{ij} could be calculated by Eq. (3), where y_{ij} stands for the i^{th} experimental results in the j^{th} experiment. The results are shown in Table 3. Basically, a larger normalized result corresponds to better performance, and the best normalized results should be equal to one.

$$x_{ij} = \frac{y_{ij} - \min y_{ij}}{\max y_{ij} - \min y_{ij}} \tag{3}$$

Next, the grey relational coefficient was calculated to express the relationship between the ideal and actual normalized experimental results. The grey relational coefficient ξ_{ij} can be expressed as Eq. (4), where x_i^o is the ideal normalized result for the i^{th} performance characteristic and ζ is the distinguishing coefficient, which was defined in the range $0 \leq \zeta \leq 1$.

$$\xi_{ij} = \frac{\min\min\left|x_i^0 - x_{ij}\right| + \zeta \max\max\left|x_i^0 - x_{ij}\right|}{\left|x_i^0 - x_{ij}\right| + \zeta \max\max\left|x_i^0 - x_{ij}\right|} \tag{4}$$

Next, the grey relational grade was computed by averaging the gray relational coefficient corresponding to each performance characteristic. The overall evaluation of the multiple performance characteristics was based on the grey relational grade, which can be determined via Eq. (5), where γ_j is the grey relational grade for the j^{th} experiment and m is the number of performance characteristics. The results are also listed in Table 3. A higher grey relational grade means that the corresponding experimental result is closer to the ideally normalized value. Experiment No. 5 had the best multiple performance characteristics among the 9 experiments because of having the highest grey relational grade (0.693), as shown in Table 3. In other words, optimization of the complicated multiple performance characteristics can be converted into optimization of a single grey relational grade.

$$\gamma_j = \frac{1}{m}\sum_{i=1}^{m}\xi_{ij} \tag{5}$$

Table 3. Data Preprocessing and Grey Relational Grade for each Experiment of $L_9(3^4)$

No.		1	2	3	4	5	6	7	8	9
Normalized results	Yield	0.71	0.33	0.05	0.28	0.00	0.27	1.00	0.14	0.60
	Kappa number	0.00	0.33	0.57	0.55	0.69	0.34	1.00	0.41	0.72
	Intrinsic viscosity	1.00	0.00	0.34	0.20	0.22	0.00	0.56	0.21	0.13
	Brightness	1.00	0.54	0.27	0.42	0.26	0.61	0.00	0.56	0.29
Grey relational coefficient	Yield	0.413	0.602	0.918	0.639	1.000	0.647	0.333	0.784	0.453
	Kappa number	1.000	0.601	0.469	0.476	0.419	0.598	0.333	0.547	0.411
	Intrinsic viscosity	0.333	1.000	0.597	0.710	0.698	0.997	0.473	0.701	0.791
	Brightness	0.333	0.479	0.652	0.543	0.655	0.450	1.000	0.470	0.631
Grey relational grade		0.520	0.670	0.659	0.592	0.693	0.673	0.535	0.626	0.571

It was then possible to separate the effect of each parameter on the grey relational grade at different levels. The average of the grey relational grade for each parameter level can be computed, and all the results were summarized and shown in Fig. 1. Basically, the larger the grey relational grade, the better the multiple performance characteristics. The optimal parameters combination was A2B2C3D2, which obtained the highest grey relational grade. This means that the O_{AQ} pulp with the highest pulp yield, intrinsic viscosity, brightness, and lowest kappa number could be obtained under these optimal Q_{AQ} conditions. Among these four parameters, the order of relative importance affecting pulp characteristics was B > A > D > C, which could be acquired from the ΔG of four factors.

