Kinetics of Reed Black Liquor (RBL) Pyrolysis from Thermogravimetric Data

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The pyrolysis of reed black liquor (RBL) was studied in nitrogen atmosphere by thermogravimetric analysis at six different heating rates of 5, 10, 20, 30, 40, and 50 °C·min^{-1} from ambient temperature (25 °C) to 800 °C. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained. The results show that there are three main weight-loss stages in the temperature ranges of 180 to 350, 350 to 560, and 560 to 800 °C, for which the error is about ± 10 °C. The kinetic parameters were determined by the Coats-Redfern method. A kinetic compensation effect (KCE) between activation energy *(E)* and pre-exponential *(A)* factor also was found.

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INTRODUCTION

Black liquor (BL), a by-product during the alkaline cooking process of fibrous plants, such as wood or non-wood (cereal straw, reed, elephant grass, *Phalaris arundinacea*, miscanthus, sorghum, kenaf, hemp, and sugarcane bagasse), is a water pollutant that contributes about 90% of the total wastewater in a paper mill. BL compositions are complex, containing lignin, hemicelluloses, other carbohydrates, and inorganic compounds. However, BL is also a special type of energy source because the chemicals and energy contained in its organics can be recovered and reused in pulp and paper production through special treatment technologies (Sánchez *et al.* 2005).

Currently, BL from wood is able to be burned in a conventional recovery boiler (Tomlinson recovery boiler) for generating energy and reusing chemicals in the papermaking process (Sjöström 1993). Compared with BL from wood, BL from straw contains more silicon and potassium. The high silicon content can increase the construction costs because it can reduce the concentration efficiency of evaporators. Additionally, the high potassium content can decrease the melting point of BL, which could cause a corrosion problem and decrease the boiler efficiency (Dickinson and Verrill 1988). Although the conventional recovery boiler has been used for many years, there are also some problems in safety and environment, such as low power to heat ratio, low thermal efficiency, high capital and maintenance cost, and risk of smelt-water explosion (Stigsson 1998). Therefore, an increasing amount of research has focused on alternative recovery technologies that are much safer, easier, and more energy efficient than the conventional technology (Whitty and Verrill 2004). Pyrolysis and gasification are two potential methods for gaseous production during BL capacity reduction. Some studies have been reported on the pyrolysis and gasification of wood-derived BL (Frederick *et al.* 1993; Alén *et al.* 1995). A series of studies on straw BL has been performed using

thermogravimetric analyzers, different bench scale reactors, and a pilot scale reactor (Puértolas *et al.* 2001; Gea *et al.* 2002, 2003; Sánchez *et al.* 2005).

Reed black liquor (RBL), a type of good quality straw BL, plays an increasingly important role in the Chinese paper industry. The extractability of hemicellulosic components from RBL was investigated (Hao and Shigetoshi 2014). The combined effect of ultrasound and polyferric sulphate on the RBL has been researched (Shen *et al.* 2005). The reuse from RBL has also been researched (Sun *et al.* 2006, 2007; Xu *et al.* 2012). Moreover, CO_2 gasification characteristics of reed kraft black liquor have been studied (Yang *et al.* 2012, 2013). However, little work has been published on the pyrolysis of RBL. Therefore, it is necessary to study the pyrolysis characteristics and kinetics of RBL.

The objective of this work was to investigate the thermal degradation behavior of RBL in N_2 atmosphere at different heating rates. Moreover, the kinetic parameters (*E* and *A*) of RBL pyrolysis were determined by the Coats-Redfern method. The results could accelerate the development of RBL pyrolysis and provide some useful experimental data for practical application. What's more, *E* and *A* could be used in numerical simulation models to investigate the RBL reaction behavior under different operating conditions.

