Effects of titanium dioxide as direct causticization agent on the pyrolysis and steam gasification characteristics of straw black liquor solid

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ABSTRACT: Black liquor gasification process with direct causticization using titanium dioxide (TiO_2) is considered a promising technology for black liquor recovery in the future. In this study, laboratory-scale pyrolysis and steam gasification experiments with direct causticization using TiO_2 for straw black liquor solid were performed in a thermogravimetric analyzer and a tube furnace, respectively. Effects of TiO_2 on the pyrolysis and steam gasification characteristics are discussed on the basis of product analysis. The results show that after adding TiO_2 at temperature higher than 550°C, the direct causticization reactions happened, while the thermogravimetric behavior of the black liquor solid along with releasing pattern of carbon dioxide and carbon monoxide was changed. In the presence of TiO_2, swelling and agglomeration were prevented during the pyrolysis process. Meanwhile, sodium emission was significantly decreased and the steam gasification rate of the black liquor char at 850°C was substantially improved. The melting process during gasification was suppressed with direct causticization. Moreover, the yield of hydrogen was kept constant while the yields of carbon dioxide and carbon monoxide were increased during the steam gasification process with direct causticization.

Application: Better understanding of how titanium dioxide affects the pyrolysis and steam gasification characteristics of straw black liquor solid can provide knowledge for the development of black liquor gasification technologies.

Black liquor, the spent cooking liquor from the chemical pulping process, contains about 60% organic substances (mainly lignin) and 40% inorganic chemicals (mostly alkaline salts) on a dry basis [1]. In pulp mills, black liquor is combusted in a recovery boiler to produce steam and electricity, and cooking chemicals can be recovered by a subsequent limestone causticizing process [2]. However, this traditional recovery process has several major disadvantages in terms of high capital costs, low energy recovery efficiency, and smelt-water explosion hazard. Therefore, development of alternative recovery technologies including black liquor gasification has attracted great interest and has been extensively studied [3-6].

The black liquor gasification process with direct causticization using titanium dioxide (TiO_2) is considered a promising technology for future deployment [7–9]. In this process, the recovery boiler and lime causticizing process are replaced by a gasifier and a titanate cycle for direct causticization in the gasifier, respectively. Thus, significant energy and capital savings can be obtained [10].

A great deal of fundamental studies have been carried out to investigate the gasification and titanate direct causticization of kraft black liquor during the last decades. Titanium dioxide has been proven as the only practical chemical agent for direct causticization of kraft black liquor [11]. Higher carbon conversion along with lower sodium mass loss were obtained during kraft black liquor air gasification with direct causticization using TiO_2 [12]. It was also found that various forms of sodium titanates were present, depending on the initial TiO_2/Na_2O (sodium oxide) molar ratio [13,14].

Black liquor pyrolysis as an initial stage of gasification has also been studied. Alen et al. [15] investigated thermal degradation of four kinds of black liquor by thermogravimetry and found that the mass loss occurred mainly in the temperature range between 250°C and 500°C. Mckeough et al. [16] examined the release of sodium during kraft black liquor pyrolysis and suggested that sodium emission was a result of sodium carbonate (Na_2CO_3) reduction by carbon after the black liquor devolatilization stage. Whitty et al. [16,17] found that swelling, char yields, and component release during pyrolysis were influenced by pressure [17,18].

Most studies used black liquor from kraft wood pulping. Little work has been reported using black liquor from straw soda pulping. In China, approximately 48% of the virgin pulp is from

nonwoody feedstock. Almost half (48%) of the nonwoody virgin pulp was from alkaline straw pulping in 2013 [19]. Gea et al. [20] characterized the swelling properties of straw black liquor in different gasifying environments and found that black liquor swelled more in a nitrogen (N_2) atmosphere than in oxidizing environments. Experiments on the thermal degradation of straw black liquor were also carried out in a thermogravimetric (TG) system and a fixed-bed reactor [21,22].

Relative to kraft black liquor, information about the pyrolysis and gasification with direct causticization of straw soda black liquor is very limited. The objective of our study was to investigate the effects of TiO_2 as a direct causticization agent on the straw black liquor solid (BLS) pyrolysis and steam gasification, respectively. The black liquor pyrolysis and char steam gasification experiments were carried out using a thermogravimetric analyzer (TGA) and a laboratory-scale tube furnace. The evolution patterns of volatile products from the pyrolysis process were traced by Fourier transform infrared spectrometry (FTIR). Moreover, the properties of the gas and solid products from the pyrolysis and steam gasification process are discussed.

EXPERIMENTAL

Materials

The black liquor used in this study was obtained from a straw soda pulp mill in Xinjiang Province, China. The BLS was prepared from the original black liquor with a dry matter content of about 40% in spray drying equipment. The temperature of the hot air entering the spray dryer was about 270°C. The BLS was then sieved using an 80-mesh screen and maintained in powder state with particle size smaller than 200 μm. It was dried to constant weight at 105°C in an air-dry oven and then stored in a glass desiccator until use.

Two samples were prepared in the pyrolysis experiments: (1) BLS and (2) a mixture of BLS and TiO_2 (denoted by BLS+) based on the stoichiometric ratios of direct causticization reactions 2 and 3, shown later. Complete conversion of Na_2CO_3 can be achieved in theory when using a TiO_2/Na_2O molar ratio at 5:4. In accordance with the TiO_2/Na_2O molar ratio and sodium content in BLS, the BLS+ was prepared via a solid-solid phase mechanical mixing in a high-speed rotary stirrer with BLS/TiO_2 mass ratio at 10:4.