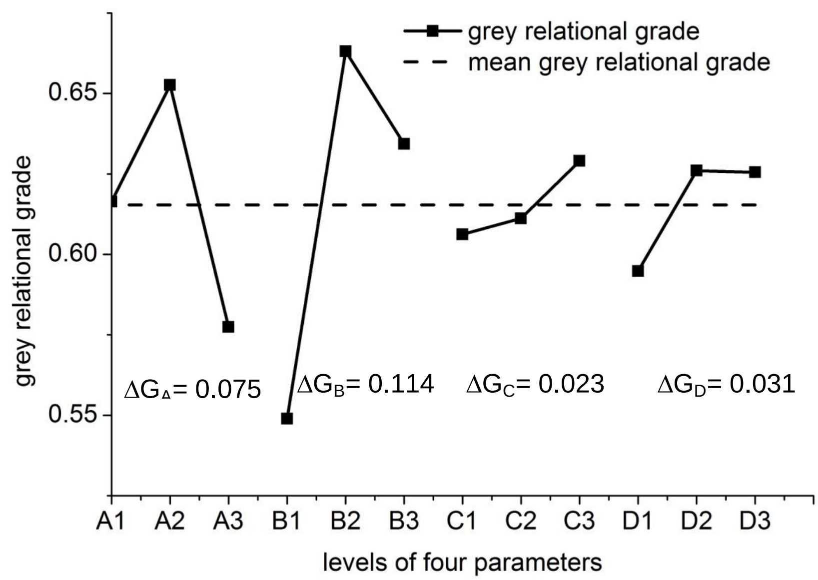

Fig. 1. Grey relational grade graph of $L_9(3^4)$
* A, B, C, and D are alkali charge, oxygen pressure, maximum temperature, and holding time at maximum temperature, respectively. 1, 2, and 3 mean the three levels of these four factors. The dashed line is the total mean value of the grey relational grade (0.615). ΔG was the effect of each parameter on the grey relational grade and it was the subtraction of the maximum and minimum grey relational grade of each factor.
Total mean value of the grey relational grade of the $L_9(3^4)$ = 0.615
Predicted grey relational grade using the optimal O_{AQ} parameters = 0.724

Analysis of variance

The purpose of variance (ANOVA) analysis was to investigate the influence of O_{AQ} parameters on the performance characteristics. This was accomplished by separating the total variability of the grey relational grades, which was measured by the sum of the squared deviations from the total mean of the grey relational grade, into contributions by each parameter and the error. First, the total sum of the squared deviations (SS_T) from the total mean of the grey relational grade (γ_m) could be calculated by Eq. 6, where p is the number of experiments in the orthogonal array and γ_j is the mean of the grey relational grade for the j^{th} experiment.

$$SS_T = \sum_{j=1}^{p} \left(\gamma_j - \gamma_m\right)^2 \tag{6}$$

The total sum of the squared deviations (SS_T) was separated into two sources: the sum of the squared deviations (SS_d) due to each O_{AQ} parameter and the sum of the squared error (SS_e). The percentage contribution by each of the parameters in the total sum of the squared deviations (SS_T) could be used to evaluate the importance of the O_{AQ} parameter change on the performance characteristic. In addition, Fisher's F-test (IIo *et al.* 2012) could also be used to determine which parameter had a significant effect on the performance characteristics. Usually, a change of the parameter has a significant effect on the performance characteristics when F is large.

ANOVA results (Table 4) indicated that B was the most important O_{AQ} parameter affecting the multiple performance characteristics. The second one was A, followed by C and D. Based on the above discussion, the optimal parameters were A2B2C3D2, which was the same as those obtained in grey relational grade analysis.

Table 4. Variance Analysis Results of $L_9(3^4)$

Symbol	Oxygen delignification parameters	Degree of freedom	Sum of square	Mean square	F	Contribution (%)
A	Alkali charge	2	0.009	0.004	9.885	26.19
B	Oxygen pressure	2	0.021	0.011	24.620	65.23
C	Maximum temperature	2	0.001	-	-	2.65
D	Holding time	2	0.002	0.001	2.237	5.93
	Error	2	0.0009	0.0004		
	Total	8				

Conformation tests

Once the optimal levels of the O_{AQ} parameters were selected, the final step was to predict and verify the improvement of the performance characteristics using the optimal level of the parameters. The estimated grey relational grade using the optimal O_{AQ} parameters can be calculated according to Eq. (7), where γ_m is the total mean of the grey relational grade of $L_9(3^4)$, $\overline{\gamma}$ is the mean of the grey relational grade at the optimal level, and q is the number of O_{AQ} parameters that significantly affects the multiple performance characteristics.

