Combustion Properties of Mixed Black Liquor Solids from Linter and Reed Pulping

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In order to find the suitable alkali recovery process for linter and reed pulping discharges, the physicochemical properties of the black liquor solids from linters pulping and black liquor solids from reed pulping were analyzed. The swelling volume index, calorific value, and pyrolysis characteristics of five samples of mixed black liquor solids were tested. The kinetics of the combustion process of the samples were further studied. The results showed that the calorific value and swelling index of the reed black liquor was higher and its inorganic content was lower. During the combustion period, the droplet undergoes four stages; drying, devolatilisation or pyrolysis, char burning, and smelt reaction. With the increase of reed pulping black liquor solids in the sample, the activation energy decreased, while the frequency factors increased. As a result, the combustion performance of the mixed solids was significantly improved.

Keywords: Black liquor; Combustion; Alkali recovery; Kinetics

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INTRODUCTION

The use of reed and cotton linters for paper production as a source of fibres has commonly been used to reduce the problem of deforestation (Hurter 1997). Linter pulping mills are mainly located in Xinjing, China. The cotton linter pulp is used in the manufacturing of cellulose nitrate (pyroxylin, kolloksilin), carboxymethyl cellulose (CMC), microcrystalline cellulose (MCC), cellulose esters, filter paper, and others (Azeez 2018). Black liquor and the effluent generated in bleaching process are major pollution sources from linter pulping mills. Only a small part of the effluent is reused; most of the effluent, which has high chroma, high pH, and unknown chemicals, is discharged (Carrier *et al.* 2011). Swelling index expresses the water binding capacity (Singh *et al.* 2005). Unlike black liquor (BL) from chemical pulping of other feedstocks, it is rarely treated through an alkali recovery system due to the small quantities with low calorific value of the linter black liquor, unless there are special favorable conditions. The COD_{Cr} concentration of the linter black liquor is up to 50000 mg/L. Once mixed with other effluents, it is very difficult to meet the integrated wastewater discharge standard of 300 mg/L according to GB 8978 (1996). With the trend of further regulating effluent treatment, it will become more difficult to meet the standards. These problems have seriously hindered the development of the domestic linter pulp industry.

To meet the discharge standards, the black liquor must be treated separately to reduce the load sent to the water treatment system. There are chemical pulping mills using reed as feedstock with an alkali recovery system. The two types of black liquor may be mixed for effective alkali recovery, reducing water pollution. Therefore, dry solids of linters pulping black liquor and reed pulping black liquor were the subjects for this study. Their physicochemical properties were analyzed, including swelling volume index, calorific value, and pyrolysis characteristics of the samples with different mixing ratios of the two BL solids. The activation energy and frequency factor of the combustion process were calculated using the Coats-Redfern method. The main objectives were to examine alkali recovery of combined linter pulping black liquor and reed pulping black liquor and to provide guidance for the design of their combustion and operating conditions.

EXPERIMENTAL

Materials

Linter pulping black liquor was produced in a laboratory cooking system in accordance with the factory cooking conditions. Reed pulping black liquor was obtained from a pulp line in Xinjiang province. The kraft pulping process was employed, which uses sodium hydroxide and sodium sulphide. The physicochemical properties were determined by correlation analysis methods. A certain amount of these liquid samples were dried at 105 °C, crushed to powder with a high speed disintegrator, and stored in a sealed plastic bag. Pulping conditions and the chemical composition of the linter and reed feedstocks are listed in Table 1.

Table 1. Pulping Process and Chemical Properties of Reed and Linter Feedstocks

Feedstock	Pulping Process	Chemical composition				
		Lignin (%)	Ash (%)	Silica (%)	Cellulose (%)	Hemicellulose (%)
Reed	Soda Cooking 15% NaOH (1:5 Liquor to reed ratio), 160 °C	19.26	5.82	0.85	42.17	25.13
Cotton linters	Soda Cooking 20% NaOH (1:5 Liquor to linter ratio), 160 °C	3.25	2.40	0.03	87.80	2.76

Analytical Equipment

The equipment used in this study included the following: Vario EL cube Elementar element analyzer, Frankfurt, Germany; TGA/DCS I STARe METTLER thermogravimetric analyzer, Zurich, Switzerland; FP6410 flame photometry, Shanghai Lepad Scientific Instruments Co., Ltd, Shanghai, China; ZDHW-5000 calorimeter, Hebi Huadian Analytical Instrument Co. Ltd. Hebi, China; EUTECH pH-700 pH meter, with a range of 0.00 to 14.00 and an accuracy of ± 0.02, Singapore; and CSR-1-20II, ASTK Technology Development Co., Ltd., Beijing, China, for bi-distilled water preparation.

