Effect of black liquor replacement in wheat straw soda-AQ cooking and lignin structure of pulps

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ABSTRACT: The effects of black liquor replacement cooking (BLRC) on wheat straw soda-anthraquinone (AQ) pulps and their lignin structures were investigated by using different black liquor replacement ratios (BLRR) and alkaline nitrobenzene oxidation and ozonation. The residual AQ, alkali, and dissolved lignin, as well as carbohydrates in the wheat straw black liquor, greatly influence wheat straw soda-AQ cooking. The influence could be controlled by different BLRR. The BLRC with around 60% BLRR resulted in superior delignification selectivity. The residual AQ and dissolved carbohydrates in the black liquor are beneficial to delignification selectivity, while the dissolved and degraded lignin can slow the delignification rate. No obvious differences were found in the lignin condensation and β-O-4 structure degradation by the BLRC at different BLRR compared to control soda-AQ cooking. The BLRC technology has potential application because it reduces chemical charge and chemical recovery load and results in higher yield and quality of pulp.

Application: Pulp mills may be able to increase the pulp yield and improve the pulp-related properties and alkaline recover efficiency of nonwood fibers.

The use of virgin fibers for pulping increased as paper consumption grew, although recycling of fibers has reduced the use of virgin fibers in the past decade. This excess of demand over supply means there is a requirement for nonwood pulp as a supplement to conventional wood pulp [1]. Wheat straw, among nonwood fiber raw materials, is considered one of the most potentially useful nonwood pulping fiber materials because of the shortage of forest resources and the wide supply of wheat straw in the developing countries [2,3]. The soda-anthraquinone (AQ) process is the most common pulping process used for nonwood fiber raw materials. Unlike wood pulping, however, several problems restrict the application of wheat straw pulping; these problems include the difficulty in achieving effective black liquor chemical recovery (BLCR) and poor drainage in the papermaking process [3–5].

Both wood and nonwood pulping processes can produce large volumes of black liquor. The chemical recovery process can effectively recover the chemicals used in the wood cooking and the energy from the black liquor combustion [5]. However, chemical recovery of wheat straw black liquor (WSBL) is difficult because of its high silica (SiO_2) content and lignin-carbohydrate complex [6]. Although several technologies – including acidification, electrodialysis, and membrane separation [6,11,12] – are available to treat black liquor and improve the chemical process, the technologies have not been successfully run on an industrial scale. The WSBL contains heat energy, lignin, carbohydrates, residual alkali, AQ, and so forth [7,8]. Many positive effects on the cooking and chemical recovery behaviors could be obtained if WSBL were used for recooking [9,10].

Our objectives were to study the effects of the residual alkali, AQ, and dissolved and degraded components in WSBL on the wheat straw soda-AQ pulps and their lignin structures by black liquor replacement cooking (BLRC) at different black liquor replacement ratios (BLRR).

EXPERIMENTAL

Material

Wheat straw (*Triticum acestivum c.v.*) was collected from Nanjing, China. The leaves and dust were removed and the straw was cut into chips of 20–30 mm in length for cooking. In addition, 40–60 mesh extractive-free wheat straw meals were prepared for alkaline nitrobenzene oxidation (NO) and ozonation. **Table I** shows the chemical composition of the straw.

Alcohol-Benzene Extractives (%)	Holocellulose (%)	Total Lignin (%)	Pentosan (%)	Ash (%)	SiO_2 (%)
3.88	77.67	20.04	24.52	4.98	3.10

I. Chemical composition of wheat straw.

Preparation of black liquor

Wheat straw black liquor was prepared in the laboratory using the soda-AQ process. The cooking was done in a glycerin bath of 8 x 1.25 L autoclaves with the conditions of active alkali (AA) 17.0% (based on sodium hydroxide [NaOH]), AQ 0.05%, liquor-to-straw ratio 4.5, maximum temperature 150°C, and time of 1 h at 150°C. The black liquor was collected and analyzed immediately after cooking (**Table II**).