$$\widehat{\gamma} = \gamma_m + \sum_{i=1}^{q}(\overline{\gamma} + \gamma_m) \tag{7}$$

Using this equation, the predicted grey relational grade using the optimal O_{AQ} parameters was then obtained, and shown in Fig. 1. A confirmation experiment was performed using the optimal O_{AQ} parameters, and the results obtained are shown in Table 5. Meanwhile, the O-stage was also conducted under the same experimental conditions to the optimal O_{AQ}-stage (0.3% alkali charge with 0.5 MPa oxygen pressure at 120°C for 85 min)), but just without AQ addition. The grey relational grade of the confirmation experiment was 0.707, which was close to predicted grey relational grade (0.724). Most importantly, it was higher than the largest grey relational grade (0.693, experiment No. 5 in Table 3) in the $L_9(3^4)$ experiments. It was clearly shown that the multiple performance characteristics in the O_{AQ} process were greatly improved by this study and the results of the confirmation test were better than those presented in Table 1.

Table 5. The Results of the Confirmation Test in Optimal Conditions

Pulp Properties	Yield (%)	Kappa number	Intrinsic Viscosity (mL/g)	Brightness (% ISO)	Grey Relational Grade
O_{AQ}[a]	87.6 ± 0.2	8.8 ± 0.2	912.5 ± 4.9	51.5 ± 0.4	0.707
O[b]	85.4 ± 0.3	8.9 ± 0.1	906.3 ± 8.8	52.2 ± 0.3	0.626
No.	Ash (%)	Glucan (%)	Xylan (%)	Araban (%)	
O_{AQ}[a]	7.1 ± 0.1	63.0 ± 0.1	16.4 ± 0.3	0.9 ± 0.1	
O[b]	7.1 ± 0.1	62.7 ± 0.2	15.7 ± 0.2	0.6 ± 0.1	

* Other conditions were constant with pulp concentration of 20% (odp), $MgSO_4$ amount of 0.5% (odp), and AQ amount of 0.05% (odp).
[a] oxygen delignification with 0.05% (odp) amount of AQ addition.
[b] conventional oxygen delignification without AQ addition.

As seen in Table 5, compared with O-stage, the pulp yield of the O_{AQ}-stage increased 2.2%. The glucan, xylan, and araban contents increased as well, but the kappa number, intrinsic viscosity, and brightness were close to the value obtained for O-stage. Therefore, the pulp obtained after O_{AQ} had the same kappa number as O-stage but higher yield, glucan, xylan, and araban contents. The intrinsic viscosity and brightness of pulp also remained at a high level.

Pulp Characteristics Variation of OAQ Wheat Straw Soda Pulp

The variation of pulp characteristics during O_{AQ} was investigated. As shown in Table 6, O_{AQ} and O were all conducted under the optimal conditions and the delignified pulps were obtained at different times. Their characteristics are presented in Fig 2 (a)-(f).

Table 6. Oxygen Delignification with Different Holding Times at the Maximum Temperature

No.	Alkali charge (%)	Oxygen pressure (MPa)	Maximum temperature (°C)	Holding time/reaction time (min)
1	3	0.5	105	0/40
2	3	0.5	120	0/52
3	3	0.5	120	30/82
4	3	0.5	120	60/112
5	3	0.5	120	90/142
6	3	0.5	120	120/172

* Other conditions were constant with pulp concentration of 20% (odp), $MgSO_4$ amount of 0.5% (odp), and AQ amount of 0.05% (odp) in O_{AQ}