Samples preparation

The two types of black liquor (linter and reed) may be mixed for effective alkali recovery, reducing water pollution. Five samples were prepared from mixing linter and reed solid mass in a five linter:reed ratios; 0:1, 1:2, 1:1, 2:1, 1:0.

Elemental Content Analysis

The C, H, N, and S contents of the sample were determined by elemental analyzer under the following conditions. The temperature of oxidation furnace and reduction furnace were 1150 °C and 850 °C, respectively. The pressure of He and O_2 were 0.12 to 0.125 MPa and 0.22 MPa, respectively; K and Na content were determined by flame photometer. Si and Cl were determined by chemical titration method; O content was calculated.

Determination of the Swelling Index

The swelling Index of reed and linter were determined using the following equation (Poosarla and Muralikrishna 2015),

$$VIE=\frac{V_0-\frac{m_1}{\rho}}{m_0} \tag{1}$$

where V_0 is the initial volume of crucible; m_1 is the weight of particles filling the upper blank space of the crucible with black liquor char at the bottom; m0 is the weight of dry black liquor solid; ρ is the density of the particles.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was carried out with high purity nitrogen to protect the inert atmosphere in the furnace, remove the volatile products of pyrolysis from the sample with time, and reduce any sample alteration due to possible secondary reaction. Mixing solids of linter pulping black liquor and reed pulping black liquor was heated by rate of 10 °C/min from 50 °C to 1000 °C. The relationship between the physicochemical properties of the sample and temperature were measured. The sample weight was less than 5 mg to avoid the influences of heat transfer, secondary gas-solid reaction, and mass diffusion factor.

RESULTS AND DISCUSSION

Physicochemical Properties Analysis of Linter Pulping Black Liquor and Reed Pulping Black Liquor

Physicochemical properties are vitally important for black liquor alkali recovery. The physicochemical properties results of linter pulping black liquor and reed pulping black liquor including pH, solids, organic matter content, inorganic matter content, elements, calorific value, and swelling volume index are shown in Table 2.

The pH of the linter pulping black liquor was higher than that of reed pulping black liquor, which was caused by high active alkali chemical to linter ratio, as high as 18% to 20%. The corresponding Na, K, and inorganic matter content of linter pulping black liquor were higher. The ratio of organic matter and inorganic matter was only 1.17, and the solid heat value was lower as well, which is not good for combustion. In addition, the holocellulose content in the raw materials of linter was as high as 90%, and the pulp yield was about 80% at the same cooking concentration.

Table 2. Physico-chemical Properties of Linter Pulping Black Liquor and Reed Pulping Black Liquor

Property		Linter Pulping Black Liquor	Reed Pulping Black Liquor
pH		14.13	12.39
Solids content (%)		7.51	12.14
Organic matter content (%)		53.91	59.48
Inorganic matter content (%)		46.09	40.52
Organic matter/ inorganic matter		1.17	1.47
Elements (%)	C	32.17	30.59
	H	3.21	3.27
	O	32.11	38.07
	N	0.98	0.14
	S	1.39	1.81
	Na	26.86	23.09
	K	1.86	0.54
	Si	0.18	1.29
	Cl	1.04	1.00
	Inert oxide	0.20	0.20
Calorific value (MJ·kg-1)	Gross	11.15	12.33
	Net	10.46	11.65
Swelling volume index (mL·g^{-1})		0	28.56
Lignin (%)		3.3	29.6
Silica (%)		0.05	0.81

The solids content of linter pulping black liquor was only 7.51%, far lower than that of reed, which was 12.14%. If linter pulping black liquor would be treated by alkali recovery process, its solid content needs to be enriched to more than 50% through evaporation, such that over 0.84 ton of water would need be removed for each ton of black liquor. The large energy cost of this process is one reason that linter pulping mills are not willing to install alkali recovery systems. In addition, the swelling volume index of linter pulping black liquor solid was almost zero, which was unfavorable for alkali recovery, reflecting its bad combustion performance.