One black liquor carbon (BLC) sample used in the steam gasification experiments was derived from the pyrolysis of BLS at 500°C in N_2 atmosphere (denoted by BLC500). Based on the similar principle of BLS+ preparation, the mixture of BLC500 and TiO_2 (denoted by BLC500+) was also prepared based on the BLC500/TiO_2 mass ratio at 10:6. The same mixing process for preparing BLS+ was used. The BLC500 and BLC500+ were ground and sieved to result in particle size of approximately 200 μm for the subsequent steam gasification experiments.

Procedure

The analyses of organic elements, including carbon, hydrogen, nitrogen and sulfur in BLS and BLC500, were performed using an ELCHNOS elemental analyzer (Variosystems; Southland, TX, USA). Meanwhile, inorganic elements including sodium, potassium, silicon, and chlorine in BLS and BLC500 were analyzed with a wavelength dispersive AXIOS^{mAX}-PETRO X-ray fluorescence (XRF) spectrometer (PANAlytical; Almelo, The Netherlands). The proximate analysis of the samples was carried out in compliance with ASTM E870-82(2013) "Standard test methods for analysis of wood fuels." The results of the ultimate and proximate analysis of BLS and BLC500 are shown in **Table I**.

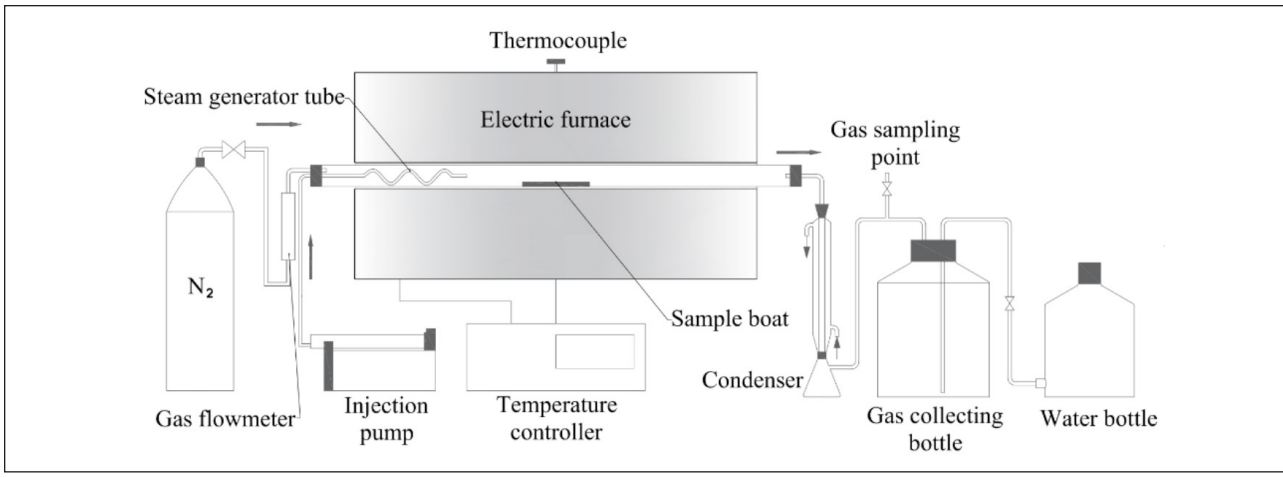
The TGA-FTIR experiments of BLS and BLS+ were carried out on a STA-449F3-Jupiter TGA (Netzsch Group; Selb, Germany), coupled with a TENSOR 27 Fourier transformation infrared spectrometer (ThermoFisher Scientific; Waltham, MA, USA). The weight loss characteristics and evolved patterns of volatiles during pyrolysis process were investigated. The experiments were conducted at a heating rate of 20°C/min within the temperature range of 100°C–900°C. High-purity argon was used as carrier gas at a flow rate of 20 mL/min. A sufficient amount of sample (30 mg) was used. The volatiles released from pyrolysis were transferred into a FTIR gas cell through a tube preheated to 150°C. The infrared spectrum range was 4000–667 cm^{-1} with resolution at 4 cm^{-1}.

In addition to TGA-FTIR experiments, pyrolysis experiments of BLS and BLS+ were performed in a laboratory-scale tube furnace at 500°C, 600°C, 700°C, and 800°C using high-purity N_2 as carrier gas with a flow rate of 300 mL/min. Gas composition and properties of the solid products from BLS and BLS+ pyrolysis were investigated. The flow diagram of the experimental apparatus is shown in **Fig. 1**.

