



# Article Nitrated Phenols and PM<sub>2.5</sub> Reduction of High-Sodium Coal Combustion by Diatomite Addition in a Typical Residential Stove

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Abstract: Nitrated phenols from residential combustion aggravate the greenhouse effect and endanger human health. To search for an ideal residential fuel which produces low nitrated phenols, high-sodium coal, conventionally used in coal-fired power plants, has been used for residential combustion considering that the construction of civil stoves makes it easy to deal with slag fouling. In this study, we investigated pollutant emissions by comparing those produced by Jinyu coal, high-sodium coal and high-sodium coal with 5% diatomite. It was found that high-sodium coal mixed with 5% diatomite showed the most desirable nitrated phenols emission factors (EFs) and particle matter (PM) EFs. Originally, high-sodium coal generated more PM EFs because its more easily vaporized composition of sodium (Na) derived from Na compounds in high-sodium coal generated more condensation nuclei of particles. PM2.5 EFs of the high-sodium coal were as high as  $3.23 \pm 0.11$  mg/kJ, 11% more than that of Jingyu coal. However, it had lower EFs of nitrated phenols, whose nitrated phenol EFs in PM<sub>2.5</sub> were 2.3  $\pm$  0.2 mg/MJ, remarkably lower than that of Jinyu coal  $(4.0 \pm 0.4 \text{ mg/MJ})$ . This can be explained by the fact that high-sodium coal has less intermediate NOx for nitrated phenols generation. However, after 5% diatomite was mixed with high-sodium coal, the nitrated phenols EFs and PM EFs dropped by 60.9% and 53.3%, respectively, during the combustion process. Its abundant silicon (Si) and aluminum (Al) formed a high-melting-point substance with Na. Consequently, considerable pollutant reduction and combustion efficiency promotion were both achieved by 5% diatomite addition to high-sodium coal. It can be concluded that high-sodium coal with 5% diatomite is a promising alternative domestic fuel featuring excellent emission reduction effects, and easy-to-handle slagging in civil stoves.

Keywords: high-sodium coal; nitrated phenols; diatomite; residential combustion

# 1. Introduction

Brown carbon (BrC) is characterized with strong light absorption performance of UV and visible light [1–3]. Being an important component of BrC [4–6], nitrated phenols account for 20%–55% of the lighting absorption contribution of BrC in the wavelength range of 300–450 nm [7]. They are not only harmful to humans by causing carcinogenesis [8], but also pose considerable damage to forests [9,10]. It is also noticeable that nitrated phenols are primarily produced in combustion processes such as biomass combustion, coal combustion and vehicle exhausts [11]. Residential combustion, as one of the main sources of nitrated phenol emissions [12–15]., is also closely associated with haze, acid rain, green house effects, etc., which threaten the living environment and health of human beings [16,17]. A variety of nitrated phenols from residential coal combustion especially pose threats to women and children who stay indoors for extended periods of time [18]. Furthermore, their unsupervised emission also generates a great impact on global warming.



**Citation:** Qi, J.; Wu, J. Nitrated Phenols and PM<sub>2.5</sub> Reduction of High-Sodium Coal Combustion by Diatomite Addition in a Typical Residential Stove. *Fire* **2023**, *6*, 89. https://doi.org/10.3390/fire6030089

Academic Editor: Ali Cemal Benim

Received: 19 December 2022 Revised: 8 February 2023 Accepted: 23 February 2023 Published: 25 February 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). There have been a number of studies on nitrated phenols from the perspective of combustion. Previous research has focused on maturity and types of coal [15,19]. For instance, nitrated phenols in smoke from bituminous coal combustion are mainly nitrocate-chol and 5-nitrosalicylic acid, while anthracite combustion mainly generates 4-nitrophenol and 3-methyl-6-nitrocatechol [20]. In the liquid phase reaction, the free radicals of NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>, and NO<sub>3</sub>, as well as the groups such as nitrite and nitrate, participate in the reaction to form nitrophenol compounds [4,21–23]. During combustion processes, polycyclic aromatic hydrocarbons (PAHs) are oxidized by NO<sub>2</sub>, NO<sub>3</sub> or N<sub>2</sub>O<sub>5</sub> to produce nitrated phenol compounds with strong lighting absorption [24–26], extending the strong absorption wavelengths to longer ones [25]. Heavy concentration of NOx and SO<sub>2</sub> facilitates the generation of nitrated phenol compounds, which are positively affected by fresh coal combustion plumes [27].

