APPLICATION OF POLYOXOMETALATE IN HYDROGEN PEROXIDE BLEACHING UNDER ACIDIC CONDITIONS

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The modified bleaching sequence $O_PA_PP_O$ from short-sequence bleaching OAP and OQP was studied in an effort to achieve higher quality straw pulp (with brightness 84.5% and acceptable viscosity 669 mL/g), which will be appropriate for more situations than straw pulp as presently produced. Though the O_P and P_O stages are recognized as the key processes used to increase the pulp's brightness, addition of hydrogen peroxide in acid pretreatment with polyoxometalate (POM) as catalyst (A_P stage) was mainly considered in this work. Phosphomolybdic acid was applied to improve straw pulp's brightness, which was 4.8% ISO higher than the pulp treated without POM. The optimum conditions of the A_P stage were: initial pH value 3, temperature 90 °C, H_2O_2 1.5%, and phosphomolybdic acid 1.0%. Comparison of the sequences O_PQP_O, O_PAP_O, and $O_PA_PP_O$ showed that the brightness of pulp bleached by $O_PA_PP_O$ was 2% and 4.7% higher than the same pulp subjected to O_PAP_O and O_PQP_O sequences, respectively. Four lignin samples (LO_P, LO_PA, LO_PA_P, $LO_PA_PP_O$) were characterized by ^{31}P NMR spectroscopy. The spectroscopic investigation showed that in LO_PA and LO_PA_P, aliphatic hydroxyls, *p*-coumaryl units, and guaiacyl phenol moieties were degraded when compared with that in LO_P. In $LO_PA_PP_O$, all these aliphatic hydroxyls and guaiacyl phenols had been destroyed and carboxylic acid functionalities increased.

Keywords: Straw pulp; Polyoxometalate; Phosphomolybdic acid; Hydrogen peroxide bleaching

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INTRODUCTION

In recent years the Chinese paper manufacturing industry has been notably improved. However, because of a shortage of wood, non-woody materials such as annual plants (cereal straw, bagasse, bamboo, reed, flax, etc.) have received increasing attention. Concern has been expressed related to severe environmental damage created when non-woody materials have been treated with traditional pulping and paper making techniques before the 1990s (Sun and Tomkinson 2001). So the elemental chlorine free (ECF) and totally chlorine free (TCF) bleaching sequences are employed popularly in non-woody pulp bleaching to reduce COD (chemical oxygen demands) and AOX (absorbable organic halides) contents of the effluent. Due to the capital cost savings related to ClO_2 production and the avoidance of organochloride, the short-sequence bleaching sequences OAP and OQP are being widely applied in Chinese pulp mills. Preliminary pulp acid

treatment (A), as well as chelation (Q) is considered to reduce the harm from transition metal ions before hydrogen peroxide bleaching. However, the wheat straw pulp's brightness after OAP and OQP sequences still cannot reach the high standard of 85% ISO in many Chinese mills (more often reaching 70% to 80% ISO brightness), which limits the range of applications of straw pulp. Three-stage treatment $O_PA_PP_O$ according to the sequences (a) oxygen delignification with hydrogen peroxide (O_P stage), (b) addition of hydrogen peroxide in sulfuric acid pretreatment and POM as catalyst (A_P stage), and (c) oxygen pressurized hydrogen peroxide bleaching (P_O stage), was studied to achieve higher quality straw pulp (with high brightness 84.5% ISO and an acceptable viscosity of 669 mL/g).

Wójciak (2004) pointed out that hydrogen peroxide in acidic medium/alkaline medium (Pac/P) could bring advantageous effects in comparison to Pac/E. Yield values exceeding 97% were obtained. The pulp brightness was relatively high, and the viscosity results were improved. This means that the proposed stage can be useful for the bleaching sequence.

Wójciak thought that the brightness of the pulp obtained from OPac/P was 2% and 4% lower than those of the same pulps according to OAP and OQP schemes, respectively. However, little research has been conducted in applying POM as catalyst in $O_PA_PP_O$ to highly delignified pulp. The protection related to Mg^{2+} (Wójciak 2002), and catalysts Cr^{3+} and Cu^{2+} (Wójciak 2004) were studied in Wójciak's research.