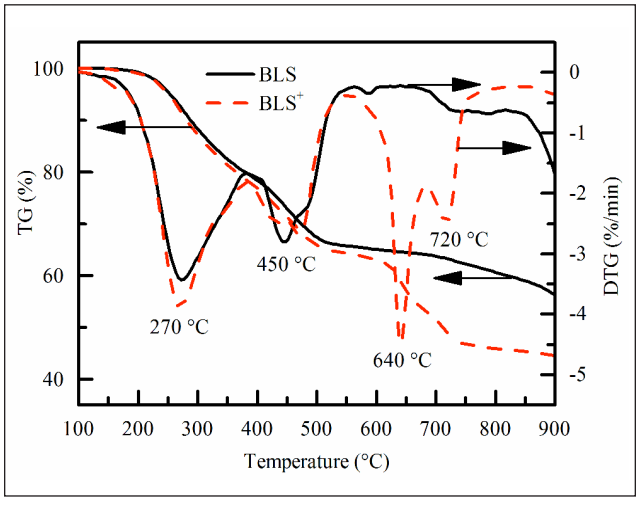
Sample	Proximate Analysis (wt%, dry basis)			Ultimate Analysis (wt%, dry basis)									Low Heating Value (MJ/kg)
	Volatiles Matter	Fixed Carbon	Ash	C	H	O[a]	N	S	Na	K	Cl	Si	
BLS	43.32	9.21	47.47	35.13	5.34	32.27	0.57	0.90	17.93	2.27	4.34	1.25	10.53
BLC500	13.28	16.57	70.15	32.44	4.42	23.23	0.30	0.98	26.18	4.08	6.36	2.01	6.81

[a] By difference.

I. Ultimate and proximate analysis of black liquor solid (BLS) and black liquor carbon (BLC500).



1. Flow diagram of the experimental apparatus.



2. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of black liquor solid (BLS) and BLS+ pyrolysis at a heating rate of 20°C/min.

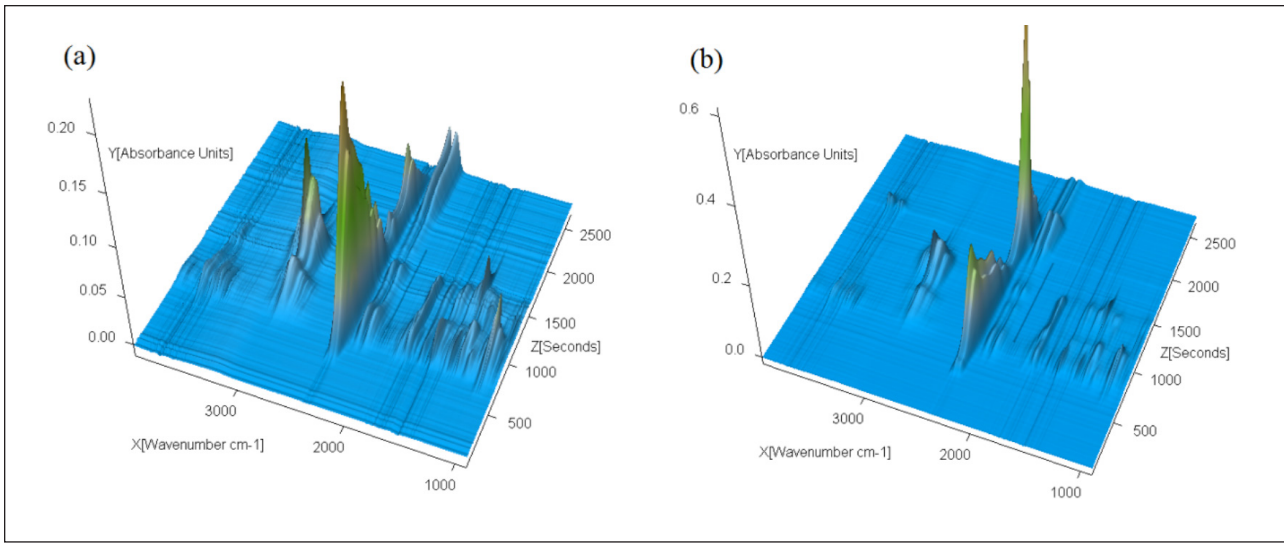
The quartz tube of the furnace was 1000 mm long with a 45 mm inside diameter. The samples were filled in porcelain boats sized 50 mm × 23 mm × 15 mm. To make more precise comparative analyses between the experimental results of BLS and BLS+, the mass of BLS in the samples used in each test was nearly the same. Here, the dosages of BLS and BLS+ used in each run were 2.50±0.01 g and 3.50±0.01 g, respectively. The residence time was set for 15 min in each run. The gas products released from pyrolysis were analyzed by a 7890A gas chromatograph (GC) (Agilent Technologies; Santa Clara, CA, USA) equipped with a thermal conductivity detector and two flame ionization detectors.

A STA-449F3 Jupiter TGA and a laboratory-scale tube furnace were employed to carry out the steam gasification of BLC500 and BLC500+ at 850°C. In the TGA experiments, high-purity N_2 was used as carrier gas at a flow rate of 20 mL/min. The temperature was raised from 100°C to 850°C at a heating rate of 10°C/min. A steam flow at a rate of 5 mL water (H_2O)/h was introduced into the system when the temperature reached 850°C and maintained for 1 h. About 20 mg black liquor char in BLC500 and BLC500+ was used in each test. In the tube furnace gasification tests, high-purity N_2 was used as carrier gas with a flow rate of 240 mL/min. The water used to generate steam was supplied by an injection pump (shown in Fig. 1) at a flow rate of 1 mL/min. The reaction temperature and residence time were set at 850°C and 8 min, respectively. For each run, 1.50±0.01 g BLC500 and 2.40±0.01 g BLC500+ were used. The gas composition and residual solids from steam gasification were analyzed by GC along with scanning electron microscopy (SEM), respectively.