Calorific Value and Swelling Volume Index of Mixing Solids of Linter Pulping Black Liquor and Reed Pulping Black Liquor

Calorific value and swelling volume index are two important parameters in alkali recovery that are determined by its combustion performance and economic efficiency. Swelling volume index describes the swelling properties of black liquor solids during dehydration and carbonation, and it has a great influence on blank liquor solid combustion conditions in the furnace.

The carbonation of the black liquor with high swelling volume index normally has a crisp shell, composed mostly of spongy material, internal holes and bubbles, which facilitate the rapid transfer of oxygen and rapid discharge of decomposition gas that can shorten the combustion time (Hu *et al*. 2007). The calorific value and swelling volume index of mixing solids, with the proportion based on bone dry weight of the linter pulping black liquor solids and reed pulping black liquor solids of 1:0 and 0:1, 1:2, 1:1, and 2:1 were determined. The results are shown in Table 3.

Table 3. Solid Samples and their Composition, Calorific Value, and Swelling Volume Index

Sample	Black Liquor Solid Composition (linter: reed ratio)	Calorific Value (mJ/Kg)		Swelling Volume Index (mL/g)
		gross	net	
1	0:1	12.37	11.89	28.56
2	1:2	12.21	11.53	4.10
3	1:1	12.12	11.43	3.44
4	2:1	11.23	10.57	2.41
5	1:0	11.15	10.46	0

The data in Table 3 show that adding the reed pulping black liquor had a positive effect on combustion of linter pulping black liquor solids. With the increase of reed pulping black liquor solids ratio, the calorific value of mixed liquor solids increased gradually, but the percentage was less than 12%. The swelling volume index indicates the rate of dissolubility. The swelling volume index increased significantly, increased from 0 ml/g to 28.56 ml/g. Swelling increases in proportional with time because the weight were increased with hydration rate and granular concentrations. The swollen granules resulted in the formation of a viscous mixture after water contact.

The combustion process of alkali recovery can be divided into four stages (Grace *et al.* 1986), (1) Drying of black liquor: drying is the first process to occur after the liquor is introduced to the furnace. The liquor temperature remains near the boiling point until the water is gone. This delays the inception of other higher temperature processes until the liquor is dry. With macroscopic sized particles, pronounced gradients of temperature and dryness can exist within the particle. The viscosity of the liquor in the drop increases gradually. The outer layers of the drop become solid, while the inside is still a highly viscous liquid. The final shape varies from drop to drop but is often partially hollow. (2) De-volatilization or pyrolysis: Pyrolysis is the production of volatile combustibles through the thermal degradation of complex organic compounds. Pyrolysis reactions are irreversible degradation reactions caused by thermal effects. They are not oxidation reactions, although they may be accompanied by parallel oxidation reactions. The gas formed during pyrolysis makes the particle volume swell rapidly, with some particles reaching 10 to 30 times their initial volume. (3) Char burning: If the particle swells well, its combustion time is short, and its combustion efficiency is high. Thus, alkali and energy recovery of the furnace can be improved. (4) Smelt coalescence: In this step, solids such as sodium carbonate compounds and sodium sulfate melt. Sodium sulfate is reduced to sulfide again. Studies of the combustion process related to swelling generally refer only to the first two stages of the combustion. Hupa *et al.* (1985) revealed that evaporation and thermal decomposition time are similar for all liquors, but the char burning times sometimes exhibit a 5- to 6-fold difference. Generally, black liquor combustion is closely related to its swelling volume index. The combustion rate increases by 3.8-fold when its swelling volume index increases by 6-fold (Milanova 1988).

In general, the following conditions are required for a better swelling volume index: (1) Gas released; (2) The softening of the material. Due to the lower hemicellulose content in linter (only about 2.76%), the amount of hydroxy acids converted from hemicellulose during cooking process is relatively low, which leads to escape of the gas generated. The swelling volume index is related to its low lignin content and the content of other substances which need more research study.

