



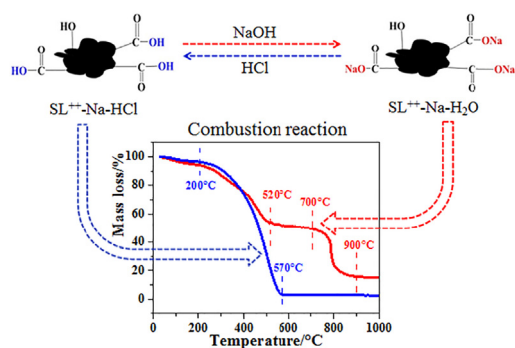
# Suppression of crosslinking combination of carboxyl functional groups with NaOH on combustion performance of Shengli lignite



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## GRAPHICAL ABSTRACT



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## ABSTRACT

It is important to inhibit the spontaneous combustion of lignite for its safe transportation and efficient utilization. Shengli lignite was treated with a NaOH solution and the as-prepared coal samples were extensively characterized by SEM-EDS, XRD, FT-IR, XPS, and Raman spectra techniques. The combustion properties of NaOH treated lignite were determined by TGA. The results show that NaOH treatment played a significant inhibitory effect on the combustion performance of Shengli lignite. The NaOH treated lignite showed two weight loss temperature regions. The temperature corresponding to the maximum combustion rate of Shengli lignite after the NaOH pretreatment was about 350–400 °C, higher than that of untreated sample, indicating that NaOH treatment significantly decreased the combustion reactivity of Shengli lignite. FT-IR and XPS analyses identified the analogous sodium polycarboxylic acid, originating from the crosslinking combination of carboxyl functional groups with NaOH. It is deduced that the suppressing effect of NaOH treatment on the combustion performance of lignite maybe attributed to the higher stability of analogous sodium polycarboxylic acid.

## 1. Introduction

Coal is the main energy source in the world, and its clean and

efficient utilization not only reduces environmental pollution, but also provides a vital chemical raw material [1–3]. Many low-rank coals such as subbituminous coal and lignite have been mined due to the changes

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in energy supply mode, especially in China. Lignite has a complex structure and mainly consists of three-dimensional macromolecule networks, various small organic molecules, and inorganic materials [4,5]. The number of volatiles and oxygen-containing functional groups present in lignite are much higher than that of high-rank coals [6–8]. These structural features make the lignite suffer from many disadvantages such as a high content of water and volatiles, low calorific value, lower ignition temperature, and a high tendency of spontaneous combustion [9–12]. The reaction of lignite with oxygen may result in self-heating and subsequent spontaneous combustion of coal mines and stock piles, leading to severe safety problems and property losses. This limits the utilization of lignite and causes safety problems [13].

Various factors such as inherent inorganic matter [14,15] and diverse functional groups, including alkyl, aryl, carbonyl, carboxyl and hydroxyl moieties affect the reactivity and stability of lignite in air. Some of these groups are more active in coal oxidation than others and trigger a series of exothermic reactions. These functional groups mainly determine the tendency of spontaneous combustion in coal [16,17]. Therefore, the inherent composition and structural characteristics of lignite are responsible for its spontaneous combustion. The presence of side chain linking to aromatic structures, bridge bond and low molecular weight organic components in lignite makes it highly chemically reactive, highly oxidizable at a low temperature and susceptible to spontaneous combustion [18,19]. Shengli lignite, a typical low-rank coal in Inner Mongolia, China, shows a high chemical reactivity because of the presence of many oxygen-containing groups [18].

Extensive studies have been conducted on the inhibition of spontaneous combustion of lignite [20–22]. At present, many different inhibitors are used to prevent the spontaneous combustion of coal. These inhibitors have two main roles in reducing coal oxidation: by preventing oxygen from reaching the active centers on coal surface and adsorbing water. Phase-transition aerosol and some inorganic salts such as NaCl, MgCl<sub>2</sub> and CaCl<sub>2</sub> function in this role [14,15,23]. However, their inhibition effects cannot be maintained for a long time due to the air flow and moisture, which indicates that they cannot continually play efficient prevention roles in the spontaneous combustion of coal [24]. The second type of inhibitor reacts with the active functional groups on coal surface, decreasing the number of active groups or inhibit free radical reactions. Oxidizing agents [25], such as permanganate, perchlorate and peroxide, as well as ionic liquids [26] and several inorganic salts [27], such as Na<sub>3</sub>PO<sub>4</sub> and Mg(Ac)<sub>2</sub>, work on this principle. However, the distribution of functional groups varies from coal to coal [28], and the reported inhibitors have neglected these variations in functional groups as well as the structural diversity of coal. Some of the inhibitors also have some disadvantages, such as an unstable inhibitory effect when combined with certain types of coal [29]. Therefore, it is essential to select a suitable inhibitor for a given type of coal and an efficient approach should be developed in selecting inhibitors to decrease the spontaneous combustion of coal. Alkali (NaOH) treatment is one of the effective methods for suppressing the spontaneous combustion of lignite, because this method can reduce the content of organic matter in coal, especially oxygen functional groups. Although many studies have been conducted on the NaOH treatment of lignite, the results are inconsistent and contradictory, mainly because of the complexity of coal microstructure. Nasir et al. [30] found that the alkali treatment removed minerals or oxygen-containing functional groups. Liu et al. [31] reported that the ignition temperature and activation energy of lignite changed after NaOH treatment. Feng et al. [32] reported that NaOH mainly reacted with the acid functional groups in lignite at low NaOH concentrations, but the changes in pore volume were not clear. Mohammad et al. [33,34] studied the effect of densification with NaOH on the thermal oxidation behavior and structure of Victorian brown coal. It revealed that a low concentration of NaOH made the brown coal more vulnerable to the spontaneous combustion, by disrupting the hydrogen bonding network and suppressing the crosslinking reactions that occur during the heating. In contrast, the