In Fig. 2, the pulp yield, kappa number, viscosity, holocellulose, and α-cellulose decreased, while brightness increased with reaction time, which were caused by delignification and carbohydrate degradation throughout the whole process. The process can be divided into three stages. During the initial stage (0 to 40 min), as the temperature was raised from room temperature to 105 °C, the pulp kappa number decreased from 23.1 to 18.3 (O) and 17.2 (O_{AQ}), and the holocellulose dropped slightly from 82.6% to 81.0% (O) and 82.4% (O_{AQ}). These results mean that a higher temperature, higher oxygen pressure, and greater alkali charge could lead to faster delignification, followed by slight degradation of carbohydrate, which also resulted in an increase of brightness and elevation of intrinsic viscosity. However, the degradation of carbohydrate during O_{AQ} was milder than O. In the second stage (40 to 115 min), the pulp yield, kappa number, intrinsic viscosity, holocellulose, and α-cellulose contents decreased dramatically and the pulp brightness rose significantly. These findings indicated that the rise of temperature and extension of reaction time promoted the severe degradation of lignin and carbohydrate. The degradation of lignin and carbohydrate in the first two stages consumed most of the alkali. There were also substantial acid substances generated that came from the alkaline degradation of carbohydrate, ester bonds broken between lignin and carbohydrate, and the hydrolyzation of uronic acid substitutions and acetyl groups on hemicelluloses, so the pH decreased dramatically in the first two stages. In the last stage (115 to 175 min), almost all the residual lignin consisted of nonphenolic lignin units that cannot be removed in an oxygen delignification process. Additionally, there was not enough alkali in these oxygen delignification systems to react with the residual lignin and carbohydrate. Hence, the pulp characterizations did not vary greatly in the last stage, although the reaction time was prolonged.

It was interesting that the pulp yield, holocellulose, and α-cellulose of the six O_{AQ} pulps were higher than the corresponding values for the six O pulps. On the other hand, the kappa number and intrinsic viscosity were close in value at the same reaction time. AQ in oxygen delignification could protect the carbohydrate, but it did not enhance delignification. Generally, the catalytic effects of AQ in alkaline pulping are reasonably well understood as a result of extensive research conducted by numerous investigations. AQ can enhance carbohydrate stabilization and the pulp yield, and the AHQ intermediate generated in the process can enhance delignification, leading to a decrease in kappa number (Falk *et al.* 1984; Parthasarathy *et al.* 1995). However, the addition of AQ during oxygen delignification improved the pulp yield, but it did not enhance delignification, which is different from what has been observed in alkaline digesting. In O_{AQ}, AQ is reduced to AHQ through oxidation of the cellulose or hemicelluloses-reducing end group, and the pulp yield improves. AHQ may be readily oxidized in the presence of strong oxidants, especially hydroxyl radicals (OH·) generated through a step-wise reduction of oxygen. Hence, the added AQ in the system might act as a hydroxyl radical scavenger and reduce cellulose or hemicelluloses degradation as a result of the ability of the hydroxyl radical to attack both lignin and cellulose unselectively. Thus, the positive effect of AQ on delignification was diminished. The oxidation of cellulose-reducing end groups by AQ to alkali-stable aldonic acid groups will also retard the further end group peeling reaction (Leh *et al.* 2008). The results indicated that AQ addition in oxygen delignification, even though it did not promote delignification, might counteract the negative effect on pulp yield.