Black liquor replacement soda-AQ cooking

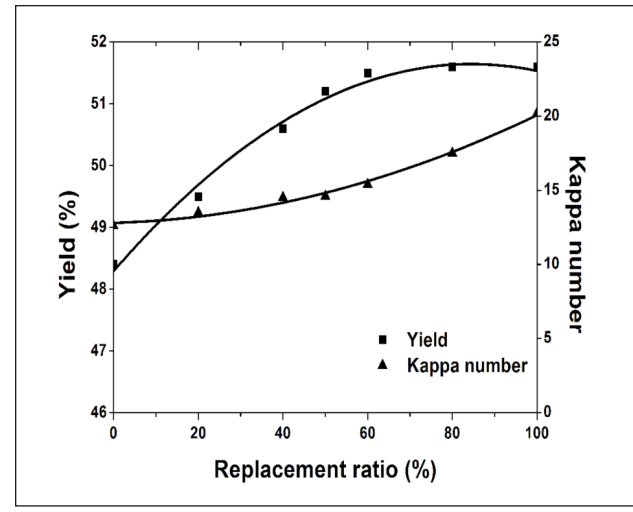
The BLRR (the volume percentage of replacement black liquor in total cooking liquor) was designed as 0% (control), 20%, 40%, 50%, 60%, 80%, and 100%. The additional NaOH was calculated and added based on the residual alkali in the liquor and AA requirement. The same cooking technical conditions were adopted as for the preparation of WSBL. The black liquor was collected and analyzed immediately after the BLRC.

Analytical methods

The raw material and pulp were characterized in accordance with the applicable TAPPI Standard Methods: alcohol-benzene extractives (TAPPI T204 om-97, "Solvent extractives of wood and pulp"), holocellulose (TAPPI T9 wd-75, "Holocellulose in wood"), pentosan (TAPPI T223 om-01, "Pentosans in wood and pulp"), lignin (TAPPI T222 om-02, "Acid-insoluble lignin in wood and pulp"), ash (TAPPI T211 om-02, "Ash in wood, pulp, paper and paperboard: combustion at 525°C"), SiO_2 (TAPPI T244 cm-99, "Acid-insoluble ash in wood, pulp, paper, and paperboard"), Kappa number (TAPPI T236 cm-99, "Kappa number of pulp"), and viscosity (TAPPI T230 om-04, "Viscosity of pulp [capillary viscometer method]"). NO and ozonation were analyzed based on references [14,15].

Residual Alkali as NaOH (g/L)	AQ (g/L)	Lignin (g/L)	Carbohydrate (g/L)	SiO_2 (g/L)
6.85	0.0178	40.9	65.5	3.20

II. Properties of the replacement black liquor.



1. Effect of BLRR on pulp yield and kappa number.

RESULTS AND DISCUSSION

Effect of BLRR on chemical composition in BLRC liquor

The effects of BLRR on the alkali, lignin, carbohydrate, AQ, and SiO_2 concentrations in the cooking liquor are shown in **Table III**. The concentration of the chemical composition in the initial cooking liquor increased with the BLRR increase. At 100% replacement ratio, the black liquor contained NaOH 37.8 g/L, lignin 40.9 g/L, carbohydrate 65.5 g/L, AQ 0.129 g/L, and SiO_2 3.20 g/L. On the basis of the principle of chemical reaction balance, these substances in the liquor can reduce alkali consumption and dissolution of the relevant substances in the pulp [16]. The extra AQ from the liquor can restrict the peeling reaction of carbohydrates and effectively break more lignin β-O-4 structure, which could affect pulp yield, kappa number, viscosity, and lignin structure.