The α-Keggin type polyoxometalates (POMs) were originally proposed as catalysts for oxygen delignification about a decade ago. In particular, POMs with molybdenum to activate hydrogen peroxide bleaching have been shown to be efficient for the delignification of pulps by some researchers (Eckert 1982; Jäkärä et al. 1995; Kubelka et al. 1992; Rabelo et al. 2008). The catalysis of POMs is based on the concept that they react selectively with phenolic lignin structures in lignocellulosic fibers and can sometimes be regenerated by re-oxidation with molecular oxygen (Weinstock et al. 1994 1997). Although POMs have been investigated for a long period, they have not yet been applied in the pulp industry (Kang et al. 1997). Difficulties in the POM re-oxidation, in particular of those POMs that have shown to be the most selective for the delignification, are important limitations to consider (Gamelas et al. 2005, 2007). Moreover, the pH of bleaching has been another important factor to explain the limited usage of POMs in industry. In general, α-Keggin type POMs are stable and effective under acidic conditions. For instance, it was reported that $Na_5H_4[PV_6Mo_6O_{40}]$ was not stable at a pH value of higher than 4 (Ruuttunen and Vuorinen 2007). However, oxygen delignification and hydrogen peroxide bleaching are usually performed under alkaline conditions. By contrast, under acidic conditions both oxygen and hydrogen peroxide have limited reactivity toward lignin in pulp. POMs have been widely used in the O stage under acidic conditions, but often they have not been shown to be more effective to remove residual lignin than conventional oxygen-alkaline process. So we gave up on the use of POM in the O_P stage. But it is still worth considering application of POM in hydrogen peroxide bleaching under acidic conditions, for reaction with chromophoric groups in lignin. That is the focus of the present article. Therefore, POMs as catalysts were not used in the oxygen delignification stage, but in an A_P stage.

The sequences O_PQP_O, O_PAP_O, $O_PA_PP_O$ were compared to illustrate the efficiency of $O_PA_PP_O$. In order to reveal the chemical features, the lignin isolated from the pulps obtained after O_P, O_PA, O_PA_P, $O_PA_PP_O$ (LO_P, LO_PA, LO_PA_P, $LO_PA_PP_O$) were characterized by means of ^{31}P NMR spectroscopy (Salanti et al. 2010).

MATERIALS AND METHODS

Soda-AQ Pulping

Soda-AQ straw pulp was cooked by us with the wheat straw obtained from a mill in Hebei province, China. The brown pulp parameters were kappa number 12.6, brightness 33.8% ISO, and viscosity 1076 mL/g (conditions of NaOH charge 17%, AQ charge 0.1% vs. oven-dry wheat straw, liquor-chips ratio 5:1, maximum temperature 165 °C, heating time 60 min, and time at the maximum temperature 30 min).

Pulp Bleaching Procedure

Oxygen delignification with hydrogen peroxide (O_P stage)

The following initial conditions of O_P stage bleaching were defined: oxygen pressure 0.55 MPa, NaOH charge 4%, H_2O_2 1%, $MgSO_4$ 0.1%, Na_2SiO_3 1%, $EDTANa_2$ 0.1% vs. o.d. pulp, pulp consistency 12%, treatment time 2 h, and temperature 120 °C. Pulp treatment was conducted in a 3 L oxygen bleaching tank. At the end of the reaction, the tank pressure was reduced to atmospheric level, and the pulp was collected in a bag and washed with tap water.

Under the given conditions, wheat straw pulp after the O_P stage had kappa number 3.6, brightness 65.0% ISO, and viscosity 907 mL/g.

Sulfuric acid pretreatment (A)

Acid pretreatment was carried out for 1 h at 80 °C, pH 3, and 4% pulp consistency.

Chelation (Q)

Oxygen-delignified pulp was chelated for 1 h at 80 °C, using DTPA (diethylene-triaminepentaacetic acid) at an addition level of 0.4% vs. oven-dry pulp mass, pH 4, and 4% pulp consistency.