EXPERIMENTAL

Materials

The RBL used in this work was received from a Chinese paper mill in Daqing of Heilongjiang province. The RBL has a solids content of 52.60%. Proximate analyses of RBL were obtained by drying oven (CS101-E, China) and muffle furnace (YX-HF, China) using ASTM standards. Ultimate analyses of the dried basic for C, H, O, N, and S were obtained by an organic elementary analyzer (Vario Micro cube, Germany), and other elements were tested by X-Ray fluorescence (AXIOS-PW4400, Netherlands). The results are shown in Table 1, and the net heating value was determined as 13.35 MJ·kg^{-1} (YX-ZR/Q 9704, China). Similar to other black liquor from straw [26], high ash content (20.63%) and a larger quantity of Na (17.64%), K (1.92%), Si (1.78%) and Cl (1.57%) were found. Before being used in the TGA experiment, the RBL was completely dried in a drying oven (105 $\pm$ 3 $^\circ$C). After dying, the RBL solids were smashed. Two sieves of 75 and 105 μm were used to filter RBL solid powder. The residue powder retained in the 75 μm size sieve was used in the following experimental procedure.

Table 1. Ultimate and Proximate Analyses (Dry Basis) of RBL

Element	C	H	O	N	S	Cl	K	Na	Si	other
			Ultimate analysis							
Weight (wt %)	33.76	4.15	36.37	0.38	0.95	1.57	1.92	17.64	1.78	1.48
Component		Ash		Volatile				Fixed carbon		
Weight (wt %)		24.39		50.00				25.61		

Thermal Analysis

A TGA ZRY-2P Series TG analyzer (Shanghai Precision and Scientific Instrument Co., Ltd., Shanghai, China) was used for all TGA experiments. During all the experiments, nitrogen was used as the flow gas (60 mL·min^{-1}) to ensure the occurrence of the pyrolysis reaction. The initial mass of the dry RBL powders, placed in an alumina

crucible (5 mm internal diameter and 4 mm height), was approximately 7 mg. Samples were heated from ambient temperature (25 ℃) to 800 ℃ at different heating rates (β=5, 10, 20, 30, 40, and 50 ℃·min^{-1}).

Kinetics Analytical Methods

The Coats-Redfern equation (Eq. 1) was used for analysis.

$$\ln[G(\alpha)/T^2] = \ln(\frac{AR}{\beta E}) - \frac{E}{RT}$$ (1)

During the pyrolysis of a specified substance, the reaction mechanisms should be the same. There were 30 main reaction mechanisms shown in the following reference (Zhao *et al.* 2010). Therefore, from the linear relationship between $\ln[G(\alpha)/T^2]$ and $1/T$, the parameters *E*, and *A* could be obtained from the slope and intercept, respectively. Among the 30 results, the best reaction mechanism can be chosen to be called the most probable mechanism function, according to the coefficient of determination (R^2) that is closest to one.

RESULTS AND DISCUSSION

TGA Results

The TGA and DTG curves are shown in Figs. 1 and 2, respectively. Different liquors can behave very differently in the same reactor under the same conditions (Whitty *et al.* 1997). Thermal decomposition of straw black liquor seemed to happen in two different steps which temperature ranges were 200 to 550 ℃ and 550 to 900 ℃ (Gea *et al.* 2002). The pyrolysis of black liquor from the mixture of bamboo and hardwood included 3 stages (Wu *et al.* 2007). But there was only one weight loss stage during wheat straw pyrolysis (Yang and Wu 2009). However, in this work, three weight loss stages had been found during the pyrolysis process. The three temperature ranges were 180 to 350, 350 to 560, and 560 to 800 ℃ (± 10 ℃) which were similar to the result of the thermal degradation of neutral sulfite semi-chemical pulp black liquor (Zhao *et al.* 2010).