High-sodium coal, with Na content greater than 2%, is held in reserves in large quantity in China, Australia, the United States, Germany and other countries. Because of its advantages of high volatility, low ash content and good combustion performance, high-sodium coal is an excellent coal for thermal power generation. However, its strong tendencies of slagging and contamination seriously limit its application [28]. At present, the utilization of high-sodium coal in an industrial boiler is mainly through the method of mixing it with weak contamination coal or soil [29–32]. However, this can only slow down the contamination and fails to fundamentally solve the problem [33]. Nevertheless, civil stoves have a completely different method to discharge slag from industrial boilers, which is convenient and fast. The ash and slag are released downward, and the problem of slag fouling in power plants can be avoided completely. However, there has been little research on high-sodium coal used for residential combustion to the authors' knowledge.

There are two main research questions in this study: (a) What is the combustion performance of high-sodium coal in conventional civil stoves? (b) Is the commonly used method of adding soil still effective in improving the combustion performance of high-sodium coal in civil combustion environments?

A simulated civil combustion system was constructed to investigate the combustion performance of high-sodium coal. Jinyu coal was selected as the reference object, because its composition is highly similar to high-sodium coal except for the much lower Na content. In addition, we added diatomite into high-sodium coal, following the common practice in industry for contamination reduction.

EFs of nitrated phenols, phenolics, PM, SO<sub>2</sub>, NOx, CO, CO<sub>2</sub> and metallic elements, and thermal efficiency (TE), were studied during the combustion process. Furthermore, the influence mechanisms of Na and diatomite on the emission of pollutants from the combustion of high-sodium coal were also explored. To our knowledge, this is the first attempt to study the adsorption effects of diatomite on nitrated phenols and PM discharge from high-sodium coal combustion. Our aim is to provide data and theoretical support for the application and promotion of high-sodium coal as a residential fuel.

#### 2. Materials and Methods

#### 2.1. Experimental Materials and Combustion Scheme

In this study, high-sodium coal from Wucaiwan coal mine of the East Junggar Basin of Xinjiang in China was selected for research, where a 390 billion ton reserve of high-sodium coal has been predicted to exist [33]. Meanwhile, a typical non-high-sodium coal, bituminous coal from the Jingyu coal mine, was chosen for comparative research. It is very similar to high-sodium coal except for its Na content. Table 1 details quality parameters of the coal samples. According to the chamber size of the most commonly used residential stoves and the usage habits of the residents, chucks with diameter of 3–5 cm were adopted for both the Jingyu and high-sodium coal samples. Although mixing soil with high-sodium coal is a conventional method to address the problem of slagging and contamination in coal-fired power plants, we made an innovative attempt to add diatomite from Shengxian County of Zhejiang Province as a third combustion sample because of its larger specific

surface area and strong adsorption performance. According to our pilot research, samples with 5% of diatomite outperformed the other samples with 1%, 3%, 7% and 10% diatomite contents (see Table S1). Therefore, 5% diatomite was dry-mixed with the high-sodium coal. In order to mix more evenly and fully, the diatomite was first crushed to  $\leq 1$  mm. The mineral composition of raw materials was then tested by an XRD analyzer (empyrean, panalytica B.V), with a scanning rate of 4°/min and scanning angle of 20°–80°. Detailed information of the ash composition of raw materials is listed in Table 2. For each coal sample, the combustion test was repeated 5 times to ensure the reliability and repeatability of the experiments.