Sulfuric acid pretreatment with hydrogen peroxide and POM (A_P stage)

The reaction time of the A_P stage was 1h, and a pulp consistency of 4% was used. Investigations on the A_P stage were made with four independent variables (initial pH value, temperature, charges of hydrogen peroxide and POM, and types of POM). (1) Pulp treatments were carried out at the following levels of pH 2.0, 3.0, 4.0, 5.0, and 6.0, with temperature 60 °C, H_2O_2 2%, and phosphomolybdic acid 1%. (2) Reactions were performed at pH 3.0 with variable temperature (60, 70, 80, and 90 °C). (3) The pulps were bleached with hydrogen peroxide charge (1.0%, 1.5%, and 2.0%) at variable phosphomolybdic acid charge (0.5%, 0.8%, and 1.0%) with pH 3.0, and temperature 90 °C. (4) The influences of different POMs as catalysts were compared. Three POMs (silicontunstic acid $H_4[Si(W_3O_{10})_4]$, phosphtunstic acid $H_3[P(W_3O_{10})_4]$, and phospho-

molybdic acid $H_3[P(Mo_3O_{10})_4])$ were evaluated with POM's charge 1%, hydrogen peroxide 1.5%, temperature 90 °C, and an initial pH of 3.

Acid pretreatment (A), chelation (Q), and the A_P stage treatment were carried out in polyethylene bags in a water bath for temperature control.

Oxygen pressurized hydrogen peroxide bleaching (P_O stage)

The following conditions of the P_O stage were defined: oxygen pressure 0.5 MPa, NaOH charge 2.5%, H_2O_2 5%, $MgSO_4$ 0.1%, Na_2SiO_3 1% vs. o.d. pulp, pulp consistency 10%, treatment time 2 h, and temperature 120 °C.

Analysis

The pH value was determined with a DELTA 320 pH meter at a temperature of 22 °C. The pulps were characterized in terms of kappa number, brightness, and viscosity, which were determined according to GB/T 1546-2004 (same as ISO 2470), GB/T 7974-2002 (same as TAPPI UM 246), and GB/T 15480-2004 (same as ISO 5351/1), respectively.

^{31}P NMR Analysis

The four lignin samples (LO_P, LO_PA, LO_PA_P, and $LO_PA_PP_O$) were isolated by the enzymatic/acidolysis method (EMAL) (Wu and Argyropoulos 2003; Wang and Wu 2006; Yu et al. 2009). A solvent mixture composed of pyridine and deuterated chloroform in a 1.6/1 v/v ratio was prepared. Two solutions were then prepared by utilizing the solvent mixture, and chromium (III) acetylacetonate (3.6 mg/mL) and cyclohexanol (4.0 mg/mL) served as relaxation reagent and internal standard, respectively. Twenty-five milligrams of lignin was accurately weighed into a 1 mL volumetric flask. The lignin sample was then dissolved in 400 μL of the solvent mixture. Then, 75 μL of phosphorizing agent 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was added, followed by the internal standard and the relaxation solution(150 μL each). Finally, the solution was made up to the 1 mL mark with the solvent mixture. The flask was shaken to ensure thorough mixing. The clear solution of the flask was moved to the tube (Salanti, et al. 2010). ^{31}P NMR spectra were recorded on a Bruker 400 MHZ instrument. The content of hydroxyl (-OH) groups were calculated according to the following equation,

$$A = \frac{\dfrac{\rho \times 150 \times 10^{-6}}{100.16} \times \dfrac{A_2}{A_1}}{m} \times 1000 \qquad (1)$$

where A is the content of the group in the lignin sample, mmol/g; ρ is the consistency of cyclohexanol solution, mg/mL; and A_1 and A_2 are hydroxy (-OH) integration areas of cyclohexanol and the lignin sample, respectively. The denominator m is the weight of lignin sample, g. The number 150 μL and 100.16 g/mol were the volume and the molar mass of cyclohexanol, respectively.