RESULTS AND DISCUSSION

Effects of TiO_2 on the TG behavior of BLS pyrolysis

The TG and derivative thermogravimetric (DTG) curves for pyrolysis of BLS and BLS+ are shown in **Fig. 2**. The TG and DTG curves were calculated on the basis of the initial content of black liquor solid in BLS and BLS+. The pyrolysis process of both BLS and BLS+ can be divided into two stages between 100°C and 900°C. For BLS, the first stage corresponded to heating from 200°C to 550°C, accounting for 33.61% weight loss. Two DTG peaks occurred at about 270°C and 450°C, corresponding to the thermal decomposition of organics in black liquor. The second stage occurred at temperatures above 550°C, accounting for 9.72% weight loss. Maximum weight loss rate occurred at 900°C, perhaps due to the thermal decomposition of the organic compounds along with the reduction of Na_2CO_3 and the evaporation of elemental sodium produced from the black liquor char. The thermal mass loss behavior of BLS was consistent with earlier results reported for straw black liquor [21]. For BLS+, the first stage from 200°C to 550°C had 34.87% weight loss with two DTG peaks at about 270°C and 450°C, which was approximately the same as BLS. The second stage occurred between 550°C and 750°C, accounting for 17.59% weight loss with two DTG peaks at approximately 640°C and 720°C. This suggests the reaction between TiO_2 and Na_2CO_3 in black liquor char had occurred in addition to devolatilization of the black liquor char. When



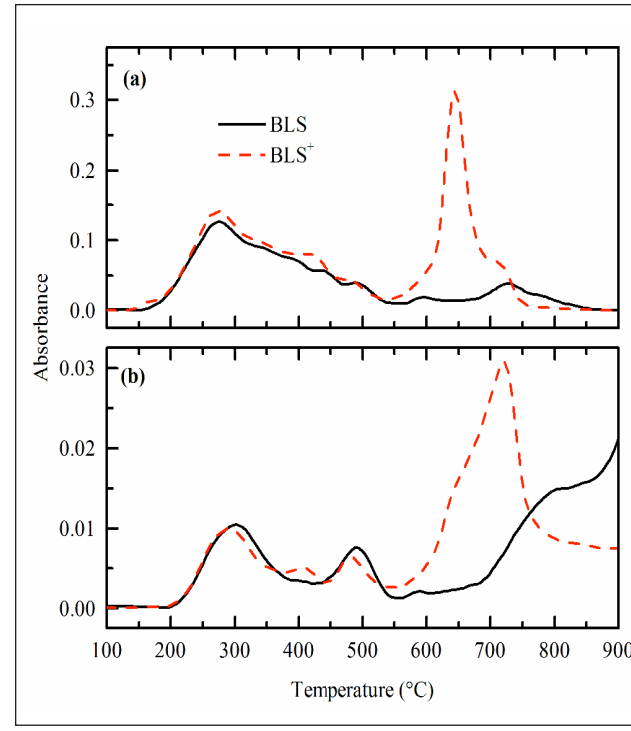
3. Three-dimensional Fourier transform infrared spectrometry (FTIR) spectra from pyrolysis of (a) BLS and (b) BLS+.

the temperature reached 900°C, 55.95% and 44.46% of the original weight remained for BLS and BLS+, respectively.

It could be concluded that the addition of TiO_2 mainly impacted the TG behavior of black liquor when the temperature exceeded 550°C but had no significant effects on the decomposition of organics in black liquor below 550°C. Analyzing the releasing patterns of evolved products during the pyrolysis can shed more light on this phenomenon, as seen in the next section.

Wavenumber (cm^{-1})	Functional Group	Vibration	Evolved Product
3559–3964	O-H	Stretching	H2O
1275–1775	H-O-H	Bending	
2058–2131	C-O	Stretching	CO
2150–2212	C-O	Stretching	
2240–2402	C=O	Stretching	CO_2
3024	-OCH3	Stretching	CH_4
2850–3200	C-H	Stretching	
1300–1400	O-H	Stretching	Phenols
1495–1525	⬡	skeleton	Aromatics
1145–1211	C-C	Stretching	Ketones
1700–1740	C=O	Stretching	
960–1131	C-O	Stretching	Alcohols
3559–3964	O-H	Stretching	

II. Main products of pyrolysis by three-dimensional infrared spectra.



4. Evolution profiles of (a) CO_2 and (b) CO from BLS and BLS+ pyrolysis.

Effects of TiO_2 on the releasing of evolved products during BLS pyrolysis

The three-dimensional (3D) plots of the FTIR spectra during pyrolysis of BLS and BLS+ are shown in **Fig. 3**. The functional groups, properties, and evolved products and corresponding wavenumbers are listed in **Table II** based on those reported in the literature [23, 24]. From Fig. 3 and Table II, it can be observed that carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and H_2O were the main light gases released, while phenols, ketones, aromatics, and alcohols were

the primary condensable volatile products. For these two samples, H_2O, CH_4, phenols, ketones, aromatics, and alcohols were released between approximately 600 s and 1600 s (from about 200°C to 550°C). This corresponds to the first pyrolysis stage in the TG curves (Fig. 2). After 1600 s (about 550°C), CO_2 and CO were the main gaseous products evolving from the process. The releasing of CO_2 and CO were substantially different between these two samples.