Table 1. Fuel quality information.

Parameter	M <sub>ad</sub> <sup>a</sup>	M <sub>t</sub> <sup>a</sup>	A <sub>d</sub> <sup>b</sup>	V <sub>d</sub> <sup>b</sup>	FC <sub>d</sub> <sup>b</sup>	S <sub>t, d</sub> <sup>b</sup>	N <sub>ad</sub> <sup>c</sup>	C <sub>ad</sub> <sup>c</sup>	O <sub>ad</sub> <sup>c</sup>	H <sub>ad</sub> <sup>c</sup>	Q <sub>net, ar</sub> <sup>a</sup>
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(MJ/kg)
High-sodium coal	15.30	20.42	11.19	41.51	42.18	0.49	0.76	53.91	16.80	4.27	24.58
Jingyu coal	1.92	1.19	39.68	23.36	36.23	1.69	0.89	48.45	7.69	3.35	17.18

<sup>a</sup>  $Q_{net, ar}$ ,  $M_{ad}$  and  $M_t$  represent the net calorific value, moisture content in dry air and total moisture content, respectively. <sup>b</sup>  $S_{t, d}$ ,  $A_d$ ,  $V_d$ , and  $FC_d$  are total sulfur contents, dry ash, volatile matter and fixed carbon, respectively. <sup>c</sup>  $N_{ad}$ ,  $C_{ad}$ ,  $O_{ad}$ ,  $H_{ad}$  are the air-dried basis carbon, hydrogen, oxygen, and nitrogen contents, respectively.

Coal	SiO <sub>2</sub> (%)	$Al_2O_3$ (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	CaO (%)	MgO (%)	Na <sub>2</sub> O (%)	K <sub>2</sub> O (%)	TiO <sub>2</sub> (%)	SO <sub>3</sub> (%)
High-sodium coal	20.85	13.44	4.55	36.70	6.43	6.76	0.66	0.31	8.75
Jingyu coal	56.78	27.43	1.60	2.2	0.86	0.18	0.38	1.92	1.35
Diatomite	78.56	9.98	5.87	0	0.87	0.58	1.36	0.92	0.47

#### 2.2. Sampling Method

The sampling system used in this study was a dilution system composed of a combustion chamber and an exhaust pipe, which has been described in detail in previous papers [34-36]. It is briefly summarized as follows. The combustion chamber was a cube with a volume of 10 m<sup>3</sup>, where flue gas was diluted by injecting fresh air with an air blower built into the side. A stove and a kettle were positioned in the stainless-steel box. The diluted smoke was then sucked into a pipe by a high-power fan installed at the end of the exhaust pipe to keep the flue gas discharging smoothly. Sampling was conducted on the exhaust pipe (diameter of 22 cm) 4 m away from the combustion chamber. The inner wall of the combustion chamber was cleaned with fresh air for one hour before each test. The kettle was placed on the stove to test TE, and a control display unit at the spout was used to record the water temperature. In order to avoid the water vapor being released into the exhaust, the kettle with 4.0 kg of water was replaced with the new one as soon as the temperature reached the fixed maximum temperature of 90 °C. According to the capacity of the fuel chamber, a fixed 2.0 kg fuel was added to stove chamber each time. The burn-out (not being put out) method was adopted, and ash was cleaned from the bottom.