RESULT AND DISCUSSION

Optimization of POM Effectiveness in the A_P stage

The aim of the investigation was to determine the influence of the initial pH value, temperature, peroxide charge, POM charge, and the type of POMs employed for the pulp treatment in the A_P stage.

Influence of initial pH in the A_P stage on the pulp's properties

It was found that decreasing the pH of the reaction medium could cause a significant brightness increase within the range of 6 to 3, but then brightness decreased at pH 2.
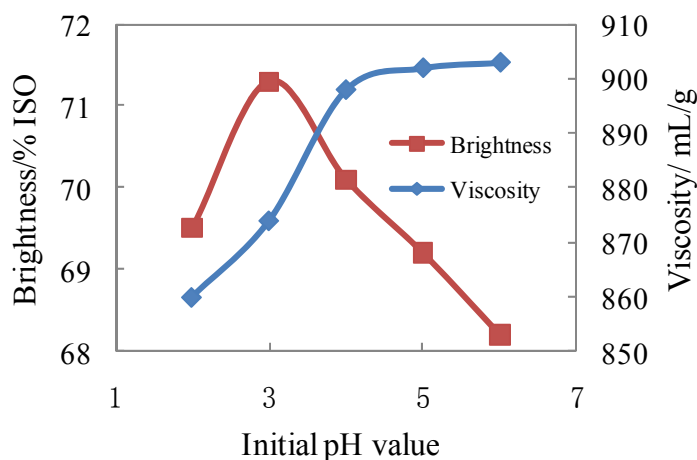

Fig. 1. Effect of initial pH in the A_P stage on pulp properties (Pulp treatment was carried out in such conditions at variable pH parameters: 2.0, 3.0, 4.0, 5.0, and 6.0, with temperature 60°C, H_2O_2 2%, and phosphomolybdic acid 1 %.)

As shown in Fig. 1, the decrease of initial pH value (from 6 to 3) led simultaneously to a reduction of viscosity, and an increase in brightness. For example, when the initial pH value decreased from 6 to 3, the viscosity decreased from 903 ml/g to 874 ml/g, and the brightness increased from 68.2% ISO to 71.3% ISO. However, when the initial pH was 2, compared to pH 3, the viscosity decreased, the brightness also decreased from 71.3% ISO to 69.5% ISO.

Rabelo et al. (2008) studied molybdenum catalyzed hydrogen peroxide bleaching (P_{Mo} stage) under acidic conditions). They reported that with increasing pH in the range of 1.5-5.5 the efficiency of bleaching decreased (kappa number and HexA group removal decreased). Although, in their research, the tendency of the brightness improvement was not significant, this effect can be used to explain why the brightness of the pulp in our work could be increased as the initial pH value decreased from 6 to 3. However, when the pH was 2, the brightness efficiency of hydrogen peroxide decreased with excessive inefficient decomposition of peroxide. The other possible reason was the fact that phosphomolybdic acid cannot work effectively at pH 2. Thus, an initial pH value 3 was considered to be optimum.

Influence of temperature in the A_P stage on the properties of the pulp

Temperature is an important factor during hydrogen peroxide bleaching. As shown in Fig. 2, when the bleaching temperature increased from 60 °C to 90 °C, the pulp's viscosity decreased from 874 mL/g to 836 mL/g, and the brightness increased from 71.3% ISO to 74.4% ISO. Because the reaction took place under constant pressure in a water bath, a temperature of 90 °C was suitable for the A_P stage.
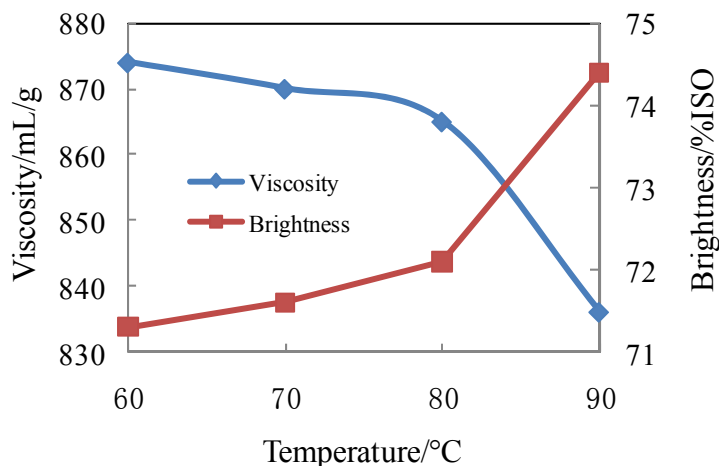