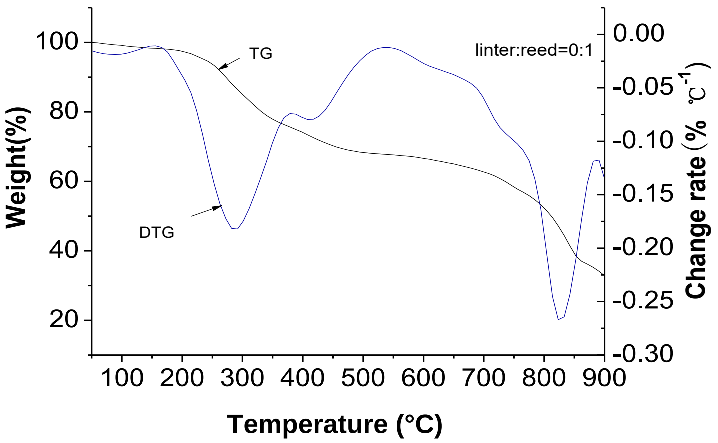
Pyrolysis of Mixing Solids of Linter Pulping Black Liquor and Reed Pulping Black Liquor

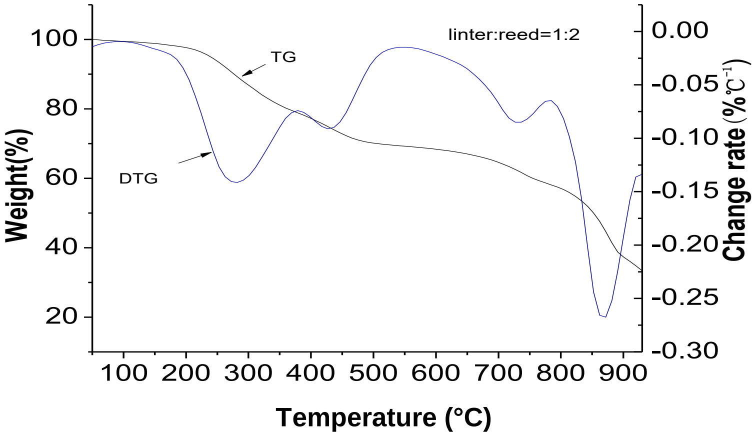
To investigate the combustion performance of the mixing solids, the relationship between the physicochemical properties of the sample and temperature was measured by TGA with heating rate of 10 °C/min as the temperature was increased from 50 °C to 1000 °C. Figure 1 illustrates the pyrolysis curve of the mixing solids of linter pulping black liquor and reed pulping black liquor with different proportions. The weight loss parameters of pyrolysis for each of the samples are listed in Table 4.

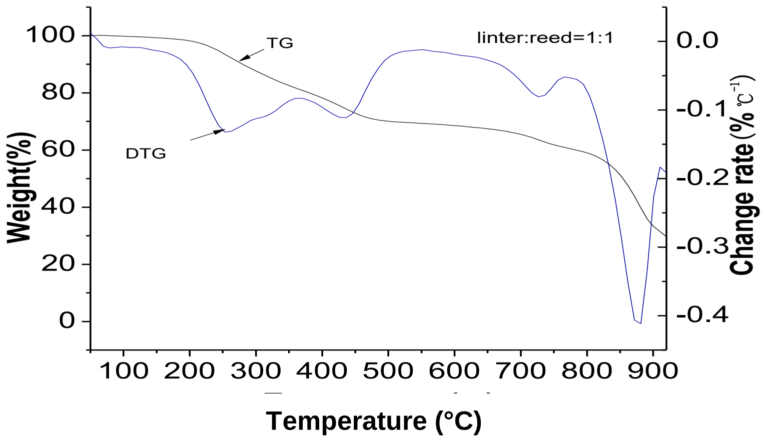
Table 4. Weight Loss Characteristic Parameters of the Samples in Different Pyrolysis Zone Heating Rate /(10 °C . min^{-1})

Sample	T_1 (°C)	T_2 (°C)	T_3 (°C)	W_1 (%)	W_2 (%)	W_3 (%)	da_1/dT (%·°C^{-1})	da_2/dT (%·°C^{-1})	da_3/dT (%·°C^{-1})	M_∞ (%)
1	272	408	843	89.98	73.41	41.39	-0.19	-0.08	-0.30	17.44
2	272	427	872	90.67	74.90	44.64	-0.16	-0.09	-0.32	18.82
3	253	437	881	93.50	74.35	39.68	-0.13	-0.11	-0.41	19.51
4	263	437	910	91.91	73.25	30.83	-0.14	-0.13	-0.54	22.20
5	243	456	978	89.38	68.23	33.17	-0.16	-0.07	-0.09	29.39