Simultaneous samples in two branches (PM<sub>2.5</sub> and TSP) with a cyclone (URG Corporation, Chapel Hill, NC, USA) were gathered on quartz (2500QAO-UP; 47 mm diameter, Pall Corp., Show Low, AZ, USA) and teflon membrane (47 mm diameter, Pall Corp., Show Low, AZ, USA). Each branch had two sampling ports for parallel sampling. Teflon film collecting PM<sub>2.5</sub> samples was measured to determine the concentration of Na, Al and Si elements per unit area by X-ray fluorescence spectrometer (NAS100, Nayur Technology Co., Ltd., Beijing, China). The gas composition was recorded and analyzed by the online gas analyzer. The flue gas, which was filtered via a quartz filter, flowed continuously into three flue gas analyzers over the entire combustion process. NO<sub>X</sub>, SO<sub>2</sub> and CO were monitored by flue gas analyzers (Model 43i, Model 42i and Model 48i, Thermo Environmental Instrumental Inc., Waltham, MA, USA). CO<sub>2</sub> was analyzed by CO<sub>2</sub> m (Model GC-0012, Gas Sensing Solutions Ltd., Cumbernauld, Scotland). Polyurethane foam (PUF, Tisch, Sparks, NV, USA) located below was used to collect the gas-phase SVOCs.

#### 2.3. Calculation Method of PM and Gaseous Pollutants EFs, and TE

EFs and TE were calculated in the same method as our previous reports [34–36]. The received mass-based  $EF_m$  of TSP and  $PM_{2.5}$  was calculated as Equation (1).

$$EF_m = M_f \times F/M_c \tag{1}$$

where  $M_f$  stands for particle mass collected, Mc represents the mass of burnt fuel, and F is the ratio of total flow rate in the dilution tunnel to the sampling flow rate.

The EFs of  $SO_2$ , NOx, CO, CO<sub>2</sub> were estimated as Equation (2).

$$EF_m = \frac{Q_f \rho_s}{M_c} \int_{\text{start time}}^{\text{extinction time}} C_s \, dt \tag{2}$$

where *Cs* is measured concentration of SO<sub>2</sub>, NOx, CO or CO<sub>2</sub>,  $\rho_s$  is the species density,  $Q_f$  is the gas flow rate in the tunnel.

 $EF_t$  (delivered energy-based EF) is derived by  $EF_m$  following the equation (see Equation (3)).

$$EF_t = EF_m / (TE \times Q_c) \tag{3}$$

The TE is derived from the increased temperature ( $\Delta T$ ) of the water in kettle. It can be expressed as Equation (4).

$$TE = M_w C_w \Delta T / M_c Q_c \tag{4}$$

where  $M_w$  is water mass in kettle,  $C_w$  stands for heat capacity of water, and  $Q_c$  is net calorific value as received.

The modified combustion efficiency (MCE) was determined as Equation (5).

$$MCE = \Delta CO_2 / (\Delta CO_2 + \Delta CO)$$
<sup>(5)</sup>

where  $\Delta CO_2$  and  $\Delta CO$  are the fire-integrated excess molar mixing ratios of CO<sub>2</sub> and CO, respectively, and refer to the EFs of the overall combustion process of CO<sub>2</sub> and CO.

#### 2.4. Phenolics and Nitrated Phenols Analysis

Nitrated phenols and phenolic compounds were extracted from the  $PM_{2.5}$  and TSP samples on the quartz membranes, which was treated in methanol under the condition of ultrasonic bathe. Then filtration, concentration with roto-evaporation, and evaporation under high-purity N<sub>2</sub> flow were performed successively. The concentrated liquid composed of nitrated phenols and phenolic compounds, etc., was detected by an ultrahigh performance liquid chromatography (UHPLC, Thermo Scientific, Waltham, MA, USA) tandem mass spectrometer (MS, LCQ Fleet, Thermo Scientific, Waltham, MA, USA), where negative ion mode and scanning mode were selected. This method was used in previous reports [20]. According to detection results, 12 nitrated phenols (including 2-methyl-4-nitrophenol, 2,4-dinitrophenol, 2,6-dimethyl-4-nitrophenol, 3-nitrosalicylic acid, 3-methyl-4-nitrophenol, 3-methyl-5-nitrocatechol, 3-methyl-6-nitrocatechol, 4-nitrocatechol, 4-nitrophenol, 4-methyl-2,6-dinitrophenol, 4-methyl-5-nitrocatechol, and 5-nitrosalicylic acid) and 8 phenolic compounds (including catechol, m-cresol, phenol, 3-methylcatechol, 4-methylcatechol, o-cresol, p-cresol, and salicylic acid) were calculated for  $EF_S$  based on quality and delivered energy, respectively. The PUF samples were cut into small pieces, and then extracted with 55 mL methanol on an orbital shaker for 2 h. Then the PUF sample was processed in the same way as the PM samples.