Fig. 2. Effect of temperature in A_P stage on pulp properties (Pulp treatment was carried out in such conditions at pH 3.0 with variable temperature 60, 70, 80 and 90°C, H_2O_2 2%, and phosphomolybdic acid 1 %)

Influence of dosage of H_2O_2 and phosphomolybdic acid in the A_P stage

Table 1. Pulp Properties under Variable Conditions in the A_P Stage (in pH 3, temperature 90°C)

H_2O_2 %	Phosphomolybdic acid %	Kappa number	Viscosity ml/g	Brightness % ISO
	0.5	2.5	899	72.9
1.0	0.8	2.4	882	73.2
	1.0	2.2	876	73.9
	0.5	2.4	898	73.9
1.5	0.8	2.1	865	74.4
	1.0	1.5	852	75.3
	0.5	2.3	895	73.8
2.0	0.8	2.2	864	74.1
	1.0	2.1	836	74.4

As shown in Table 1, using the same dosage of hydrogen peroxide, with the increasing charge of phosphomolybdic acid, the kappa number and the viscosity decreased, and the brightness increased. However, using the same dosage of phospho-

molybdic acid, the brightness of the pulp with H_2O_2 1.5% was higher than the pulps with H_2O_2 1.0% and H_2O_2 2.0%. In general, the kappa number and the viscosity of the pulp with H_2O_2 1.5% were lower than that with 1.0% H_2O_2 and 2.0% H_2O_2, respectively. The possible reason was that H_2O_2 at the 1.5% level and phosphomolybdic at the 1.0% level were a good combination at pH 3 and with a temperature of 90 °C. Therefore, the brightness of the pulp with 1.5% H_2O_2 and 1.0% phosphomolybdic acid was highest.

Influence of POMs in the A_P stage

The results with different POMs are presented in Table 2. Result No.1[#] was without any POM and 1.5% H_2O_2; No.2[#], No.3[#] and No.4[#] were with silicotungstic acid, phosphotungstic acid, and phosphomolybdic acid as POM catalyst, respectively, and H_2O_2 1.5%.

Table 2 shows that POMs as catalysts had a sharp influence on the A_P stage. The brightness of the pulp in No.2[#], 3[#], and 4[#] experiments was evidently higher than that obtained in the reference experiment No.1[#]. Phosphomolybdic acid as catalyst in the A_P stage could increase the brightness by 4.8% ISO relative to the same pulp treated in the absence of POM. The brightness of the pulp with experiment No.4[#] was the highest. It appeared that phosphomolybdic acid was the most effective of the three catalysts evaluated for the A_P stage.

Table 2. Pulp Properties with Different POMs in the A_P Stage
(in pH 3, temperature 90°C)

Test number		H_2O_2 %	POMs %	Kappa number	Viscosity ml/g	Brightness % ISO
1[#]	Hydrogen peroxide	1.5	-	3.1	899	70.5
2[#]	Silicotungstic acid	1.5	1	2.6	865	73.8
3[#]	Phosphotungstic acid	1.5	1	2.2	864	74.1
4[#]	Phosphomolybdic acid	1.5	1	1.5	852	75.3