Note: T_1, T_2 and T_3 are peak temperature; W_1, W_2, W_3 is the residue weight at different peak temperature; da_1/dt, da_2/dt, and da_3/dt are maximum pyrolysis rate of the samples; M^∞ is the final residue weight of the sample.




linter:reed=1:2
TG
DTG
Weight(%)
100
80
60
40
20
Change rate (%℃$^{-1}$)
0.00
-0.05
-0.10
-0.15
-0.20
-0.25
-0.30
100 200 300 400 500 600 700 800 900
Temperature (°C)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TG
DTG
Weight(%)
100
80
60
40
20
0
Change rate (%℃$^{-1}$)
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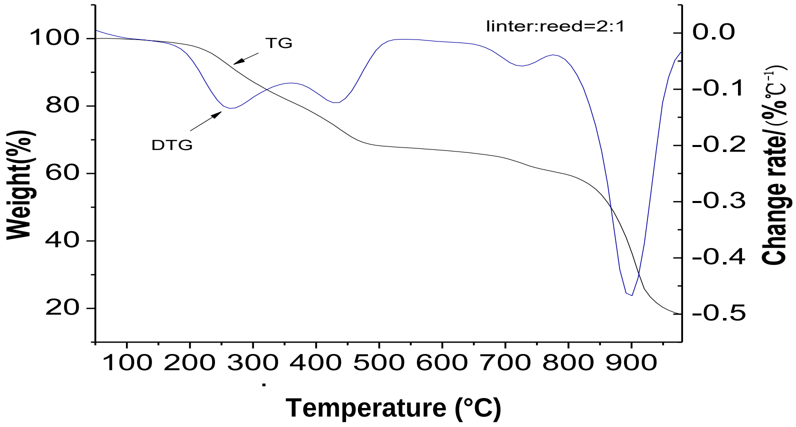
-0.1
-0.2
-0.3
-0.4
100 200 300 400 500 600 700 800 900
Temperature (°C)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TG
DTG
Weight(%)
100
80
60
40
20
Change rate/(%℃$^{-1}$)
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
100 200 300 400 500 600 700 800 900
Temperature (°C)

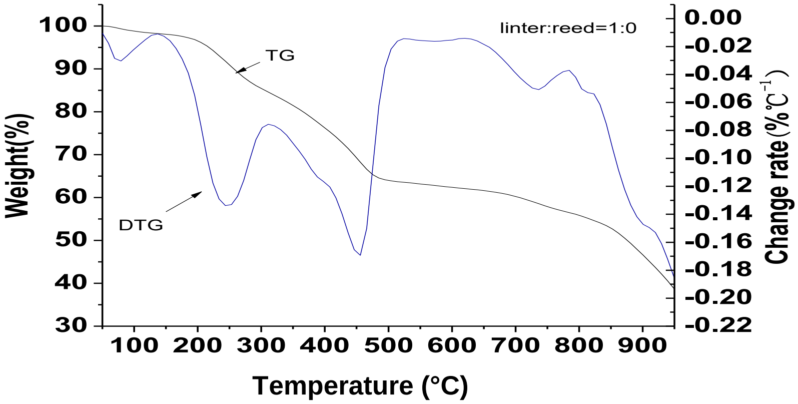

Fig. 1. Pyrolysis curve of the mixing solids of linter pulping black liquor and reed pulping black liquor

Pyrolysis processes of the samples can be described by several different stages with the increase of temperature, as shown in Fig. 1. According to the characteristics of the DTG curve, weight loss of the samples can be divided into 4 regions. The first region was from room temperature to 170 °C. The DTG curve shows several small fluctuations as part of combined water crystals, and some low molecular weight substances such as some low molecular weight volatile acids were separated from the samples. The weight loss rate of the five samples in this area were 1.94%, 1.67%, 1.12%, 1.27%, and 2.42%, respectively. The second region was from 170 °C to 380 °C. There was a large peak on the DTG curve, the peak temperature of maximum weight loss was at 273 °C, The weight loss percentages of the five samples in this region were 22.41%, 19.45%, 19.07%, 18.93%, and 18.71%, respectively. Lignin is an aromatic polymer with amorphous network structure; its pyrolysis occurs from 200 °C until to the end of pyrolysis (Raveendran *et al*. 1996). The third region was from 380 °C to 550 °C, where the weight loss peaks of DTG may come from further decomposition and carbonized reactions of polymer compounds. The maximum pyrolysis rate of the five samples were at 417 °C, 427 °C, 437 °C, 437 °C, and 446 °C, with corresponding weight loss rates of 8.08%, 10.90%, 12.13%, and 15.52% respectively. The fourth region was from 600 °C to 1000 °C, and there was a weight loss platform in the TG curve in this region. Alkali metal salt melting, evaporation, decomposition, and combustion of fixed residue carbon occur in this temperature range, producing a large number of volatile components, such as CO and CO_2 (Song *et al*. 2007; Su *et al*. 2015). The weight loss rate of the five samples was 49.56%, 49.17%, 49.01%, 44.67% and 32.97%, respectively (Su *et al.* 2013a,b).