#### 2.5. Calculation Method of PM and Gaseous Pollutants EFs, and TE

Optical characteristics of the previously treated methanol extract samples used for nitrated phenols and phenolics detection (pretreatment solution in Section 2.4) were examined with an ultraviolet visible spectrometer (UV-4802S, UNIC, Shanghai, China). The calculation methods of a variety of parameters were taken into consideration, including absorption coefficient (Abs), mass absorption efficiency (MAE), and absorption angstrom index (AAE). Abs is the absorption coefficient under air condition. AAE and MAE are used to characterize the light absorption with the change of wavelength.

Abs at 365 nm (Abs<sub>365</sub>) was calculated as Equation (6).

$$Abs_{365} = (ATN_{\lambda} - ATN_{700}) \times \frac{V_1}{V_a \cdot l} \times \ln(10)$$
(6)

where  $V_1$  (mL) represents the volume of the PM<sub>2.5</sub> extracting solution, Va (L) stands for PM sampling volume, l (m) is the absorption optical path length,  $ATN_{\lambda}$  is light attenuation at a definite wavelength which can be indirectly measured by ultraviolet spectrophotometer, and  $ATN_{700}$  represents the light attenuation at 700 nm, used as the baseline for deduction.

 $ATN_{\lambda}$  was estimated as Equation (7).

$$ATN_{\lambda} = -\log(\frac{I}{I_0}) = l \times \sum_{i} (c_i) \times \varepsilon_{i,\lambda}$$
(7)

where  $c \pmod{L}$  is the concentration of lighting absorbing substances,  $\varepsilon$  stands for the proportional constant,  $l \pmod{r}$  represents the length of optical path.

MAE at 365 nm (MAE<sub>365</sub>) can be expressed as Equation (8).

$$MAE_{365} = \frac{Abs_{365}}{M}$$
 (8)

where *M* is the quality concentration of the soluble organics of the tested sample.

AAE was calculated as Equation (9)

$$Abs = K \cdot \lambda^{AAE} \tag{9}$$

where *K* is the constant of the PM mass concentration.  $\lambda$  (nm) is the wavelength of the light. *AAE* is obtained by linear fitting of Abs<sub>365</sub> in the wavelength range of 310–450 nm.

#### 3. Results

# 3.1. High-Sodium Coal: Lower EFs of Nitrated Phenols but Higher EFs of PM

The EFs of phenolics and nitrophenols obtained from the collected samples of  $PM_{2.5}$ , TSP, and gas phase for each burned fuel are exhibited in Figure 1 (details in Table S2). The average values of total phenolics in  $PM_{2.5}$  were  $0.9 \pm 0.1$  and  $1.8 \pm 0.2$  mg  $MJ^{-1}$  for high-sodium coal and Jingyu coal, respectively. The countervalues of nitrated phenols were  $2.3 \pm 0.2$  and  $4.0 \pm 0.4$  mg  $MJ^{-1}$ . It is indicated that high-sodium coal outperformed Jinyu coal in terms of phenolics and nitrated phenols EFs. The TSP, gas phase and  $PM_{2.5}$  demonstrated similar trends in terms of phenolics and nitrated phenols EFs, as shown in Figure 1.



Figure 1. EFs of phenolics and nitrated phenols in PM<sub>2.5</sub>, TSP and gas phase.