To illustrate this behavior more clearly, the releasing profiles of CO_2 and CO during BLS and BLS+ pyrolysis are presented in 2D form as shown in **Fig. 4**. No differences were observed between these two samples from 200°C to 550°C. The formation profile of CO_2 had one releasing peak at 270°C, while the formation profile of CO had two releasing peaks at 300°C and 480°C in this stage. The releasing profiles of CO_2 and CO were significantly different between these two samples when the temperature reached 550°C. The releasing profile of CO_2 from BLS was fairly flat and only had a small peak at 730°C. However, CO_2 release from BLS+ was increased sharply with temperature and peaked at 640°C followed by a rapid decline at 750°C. The direct causticization reactions had occurred after adding TiO_2, with more CO_2 being released. The direct causticization reactions could be expressed by Eqs. (1) and (2) [11]:

$$Na_2CO_3\,(s)+3TiO_2\,(s)\rightarrow Na_2O{\cdot}3TiO_2\,(s)+CO_2\,(g) \quad (1)$$

$$7Na_2CO_3\,(s)+5Na_2O{\cdot}3TiO_2\,(s)\rightarrow 3(4Na_2O{\cdot}5TiO_2)\,(s)+7CO_2\,(g) \quad (2)$$

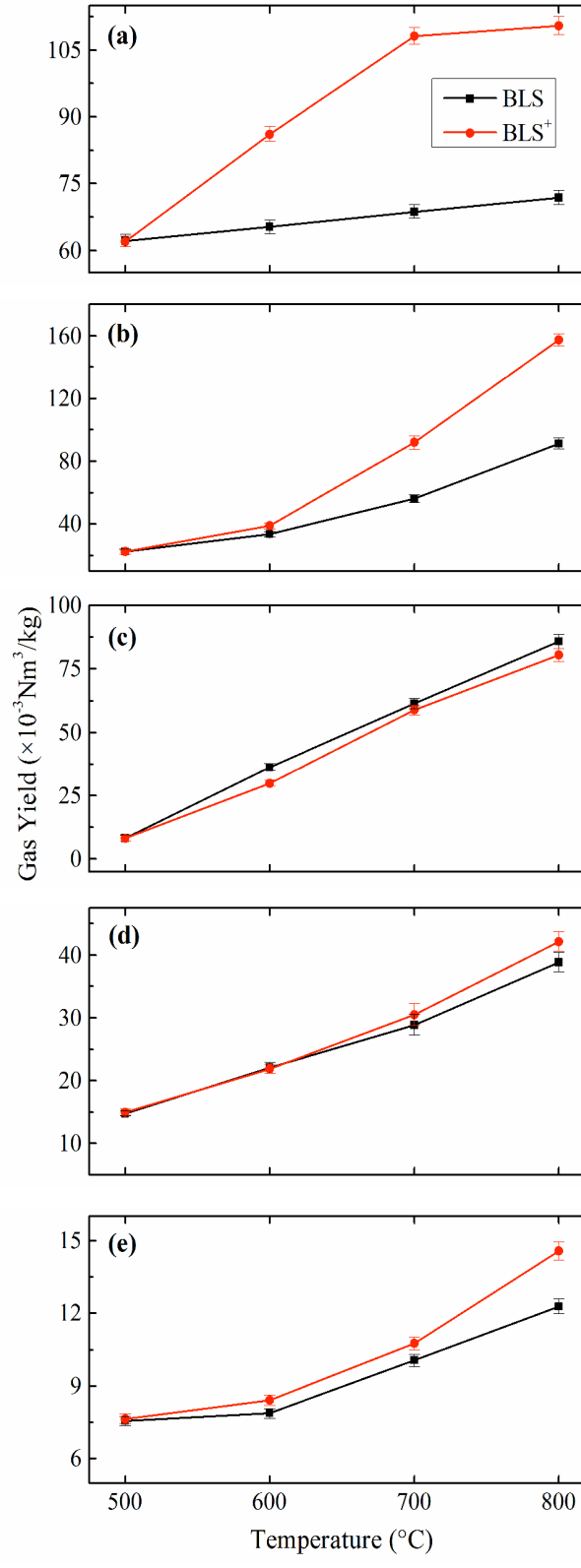
The releasing profile of CO from both BLS and BLS+ increased with temperature. However, the CO did not release from BLS until temperature reached 700°C while CO was released from BLS+ at 550°C and peaked at 720°C. The release of CO can be described by the carbothermal reduction reaction, Eq. (3), between Na_2CO_3 and organic carbon in black liquor char [25]:

$$Na2CO_3\,(s)+2C\,(s)\rightarrow 2Na\,(v)+3CO\,(g) \quad (3)$$

The gas-solid reaction between CO_2 and organic carbon in black liquor char, Eq. (4), can be substantially enhanced with a dramatic increase in CO_2 and thereby the release of CO. The direct causticization reactions, Eqs. (1) and (2), consumed a large amount of Na_2CO_3, which inhibited the carbothermal reduction reaction, Eq. (3), and reduced CO release above 800°C.

$$C(s)+CO_2\,(g)\rightarrow 2CO\,(g) \quad (4)$$

Figure 5 shows the yields of CO_2, CO, H_2, CH_4, and C_2 hydrocarbons (C_2H_6, C_2H_4, and C_2H_2) derived from pyrolysis of BLS and BLS+ between 500°C and 800°C. Here, the gas yield means the volume (at standard conditions) of the gaseous products from the pyrolysis process per unit mass of BLS. The production of all gases was increased with temperature. Gas