In the first stage, the weight loss ranged from 19.83% to 21.51%, which can be attributed to the decomposition of various organic matters, such as hemicelluloses (200 to 260 ℃), low molecular weight organic acids (200 to 300 ℃), and some lignin (280 to 500 ℃) (Oren *et al.* 1984; Gu *et al.* 1992). In the second stage, the weight loss ranged from 9.13% to 15.37%, which was mainly due to the decomposition of lignin (280 to 500 ℃) (Alén *et al.* 1995). In the third stage, the weight loss was about 11.5% to 22.11%, due to the decomposition of organic compounds and inorganic salt sodium in RBL, in addition to the reactions among salt sodium, in which carbon and a minor portion of the organic matter remained (Wäg 1996).

From Figs. 1 and 2, it can be seen that the peak temperature of each stage increased as the heating rate increased. As the heating rate increased, reaching the same temperature required shorter time, and the reaction became much stronger. In other words, the RBL was heated inhomogeneously, and some reactions did not occur while the temperature rose. Therefore, the temperature lag effect caused the peak temperatures of curves to move to the high-temperature side.
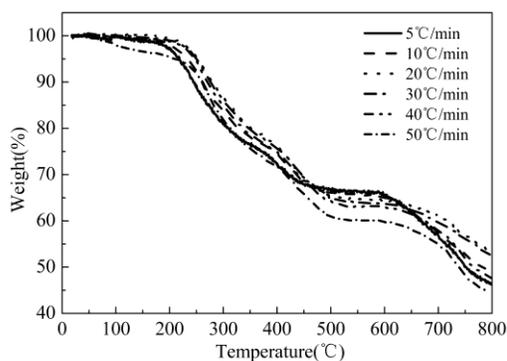
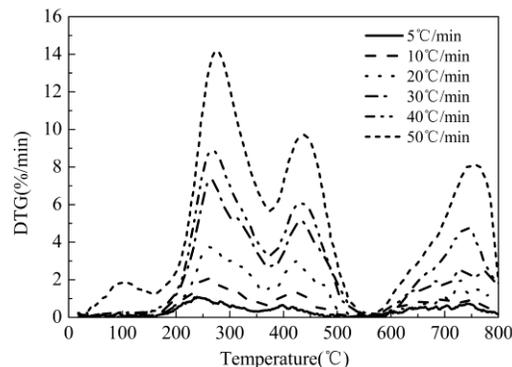**Fig. 1.** TGA curves of RBL on dry basis   **Fig. 2.** DTG curves of RBL on dry basis

Table 2 shows the pyrolysis analysis data of the RBL solid powder at different heating rates. During the wood BL pyrolysis process, final solid conversion increased as the heating rate increased, due to a higher production of volatiles, as has been found (Frederick *et al.* 1994). But Gea *et al.* (2002) found that the trend of the final solid conversion was not clear during the thermogravimetric study of alkaline straw BL. They found that these deviations may be attributed to differences of composition of BL solid powder.

In the present work, the final solid conversions of RBL used also did not show the same trend, which is evident by the last row of Table 3. However, we consider this to be a result of the deviations of the intensity of the reaction. When β is greater than 10 $^{\circ}$C·min^{-1}, as β increases, pyrolysis time decreases, reactions strengthen, and more matter is released, so the solid conversion rises. When β is smaller than 10 $^{\circ}$C·min^{-1}, the reactions are closer to an ideal process and each reaction has sufficient time to react isothermally and completely. Therefore, the final solid conversion is greater than 0.5, and the solid conversion decreases when β increases. But when β is very small, some reactions do not occur. Therefore, the final solid conversions of 5 $^{\circ}$C·min^{-1} (53.75%) and 10 $^{\circ}$C·min^{-1} (50.70%) were smaller than those of 40 $^{\circ}$C·min^{-1} (52.48%) and 50 $^{\circ}$C·min^{-1} (55.56%).