Comparison of Sequences O_PQP_O, O_PAP_O, and $O_PA_PP_O$

It can be seen from Table 3 that chelation (Q) had no significant effect on either brightness or the delignification value, and it had very little effect on the degradation of cellulose. However, sulfuric acid pretreatment (A) contributed to the increase of pulp brightness and delignification value, with a slight degradation of cellulose. The presence of hydrogen peroxide and POM in acid pretreatment (A_P) had a significant effect on increasing the pulp brightness by about 10 units, reducing the kappa number by 2.1 units, and reducing the viscosity by 55 mL/g, in comparison to O_P stage. The results of the P_O stage showed the same tendency as the above-mentioned conclusion. Besides viscosity, which was 11 and 21 units lower, the brightness of $O_PA_PP_O$ was 2% and 4.7% higher than the same pulp according to O_PAP_O and O_PQP_O sequences, respectively. Though sequences O_PAP_O and O_PQP_O were practical bleaching sequences and used widely nowadays, they were not as efficient as $O_PA_PP_O$. The pulp after $O_PA_PP_O$ had a high brightness (84.5% ISO) and an acceptable viscosity (669 mL/g).

Table 3. Pulp Properties at Variable Stages

		Kappa number	Viscosity ml/g	Brightness % ISO
	O_P	3.6	907	65.0
$O_PA_PP_O$	O_PA_P	1.5	852	75.3
	$O_PA_PP_O$	1.4	669	84.5
O_PAP_O	O_PA	3.1	899	70.5
	O_PAP_O	2.4	680	82.5
O_PQP_O	O_PQ	3.6	900	65.6
	O_PQP_O	2.5	690	79.8

^{31}P NMR Spectroscopy

Four lignin samples (LO_P, LO_PA, LO_PA_P, and $LO_PA_PP_O$) were characterized by means of quantitative ^{31}P NMR spectroscopy. Figure 4, along with Table 4, shows that
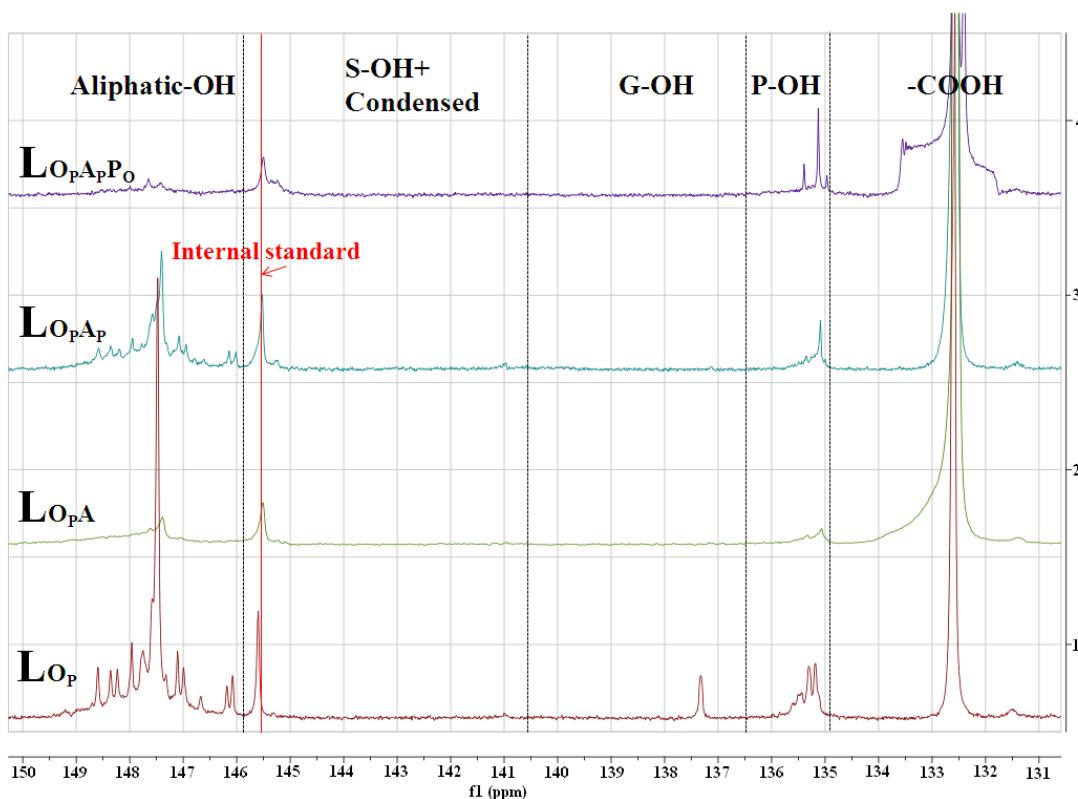