addition of NaOH at higher concentrations, decreased its spontaneous combustion tendency because of the strong electrostatic interactions.

The occurrence form of sodium in coal was also studied. Sathe et al. [35,36] studied the occurrence form of sodium in Victorian brown coal and found that coal pyrolysis was mainly affected by sodium carboxylate. However, Chen et al. [37] investigated the combustion of Xinjiang coal and found that the sodium present in the organic form promoted the combustion. The literature in material area reports that the thermal stability of a material is improved by combining alkali metal ions with small molecules of organic carboxylic acids. For example, Park et al. [38] prepared sodium batteries by utilizing the structural flexibility of small organic molecules and relatively high mobility of Na<sup>+</sup> in organic compounds. Disodium terephthalate formed by the reaction of NaOH with carboxyl functional groups in terephthalic acid increased the stability of the electrode material. Sánchez et al. [39] studied the thermochemistry of sodium, potassium, and magnesium biphenyl carboxylates and found that the strongly basic alkali and alkaline earth metal promoted the formation of thermally stable carboxylates with decomposition temperatures above 400 °C. Sodium carboxylates, e.g., RCO<sub>2</sub>Na (R = C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, C<sub>10</sub>H<sub>21</sub>, C<sub>12</sub>H<sub>25</sub>), are thermally stable compounds and therefore decompose at a high temperature, 350–560 °C, producing carbonates and ketones as the main inorganic and organic products, respectively [40]. In our previous study [41], it was also found that the ignition of Shengli lignite shifted to the high temperature region after the alkali-oxygen oxidation, and the combustion stability of lignite increased. However, the mechanism of inhibitory effect of NaOH treatment on the spontaneous combustion of lignite is not clear, and it is essential to elucidate the role of NaOH treatment by conducting more studies.

In this study, the effects of NaOH treatment on the texture and combustion properties of Shengli lignite were investigated. The structural evolution of samples by different treatments and the corresponding combustion properties were determined using XRD, Raman, FT-IR, and XPS. A possible mechanism of the inhibitory effect of NaOH treatment on the spontaneous combustion of lignite is also proposed based on the experimental results. This study provides a way to inhibit the spontaneous combustion of low-rank coals for the safe transportation and efficient utilization of lignite in industry.

## 2. Experimental

### 2.1. Materials

Air (O<sub>2</sub>: 20.94%, N<sub>2</sub>: 78.09%, Ar: 0.93%, CO<sub>2</sub>: 0.033%) was provided by Beijing Analytical Instrument. NaOH (analytically pure, purity > 96%), HCl (analytically pure, 38 wt%), and HF (excellent purity, 40 wt%) were purchased from Tianjin Fengchuan Chemical Reagent. All the chemicals were used as received without further purification.

### 2.2. Coal sample preparation

The used lignite sample labeled as SL was collected from Shengli coalfield (Inner Mongolia Autonomous Region, China). A proximate analysis showed that the received SL contained 47.6% moisture, 7.7% ash, 17.3% volatiles, and 27.4% fixed carbon. The received SL was crushed and sieved to 0.150–0.180 mm for subsequent treatment.

The demineralized SL sample was prepared using HCl and HF leaching. The lignite was crushed and ground to a fine powder with average sizes of 0.075–0.150 mm, then dried at 105 °C for 4 h. Approximately 50 g of SL was mixed with 500 mL of 19% HCl and stirred at room temperature for 24 h. The resulting slurry was filtered under vacuum, rinsed continuously with distilled water to remove the residual Cl<sup>-</sup>, and dried at 105 °C for 4 h to obtain the solid. This solid product was labeled as SL<sup>+</sup>. SL<sup>+</sup> was mixed with HF in a ratio of 1:6 (w/v) and stirred for 24 h. The resulting slurry was washed

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