It also was found that the highest weight loss occurred in the first stage and third stage at a low heating rate (5 and 10 $^{\circ}$C·min^{-1}) and a highest heating rate (β = 50 $^{\circ}$C·min^{-1}). The first stage weight loss value was similar, having a value between 19.83% and 21.51%. However, as the heating rate increased, the second stage weight loss increased at first and then decreased, and the third stage weight loss decreased at first and then increased. This may be an indication of the temperature lag effect.

Figure 2 and Table 2 also show that the devolatilization rates of RBL when β = 50 $^{\circ}$C·min^{-1} were greater than for other conditions. When β was 5 $^{\circ}$C·min^{-1}, the devolatilization rate of the second and third stages were similar, and the first stage value was the highest of the three.

Not including the 5 $^{\circ}$C·min^{-1} result, it can be seen that the devolatilization rates of the three stages were ranked as the first stage > the second stage > the third stage. Generally speaking, organic matter fraction devolatilization (T < 560 $^{\circ}$C) was higher than that of the inorganic matter fraction (T > 560 $^{\circ}$C).

Table 2. Pyrolysis Analysis Data of RBL on Dry Basis at Different Heating Rates

Heating rate (^{o}C·min^{-1})	Temperature range (^{o}C)	Peak temperature (^{o}C)	Devolatilization rate (%·min^{-1})	Weight loss (%)	Final solid conversion (%)
	180~350	244	1.0658	22	
5	350~560	432	0.4155	10	53.75
	560~800	728	0.6770	20	
	180~350	257	2.1004	21	
10	350~560	414	1.3759	12	50.70
	560~800	730	0.9546	16	
	180~350	262	3.7410	20	
20	350~560	422	2.9955	15	46.65
	560~800	729	1.9670	11	
	180~350	266	7.3183	20	
30	350~560	433	5.0940	15	47.56
	560~800	737	2.4407	12	
	180~350	268	8.9112	21	
40	350~560	430	6.0779	15	52.48
	560~800	741	4.8343	16	
	180~350	276	14.1823	20	
50	350~560	439	9.7231	9	55.56
	560~800	760	8.0907	22	

Kinetics Study

Coats-Redfern method

Comparing the 30 results, the R^2 value of the 13th reaction mechanism is closest to one, which suggests that it is the most probable mechanism function to describe the kinetics for the RBL pyrolysis in nitrogen atmosphere during all three stages. The integral form is $G(\alpha)=[-\ln(1-\alpha)]^4$, and the function of this reaction mechanism, the Avrami-Erofeev equation, is $f(\alpha)=(1-\alpha)[-\ln(1-\alpha)^{-3}]$. Therefore, the RBL pyrolysis reaction mechanism may be random nucleation and subsequent growth. This model is based on the assumption that in the course of the pyrolysis of RBL, active centers are generated at random local points, and some of the active centers produced decomposition products or become deactivated, but the others continue to produce some active centers. The reaction order was four.

Various kinetic parameters calculated with the Avrami-Erofeev equation (n=4) reaction mechanism using Coats-Redfern method are shown in Table 3. The R^2 value in the first stage was the closest to one, meaning the linear fitting relevance between this reaction mechanism and the experimental result is satisfied. This reaction mechanism can accurately describe RBL pyrolysis in the first stage. But in the second and third stages, the R^2 values are less than the first stage and far less than one, meaning that using this reaction mechanism to describe the second and third stages of RBL pyrolysis is not satisfactory, especially for the third stage. The results could also mean that pyrolysis of RBL is a complex reaction, especially in the third stage (560 to 800 ℃).