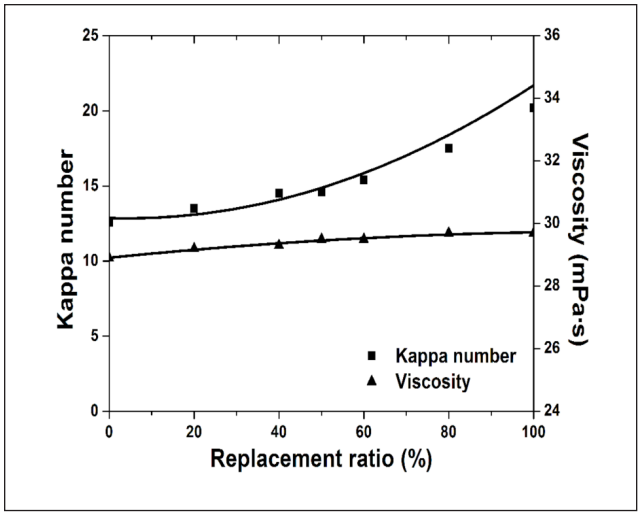
Effect of BLRR on delignification selectivity

Figure 1 shows the influence of BLRC on the yield and kappa number of pulps. Compared to the control cooking (alkali concentration 37.8 g/L, pulp yield 48.4%, kappa no.

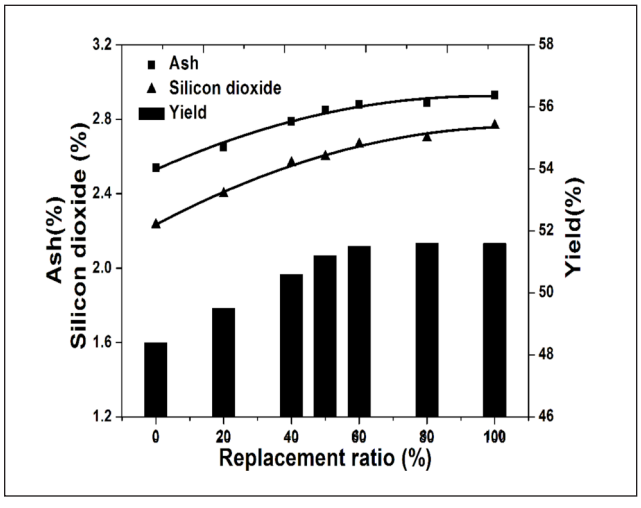
BLRR (%)	NaOH* (g/L)	AQ (g/L)	Total Lignin (g/L)	Carbohydrate (g/L)	SiO_2 (g/L)
0	37.8(0.00)	0.111	0.0	0.0	0.00
20	37.8(1.37)	0.115	8.2	13.1	0.64
40	37.8(2.74)	0.118	16.4	26.2	1.28
50	37.8(3.43)	0.120	20.5	32.8	1.60
60	37.8(4.11)	0.122	24.5	39.3	1.92
80	37.8(5.48)	0.125	32.7	52.4	2.56
100	37.8(6.85)	0.129	40.9	65.5	3.20

* The number in the brackets is standard for the NaOH from replacement black liquor.

III. Effects of black liquor replacement ratio (BLRR) on chemical composition in cooking liquor.



2. Effect of BLRR on kappa number and viscosity.



3. Effect of BLRR on the pulp ash and silica.

12.6, and viscosity 28.9 mPa·s), at 60% BLRR the new alkali consumption decreased by 10.9% (Table III) and the pulp yield increased by 6.4% while kappa number increased slightly. Increasing replacement ratio beyond 60% BLRR changed the yield slightly. When cooking of 100% BLRR was compared to the control cooking, the pulp yield increased by 6.5%, kappa number increased to 20.2, and chemical consumption decreased by 18.1%. The results indicated that at the same alkali charge, the cooking chemical consumption was reduced and the pulp yield improved significantly along with the BLRR increase in the BLRC. These results were closely related to the AQ, residual alkali, carbohydrate, and lignin in the black liquor. The dissolved and degraded carbohydrates in the black liquor limited the dissolution of the carbohydrates in the pulp [17,18].