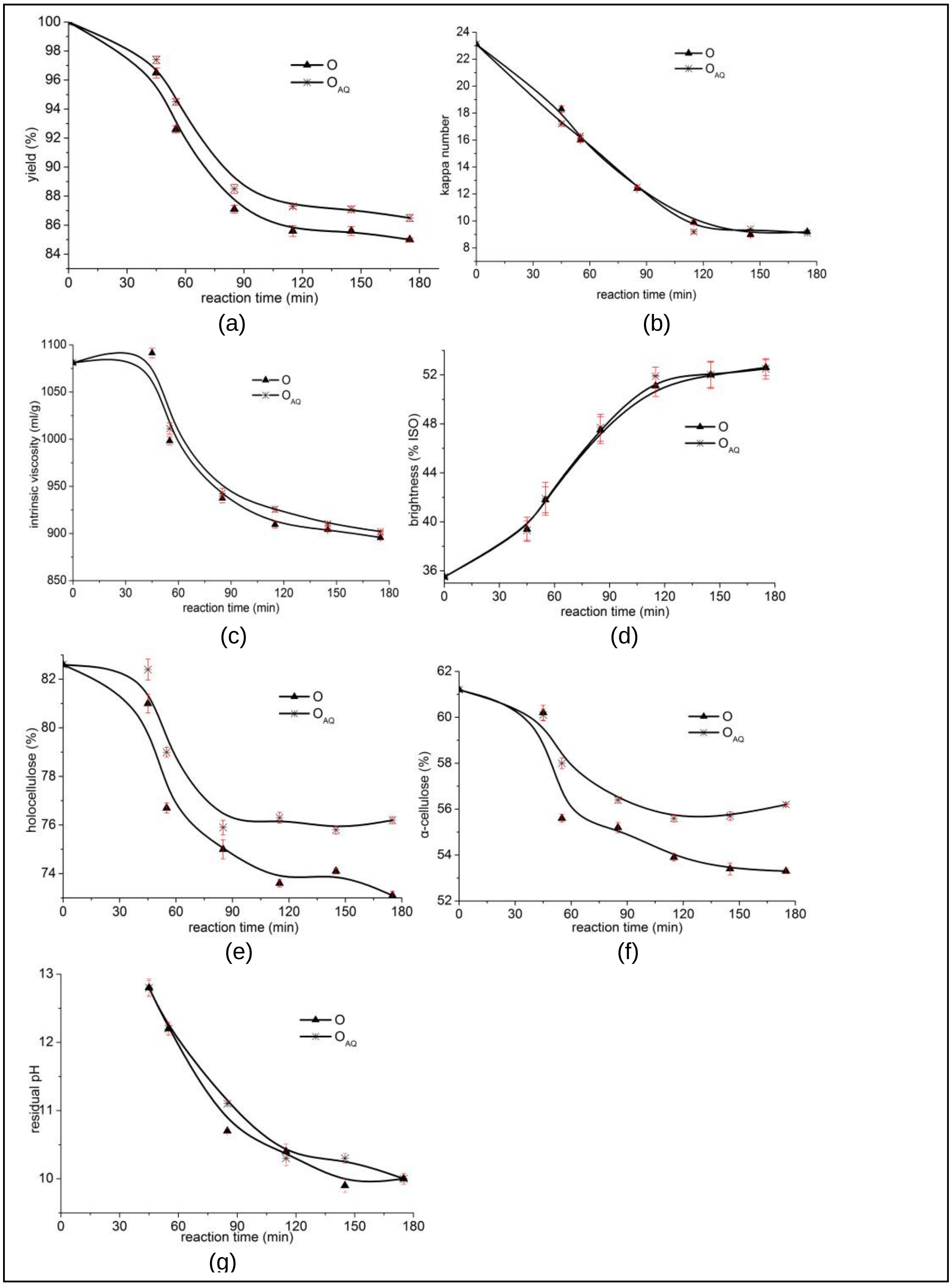

Fig. 2. The characteristics of oxygen-delignified pulp under optimal conditions with different reaction times

Note: O_{AQ} means oxygen delignification with 0.05% (odp) AQ addition; O means conventional oxygen delignification without AQ addition

CONCLUSIONS

1. The effects of four factors on an oxygen-anthraquinone stage (O_{AQ}) for bleaching of wheat straw soda pulp and the optimal parameters were determined using the Taguchi method with grey relational analysis. Oxygen pressure had the greatest impact on pulp yield and viscosity but little impact on kappa number and brightness. While the maximum temperature had a marked effect on kappa number and brightness, it had little effect on yield. In addition, holding time at the maximum temperature had little effect on intrinsic viscosity.
2. Compared with an oxygen stage (O), the pulp yield of O_{AQ} increased by 2.2%, while the kappa number, intrinsic viscosity, and brightness were close to O when the raw pulp was treated by 3% alkali charge with 0.5 MPa oxygen pressure at 120 °C for 85 min.
3. In O_{AQ}, anthraquinone (AQ) might act as a hydroxyl radical scavenger and reduce cellulose or hemicelluloses degradation because a hydroxyl radical is able to attack both lignin and cellulose unselectively. Hence, the addition of AQ during oxygen delignification could improve the pulp yield, but not enhance delignification, which was different from the effect of AQ addition in alkaline digesting.

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