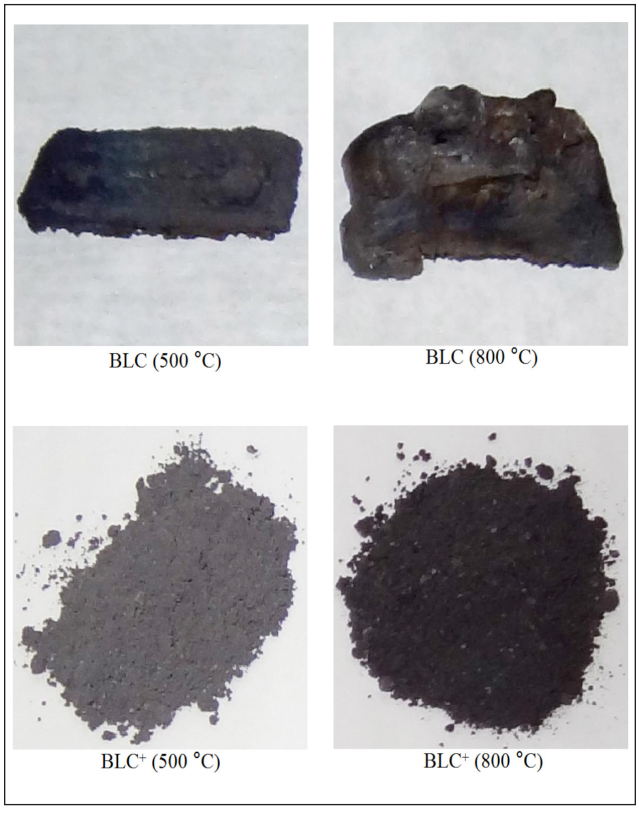


5. Yields of (a) CO_2, (b) CO, (c) H_2, (d) CH_4, and (e) C_2 hydrocarbons derived from BLS and BLS+ pyrolysis.

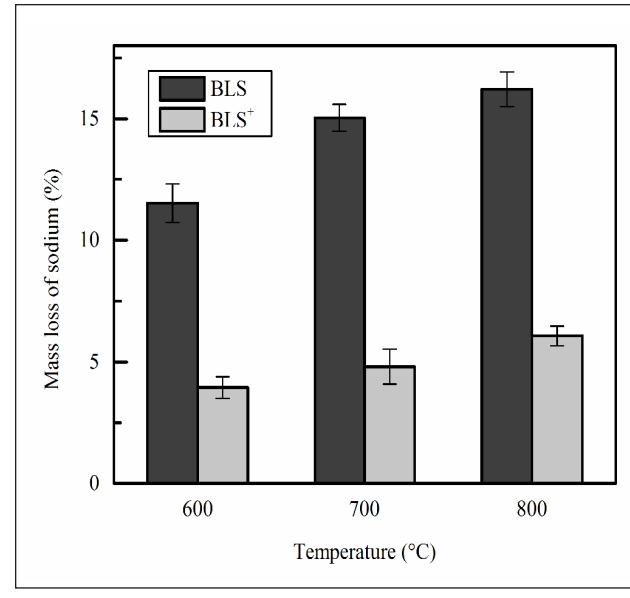
yields showed no obvious difference between BLS and BLS+ at 500°C. When the temperature reached 600°C, the yields of CO_2 and CO were substantially increased while the yields of H_2, CH_4, and C_2 hydrocarbons were unchanged with the application of TiO_2. This indicated that TiO_2 mainly affected the yields of CO_2 and CO. This is consistent with the results shown in Figs. 3 and 4. More CO_2 was generated due to the direct causticization reactions, Eqs. (1) and (2), between TiO_2 and Na_2CO_3 in black liquor char. Simultaneously, the yield of CO was increased as a result of the gas-solid reaction, Eq. (4), between organic carbon and CO_2.

Effects of TiO_2 on the solid products from BLS pyrolysis

Figure 6 shows the photographs of BLC and BLC+ derived from pyrolysis at 500°C and 800°C. It can be noted that BLC had been agglomerated and swelling of BLC had occurred at higher temperature (e.g., 800°C). This is in agreement with previous reports on the swelling behavior of black liquor during pyrolysis [18,20]. To the contrary, the BLC+ samples were maintained in good powder state and no agglomeration and swelling had happened at 500°C and 800°C. It was reported that the degree of agglomeration of black liquor could be decreased with additives such as kaolin and alumina [26]. Also, TiO_2 was proven an effective additive in reducing agglomeration during the straw black liquor pyrolysis.



6. Photographs of black liquor carbon (BLC) and BLC+ derived from pyrolysis at 500°C and 800°C.



7. Mass loss of sodium during BLS and BLS+ pyrolysis.

Swelling was mainly induced by devolatilization of the BLS [20]. Meanwhile, the agglomeration might occur during pyrolysis of BLS due to the presence of inorganic salts (primarily Na_2CO_3). However, Na_2CO_3 was converted into $Na_2O{\cdot}nTiO_2$ with TiO_2. Not only did $Na_2O{\cdot}nTiO_2$ have higher thermal stability than Na_2CO_3, it also affected the heat and mass transfer during BLS pyrolysis. Therefore, the escape of volatile matter was facilitated and the agglomeration and swelling were suppressed during the pyrolysis process as a result of adding TiO_2. It can be concluded that the form of inorganic salts has significant effects on the agglomeration and swelling behavior. Adding TiO_2 was significant for reducing the size of the equipment and maintaining good fluidity of materials during pyrolysis.