Fig. 4. Comparison among ^{31}P NMR spectroscopy of LO_P, LO_PA, LO_PA_P, $LO_PA_PP_O$ samples. Approximate integration ranges were included for aliphatic hydroxyls (Aliphatic-OH), syringyl and condensed phenolic units (S-OH+ Cond), guaiacyl phenol moieties (G-OH), *p*-coumaryl units (P-OH), and carboxylic acid functionalities (-COOH).

Table 4. Comparison by ^{31}P NMR Spectroscopy among LO_P, LO_PA, LO_PA_P, and $LO_PA_PP_O$ Samples

	Alphatic-OH mmol/g	S-OH+Condensed mmol/g	G-OH mmol/g	P-OH mmol/g	-COOH mmol/g
LO_P	2.861	0	0.0978	0.681	2.928
LO_PA	0.645	0	0	0.240	7.162
LO_PA_P	0.445	0	0	0.240	7.164
$LO_PA_PP_O$	0	0	0	0.240	9.812

wheat pulp lignin after O_P stage (LO_P) had a high content of aliphatic hydroxyls (Aliphatic-OH) and acid functionalities (-COOH), along with a few guaiacyl phenol moieties (G-OH). LO_PA and LO_PA_P, compared with LO_P, aliphatic hydroxyls (aliphatic-OH), *p*-coumary units (P-OH) and guaiacyl phenol moieties (G-OH) were degraded, and carboxylic acid functionalities were increased. Due to oxidation and the use of POM as a catalyst, LO_PA_P had lower aliphatic hydroxyls (alphatic-OH) content than LO_PA. The different hydroxyl (-OH) content modification was consistent with the fact that the pulp's brightness of the A_P stage was higher than the brightness of the pulp in acid pretreatment (A). After $O_PA_PP_O$ treatment, the pulp brightness was increased to 84.5% ISO, and the residual lignin ($LO_PA_PP_O$) had the highest content of carboxylic acid functionalities (-COOH) in four samples. These results imply that all of the aliphatic hydroxyls (Aliphatic-OH) and guaiacyl phenol moieties (G-OH) had been destroyed and the carboxylic acid functionalities (-COOH) increased.

CONCLUSIONS

1. The practical sequence $O_PA_PP_O$ could bleach straw pulp with a brightness 84.5% ISO, an acceptable viscosity 669 mL/g, and a low kappa number of 1.4. In comparison to reference pulps prepared by the sequences O_PAP_O and O_PQP_O, the viscosity was 11 and 21 units lower, respectively, and the brightness of $O_PA_PP_O$ was 2% and 4.7% higher, respectively.

2. Phosphomolybdic acid was the best catalyst among silicotungstic acid, phospho-tungstic acid, and phosphomolybdic acid. Phosphomolybdic acid was applied in the A_P stage but not in the O_P stage to improve straw pulp's brightness, which was 4.8% ISO higher than the pulp treated without POM. The optimum conditions of the A_P stage were: initial pH value 3, temperature 90 °C, H_2O_2 1.5%, and phosphomolybdic acid 1.0%.

3. ^{31}P NMR spectroscopy showed that for LO_PA and LO_PA_P, compared with LO_P, aliphatic hydroxyls (aliphatic-OH), *p*-coumary units (P-OH), and guaiacyl phenols (G-OH) were degraded, and carboxylic acid functionalities were increased. For the pulp after $O_PA_PP_O$ treatment, all of aliphatic hydroxyls (Aliphatic-OH) and guaiacyl phenols (G-OH) in residual lignin had been destroyed and the carboxylic acid functionalities (-COOH) increased.

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