Figure 2 shows the effects of the BLRR on the kappa number and viscosity of pulps. Compared to the control cooking, the kappa number increased slowly in the initial phase but increased rapidly in the following phase. The delignification was limited when the BLRR rose and the kappa number increased to about 20; however, viscosity increased to some extent when BLRR was 100%. In addition, AQ can reduce the peeling reaction of carbohydrate and protect the pulp yield and viscosity from loss [19,20]. These results were the combination effect of AQ, carbohydrates, and lignin in the liquor.

Effect of BLRR on the ash and silica contents of pulps

Figure 3 indicates the effect of BLRR on the ash and silica contents of pulps. After BLRC, ash and silica contents were higher than in the control pulp and increased with increasing BLRR. When the BLRR was about 60%, the ash and silicon contents increased by 13.4% and 7.6%, respectively, compared to the control cooking. After the 60% BLRR, the trend changed

		Lignin (%)	NO Yield (%, mol)	V:S:H* (mol ratio)	E+T** (%, mol)	E/T
	Wheat straw	20.04	41.4	1:0.88:0.32	22.19	1.74
BLRR (%)	0	3.42	22.0	1:0.90:0.38	9.31	1.11
	20	3.49	22.1	1:0.91:0.36	9.32	1.11
	40	3.69	23.2	1:0.90:0.36	8.81	1.03
	50	3.73	23.5	1:0.86:0.38	8.57	1.02
	60	3.92	23.9	1:0.85:0.36	8.36	1.07
	80	4.32	23.3	1:0.86:0.36	8.42	1.05
	100	5.16	23.2	1:0.88:0.37	8.38	1.08

*V (vanillin and vanillic acid), S (syringaldehyde and syringic acid), and H (p-Hydroxybenzaldehyde and p-Hydroxybenzoic acid) unit.
**E (erythronic acid), T (threonic acid).

IV. Nitrobenzene oxidation and ozonation at different BLRRs.

slightly; the ash and silica contents increased by 15.6% and 9.4%, respectively, when BLRR was 100%. According to the principle of chemical balance, the ash and silica in the BLRC liquor can reduce the relative component dissolution from pulp. In addition, the residual inorganic components in the black liquor can adsorb onto the pulp in the weak alkaline environment [21]. The silica in the pulp may improve its yield and application properties.

Effect of BLRR on the lignin structure

Lignin structure unit

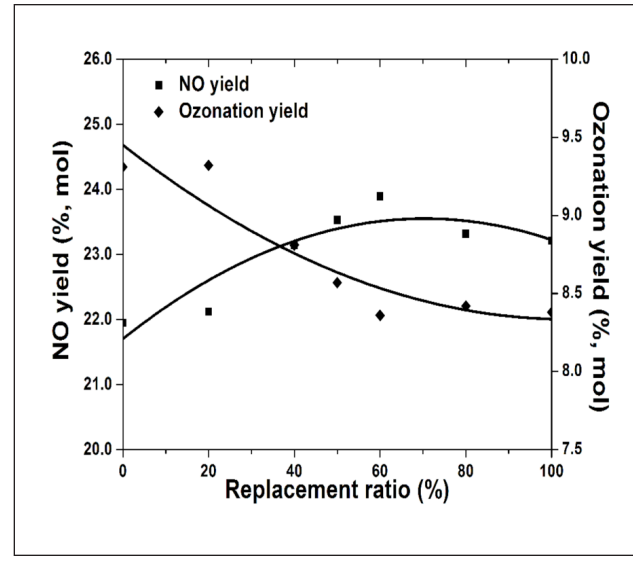
Table IV and **Fig. 4** show the results of NO and ozonation of the pulps. The NO yield reflected the degree of noncondensed lignin indirectly. Compared to wheat straw meal, the NO yield was decreased and the condensed lignin was increased after BLRC. The lignin content in the pulps increased from 3.42% to 5.16% when the BLRR increased from 0% (control cooking) to 100%, but the NO yield and its V:S:H molar ratio only changed to very limited content, especially when the BLRR was less than 60%. The lignin in the black liquor restrained the dissolution of lignin, resulting in lignin content increase and condensation in the pulp. On the other hand, AQ in the cooking liquor can accelerate lignin dissolution and protect from the lignin condensation [22]. The final data indicated that the more black liquor that was added, the more difficult lignin was dissolved. This was an integrated result of many factors based on the chemical reaction balance.