It is worth investigating the mass balance of sodium, the most important process element in the chemical recovery process. Data in **Fig. 7** show the mass loss of sodium during pyrolysis of BLS and BLS+. It was calculated on the basis of the sodium content in the black liquor solid and the black liquor char from the pyrolysis process. The mass loss of sodium became severe for both BLS and BLS+ with increasing temperature. The sodium loss of BLS pyrolysis was about 14% and only about 5% for BLS+ from 600°C to 800°C (i.e., the sodium loss was reduced approximately 9% with addition of TiO_2). A similar feature was observed in previous investigations of sodium emission during kraft black gasification with direct causticization using TiO_2 [12,27].

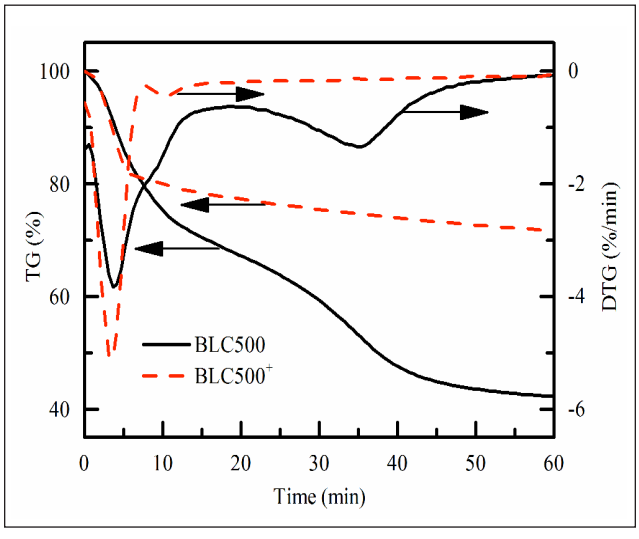
The carbothermal reduction reaction, Eq. (3), between organic carbon and Na_2CO_3 in black liquor char was accelerated with the increasing temperature [2,16,25]. Sodium emission was increased because the decomposition of Na_2CO_3 was intensified. After adding TiO_2, the carbothermal reduction reaction, Eq. (3), was suppressed owing to the direct causticization reactions in Eqs. (1) and (2). Therefore, the sodium release

was reduced, which would be helpful to improve the recovery efficiency of Na_2CO_3 in the subsequent chemical recovery process.

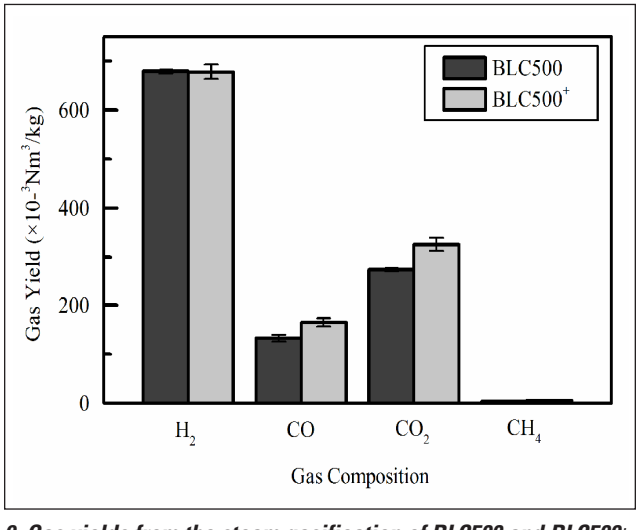
Effects of TiO_2 on the black liquor char steam gasification

Figure 8 shows the TG and DTG curves from the steam gasification of BLC500 and BLC500+ at 850°C for 1 h. The curves had been converted based on the mass of black liquor char in the samples and the normalization processing of the curves had been performed.

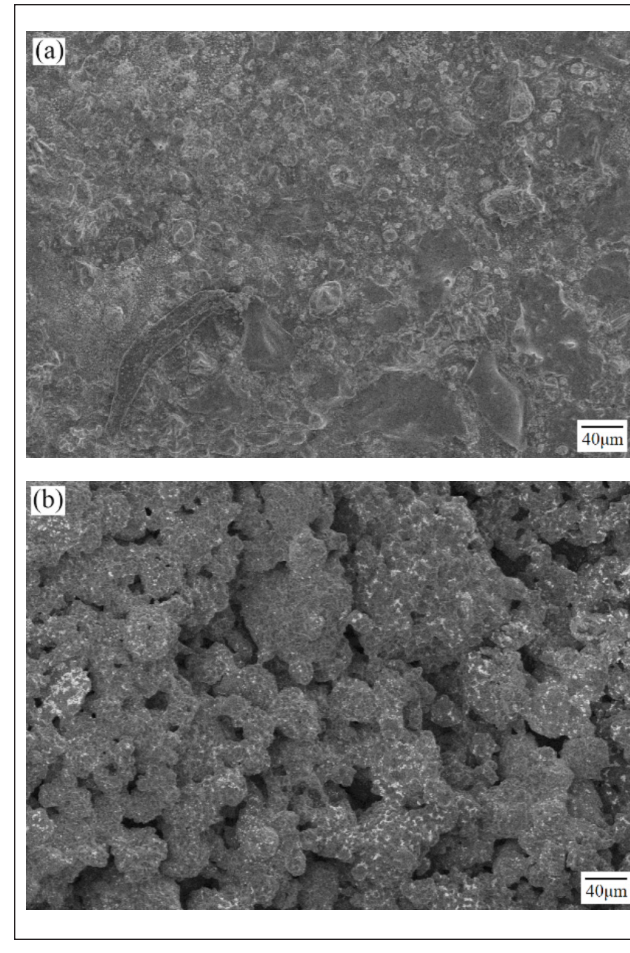
In the course of the constant temperature at 850°C for 1h, the mass of BLC500 was decreased by 57.75% accompanied by two DTG peaks at about 4 min and 35 min (-3.84% and -1.35%/min). For BLC500+, the mass was decreased by 28.30%, and a DTG peak at about 4 min (-5.13 %/min) occurred during the steam gasification process. It could be inferred that the mass loss of BLC500 during the steam gasification was probably derived from the gasification reactions between the steam and organic carbon in BLC500 and the evaporation of Na_2CO_3, which was carried out more remarkably as the organic carbon was reduced by the steam gasification. After adding TiO_2, the steam gasification of organic carbon was the main pathway for BLC500 mass loss as Na_2CO_3 had been converted into $Na_2O{\cdot}nTiO_2$ with no evaporation of Na_2CO_3. As a result, the range of BLC500+ weight loss was significantly reduced compared with that of BLC500. This suggested that the mass loss of Na_2CO_3 during the black liquor char steam gasification process was decreased enormously with the addition of TiO_2. Moreover, the DTG peak value of BLC500+ at about 4 min was apparently larger than that of BLC500, indicating that organic carbon steam gasification rate of the black liquor char had been increased significantly after adding TiO_2.