Kinetic Analysis

The Coats-Redfern method was used to analyze the combustion performance of the different samples by analyzing the weight loss data (Zhang 1996; Zhang and Yu 1999; Yao 2006; Wu *et al*. 2007). The activation energy *E* and frequency factor *A* of the combustion process were obtained, as shown in Table 5.

Table 5. Pyrolysis Kinetic Parameters of Different Samples

Sample	Temperature Range (°C)	Fitting equation	R^2	*E* (kJ/mol)	*A* (min^{-1})
1	200 - 550	y = -2209.5x – 10.317	0.9602	18.37	6.68×10^8
2	200 - 550	y =-2852.2x – 9.5858	0.9741	23.71	4.15×10^8
3	200 - 550	y = -3103.5x – 9.1658	0.9671	25.80	2.97×10^8
4	200 - 550	y = -3188.4x – 9.0404	0.9646	26.51	2.69×10^8
5	200 - 550	y = -3433.1x –8.3769	0.9715	28.54	1.49×10^8

Note: Heating rate / (10 °C . min^{-1})

Table 4 shows that the linear relationship was well fitted. Thus, the kinetic equation can be used to describe the pyrolysis reaction process of organic compounds in the selected region. The activation energy increased gradually, from 18.37 kJ•mol^{-1} to 28.54 kJ•mol^{-1}, with the increase of linter pulping black liquor solid proportion in the mixing solids, with an increase percentage up to 55.36%. The sample was more stable with less reactivity, and its reaction speed was slower. The frequency factor *A* of mixing samples was decreased with the increase of cotton pulping black liquor solids ratio, from 6.68 $\times 10^8$ min^{-1} of pure reed pulping black liquor to 1.49 × 10^8 min^{-1} of pure linter pulping black liquor, with a decline of up to 77.69%. The greater frequency factor indicates the more effective collision frequency between the active molecules. The reaction between active molecules was more violent and its speed was much faster. The combustion performance of sample reflected from the frequency factor and the activation energy was similar. Therefore, with an increased reed pulping black liquor solid ratio, the combustion performance of the sample was better in the alkali recovery process, which was consistent with the result of combustion properties predicted from swelling volume index of the two types of solids where the ratio of linter pulping black liquor solid in the mixing sample is relatively low.

CONCLUSIONS

1. There was little difference of element content between linter pulping black liquor and reed pulping black liquor. The K, Na, and inorganic matter content in the linter pulping black liquor solid was relatively high, due to the high active alkali chemical to linter ratio. The original solid content of linter pulping black liquor was low because of the high holocellulose content of linter and high pulping yield.
2. Pyrolysis of linter pulping black liquor solids, reed pulping black liquor solids, and the mixed solids of the two kinds is a complicated process, which can be roughly divided into four stages: (1) drying of blank liquor drops; (2) devolatilization or pyrolysis of organic matter to form a large number of volatile substances; (3) further decomposition of polymer compounds and char burning; and (4) melting and reduction reaction of inorganic compounds.
3. The combustion performance of linter puling black liquor solid can be improved by mixing with reed pulping black liquor. Its activation energy was reduced, and its frequency factor and swelling volume index were increased with the increase of reed pulping black liquor ratio in the mixing sample. The alkali recovery system can be run in normal operations with proper ratio of the two kinds of black liquor instead of

discharging them to an effluent treatment system. Thus, the difficulty of water pollution governance for linter pulping mill can be significantly reduced.

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