The delignification process may be the cause of the lignin structure change. The relative degradation rate of each unit can be evaluated by lignin structure unit yield and its molar ratio. The literature [23] shows that p-coumaric acid, which connects to the macromolecule lignin with ester bond, has dissolved in pulping, but there was less hydroxyphenyl alcohol glycerol-β-aryl. The β-O-4 structure exists widely in the syringyl and the guaiacyl units and is easily broken [24]. The extra AQ in BLRC can accelerate the breaking of the β-O-4 structure and lead to a relative decrease of V and S units in the pulps. However, BLRC had no obvious influence on the lignin condensation, which was coincident with the delignification rate in the BLRC system.

Lignin β-O-4 structure

The erythonic plus threonic (E+T) yield and E/T ratio of the pulp lignin by ozonation analysis are shown in Table IV. The β-O-4 structure broke significantly during soda-AQ (BLRR 0%) and BLRC processes. However, there were differences between soda-AQ and BLRR processes in aspects of the straw β-O-4 structure reaction. The (E+T) yield of soda-AQ was 9.31% while the (E+T) yield of BLRR was 8.36% at 60% BLRR. The results showed that the BLRR process was more able to delignify the β-O-4 structure than the soda-AQ process. The extra AQ in the black liquor can promote breakage of the β-O-4 structure effectively.

The E/T ratio reflects the stereochemistry of β-O-4 structure. Compared to the straw lignin E/T ratio (1.74), both the E/T ratios of soda-AQ (BLRR 0%) and BLRC processes were decreased during the cooking, indicating that erythonic and threonic structures are degraded at different rate in the processes. However, there was no obvious difference between soda-AQ and BLRC processes for the E/T ratio; the β-O-4 structure stereochemistry was not observed when different BLRR were applied.



4. Effect of BLRR on the nitrobenzene oxidation and ozonation yield.

CONCLUSIONS

The residual AQ, alkali, dissolved lignin, and carbohydrates in the WSBL have a great influence on the wheat straw BLRC characteristics. The influence can be controlled by the different BLRR. The BLRC with around 60% of BLRR resulted in a good delignification selectivity, which showed quite high SiO2 content, yield and viscosity of the pulp, and alkali saving. The delignification rate, however, was slowed to some extent.

The residual AQ content and dissolved carbohydrates in the WSBL are beneficial to the selectivity, while the dissolved and degraded lignin can restrict the delignification. Their combination effects were controlled by the principle of chemical reaction balance.

There was no obvious variation in the lignin condensation and β-O-4 structure degradation during BLRC at different BLRR compared to the normal soda-AQ cooking. **TJ**

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ABOUT THE AUTHORS

We sought to make direct use of heat energy, dissolved lignin and carbohydrates, and residual alkali and AQ in wheat straw black liquor for recooking to save energy and chemical consumption.

Our study focused on the chemical recovery of wheat straw black liquor. It differs from the previous studies in its use of the effective chemical components from the alkali recovery process. The delignification selectivity, SiO2 content, pulp yield, and viscosity were enhanced when black liquor was used for replacement cooking due to the residual AQ and dissolved carbohydrate in the black liquor. Meanwhile, the residual alkali in black liquor also decreased the alkali consumption. The black liquor replacement cooking technology has potential application in energy and chemical recovery, which is positive for both pulp cooking and alkali recovery.

While the technical aspect of this research was not particularly difficult, it could scale up the process to an industrial level. Future work would involve pilot trials and studies focused on environmental and economic analyses.

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