8. TG and DTG curves from the steam gasification of BLC500 and BLC500+ (850°C, 1 h).



9. Gas yields from the steam gasification of BLC500 and BLC500+ at 850°C.



10. Scanning electron microscopy (SEM) micrographs of residuals from steam gasification of (a) BLC500 and (b) BLC500+ at 850°C.

The yield of each gas from the steam gasification process of BLC and BLC+ is shown in **Fig. 9**. The gaseous products generated were mainly H_2, CO_2, and CO, with a small amount of CH_4. The gas could be considered as hydrogen-rich as the relative content of H_2 was about 60%. Furthermore, more CO_2

and CO were generated while the yield of H_2 was kept constant as a result of adding TiO_2. Compared with BLC500, the yields of CO_2 and CO obtained from BLC500+ steam gasification were increased by about 18.64% and 24.31%, respectively. More CO_2 was generated due to the direct causticization reactions in Eqs. (1) and (2). The yield of CO was also increased because the gas-solid reaction in Eq. (4) was facilitated by increasing release of the CO_2.

Figure 10 shows the SEM micrographs of gasification residuals from BLC500 and BLC500+ at 850°C. A serious melting phenomenon had come up and no porous structure existed for the residuals from BLC500 steam gasification. However, a slight agglomeration without melting had occurred and apparent pore structures, and good particle dispersion still existed in BLC500+ gasification residuals. One possible explanation was that Na_2CO_3 in BLC was converted into $Na_2O{\cdot}nTiO_2$ with higher melting point after adding TiO_2. The melting salts might hinder steam from reaching the carbon, which would exert a negative impact on the steam gasification process. However, the mass transfer between the steam and the carbon was intensified because the melting phenomenon was prevented after adding TiO_2. Hence, the gasification rate was improved in the char steam gasification with direct causticization at 850°C.

CONCLUSIONS

Effects of TiO_2 as direct causticization agent on the pyrolysis and steam gasification characteristics of the straw black liquor solid were presented. Thermogravimetric behavior of the black liquor solid and releasing pattern of CO_2 and CO were changed due to the direct causticization reactions after adding TiO_2 when the pyrolysis temperature was higher than 550°C. Swelling and agglomeration were prevented during the pyrolysis process in the presence of TiO_2. Meanwhile, the sodium emission was significantly decreased. In the char steam gasification with direct causticization at 850°C, the gasification rate was improved and the melting phenomenon was prevented. Furthermore, the yield of H_2 was kept constant while the yields of CO_2 and CO were increased during the steam gasification process with TiO_2. **TJ**

ABOUT THE AUTHORS

The black liquor gasification process with direct causticization using TiO_2 is considered to be a promising technology for future deployment. However, information about the pyrolysis and gasification with direct causticization of straw soda black liquor is very limited. This is the reason we chose this topic to research.

Most of the previous studies used black liquor from kraft wood pulping, and little work has been reported using black liquor from straw soda pulping. We used straw black liquor as a research object to complement the previous studies.

The most difficult aspect of this research was the detection of sodium emission during the pyrolysis process. To obtain more accurate results, we repeated the experiments more than three times. Both the X-ray fluorescence spectrometer and atomic absorption spectrophotometer were employed to analyze the sodium content in the samples.

From this research, we found that the yields of CO_2 and CO along with the releasing pattern of them were changed after adding TiO_2. In the presence of TiO_2, swelling and agglomeration were prevented during the pyrolysis process.

The most interesting thing was that the swelling behavior was prevented after adding TiO_2. From this research, we found that TiO_2 had significant effects on the solid and gaseous products from the pyrolysis and steam gasification process. Mills might optimize their existing recovery process with this information.

The presence of silica and the large amount of chlorine in the straw black liquor may affect the gasification process with direct causticization. Therefore, we will focus on these two elements in the next step.

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