Table 3. Kinetic Parameters of the RBL Pyrolysis Using Coats-Redfern Method

Heating rate-β (^{o}C·min^{-1})	Temperature range-T (^{o}C)	Activation energy-E (kJ·mol^{-1})	Pre-exponential factor-A (s^{-1})	R^2
5	180-350	155.7133	1.29E + 12	0.94446
	350-560	34.9673	6.69E + 00	0.82600
	560-800	179.3450	6.91E + 09	0.85875
10	180-350	181.6669	4.01E + 14	0.96657
	350-560	53.0240	5.33E + 02	0.90361
	560-800	169.5386	5.73E + 09	0.84554
20	180-350	261.6922	8.64E + 21	0.94332
	350-560	69.4412	3.07E + 04	0.85927
	560-800	112.3109	6.35E + 06	0.72245
30	180-350	222.8000	4.53E + 18	0.97607
	350-560	76.6747	1.73E + 05	0.96755
	560-800	116.0614	1.67E + 07	0.75433
40	180-350	208.9409	2.67E + 17	0.97206
	350-560	68.8288	3.51E + 04	0.96040
	560-800	138.0287	2.66E + 08	0.75640
50	180-350	126.1363	1.19E + 10	0.97352
	350-560	63.6319	2.23E + 04	0.95839
	560-800	138.9907	4.73E + 08	0.73965

Kinetic compensation effect

From Table 3, it can also be seen that the variation of E gave rise to a variation in A, which can be explained by a predictable relationship between E and A ($\ln(A)=aE+b$). This relationship is referred to as kinetic compensation effect (KCE). It reflects a compensation effect between the exponential and pre-exponential factors in the Arrhenius equation (Andreasen *et al.* 2005). It can be used to calculate E or A at other experimental conditions according existing experimental data to reduce the number of experiments. And it can also be used to test the experimental data. The plots of $\ln A$-E of different methods are shown in Fig. 3. The KCE relationship between E and A has been found in the thermal decomposition of RBL.

(a) Coats-Redfern: 180-350°C   (b) Coats-Redfern: 350-560°C   (c) Coats-Redfern: 560-800°C
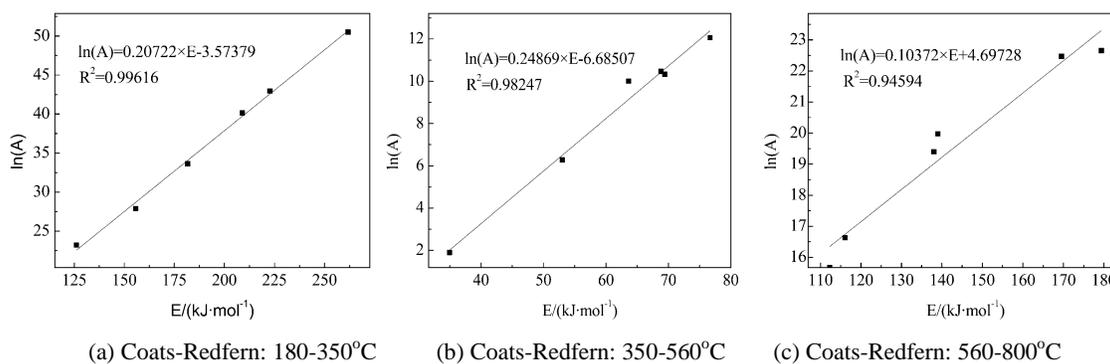
Fig. 3. Linear fitting between Y=E and X=ln(A) from Table 4 and 5

CONCLUSIONS

1. Three main weight loss stages were observed during RBL pyrolysis: 180 to 350 ℃, 350 to 560 ℃, and 560 to 800 ℃. The three stages obtained at different heating rates were similar, and the errors were within ± 10 ℃. Solid conversions were greatly influenced by the heating rates.

2. The most probable mechanism function of the RBL pyrolysis in nitrogen was determined to be the Avrami-Erofeev equation (n=4), which can be expressed in integral form as $G(\alpha)=[-\ln(1-\alpha)]^4$. It showed that during RBL pyrolysis, active centers become generated at random local points. And then, some of the active centers produced decomposition products or are deactivated, but the others continue to produce some new active centers.

3. *E* and *A* obtained by the Coats-Redfern method at different heating rates satisfied a kinetic compensation effect.

ACKNOWLEDGMENTS

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