Figure 2 (details in Table S3) shows the PM<sub>2.5</sub> and TSP EFs of each burned sample. The PM<sub>2.5</sub> EFs were  $3.23 \pm 0.11$  and  $2.92 \pm 0.11$  mg/kJ for high-sodium coal and Jinyu coal, respectively. For TSP EFs, the values were  $6.16 \pm 0.21$  and  $4.85 \pm 0.12$  mg/kJ. This indicated that more PM was produced from high-sodium coal.



Figure 2. EFs for TSP and PM<sub>2.5</sub>, and TE for the tested coal samples.

# 3.2. High-Sodium Coal with 5% Diatomite: Effects of Diatomite on Reduction EFs of PM and Nitrated Phenols

Addition of diatomite can effectively reduce the EFs of nitrated phenols (as shown in Figure 1) and PM (as shown in Figure 2). When 5% diatomite was mixed with high-sodium coal, the EF of nitrated phenols in PM<sub>2.5</sub> was  $0.4 \pm 0.1$  mg/MJ, which achieved 60.9% and 77.5% reductions compared with high-sodium coal and Jingyu coal, respectively. In particular, diatomite addition also decreased the EFs of PM. PM<sub>2.5</sub> EFs of  $1.51 \pm 0.20$  mg/kJ indicated drops of 53.3% for high-sodium coal and 48.3% for Jingyu coal. TSP EFs presented an identical trend as well, which decreased from  $6.16 \pm 0.21$  mg/kJ to  $3.63 \pm 0.11$  mg/kJ after 5% diatomite was mixed into high-sodium coal. An obvious drop of 41.07% was

achieved. The value of high-sodium coal with 5% diatomite was remarkably 25.15% lower than that of Jingyu coal, and so were the nitrated phenols in TSP and gas phase.

### 3.3. Optical Characteristics of Methanol Soluble Organic from PM<sub>2.5</sub>

Optical characteristics of methanol soluble organic from  $PM_{2.5}$  are shown in Figure 3 (details in Table S4), which also represents OC concentration in  $PM_{2.5}$ . The AAE value of methanol soluble organic in  $PM_{2.5}$  from high-sodium coal combustion (5.93  $\pm$  1.32 in the wavelength range of 310~ 450 nm) was lower than of that of Jingyu coal (5.97 $\pm$  0.96). However, the lowest value of 5.8  $\pm$  1.25 was achieved in the high-sodium sample with 5% diatomite. This indicates that Na's presence effectively reduced wavelength dependence, which was further weakened by diatomite addition. Furthermore, Jingyu coal had a higher MAE<sub>365</sub> value of methanol soluble organic in  $PM_{2.5}$  than the other two samples. The same pattern was also discovered in the values of Abs<sub>365</sub>. OC in  $PM_{2.5}$  exhibited an identical declining order, with 33.26  $\pm$  3.33 mg/m<sup>3</sup> for Jingyu coal, 30.51  $\pm$  2.67 mg/m<sup>3</sup> for high-sodium coal and 25.54  $\pm$  3.12 mg/m<sup>3</sup> for high-sodium coal with 5% diatomite.



**Figure 3.** (a) AAE, (b) MAE<sub>365</sub> and (c) Abs<sub>365</sub> for methanol soluble organic in  $PM_{2.5}$  and (d) OC concentration of  $PM_{2.5}$ .

# 4. Discussion

According to a previous study [27], high concentrations of NOx and SO<sub>2</sub> can produce more nitrated phenols. The reduction of nitrated phenol EFs of high-sodium coal can mainly be attributed to the decrease of NOx and SO<sub>2</sub>, the important compounds for the formation of nitrated phenols as shown in Figure 4 (details in Table S5). The EFs of NOx from high-sodium coal ( $3.09 \pm 0.13 \text{ mg/kJ}$ ) burning were remarkably less than that of Jingyu coal ( $4.41 \pm 0.07 \text{ mg/kJ}$ ), and the EFs of SO<sub>2</sub> were  $4.64 \pm 0.21 \text{ mg/kJ}$  for the former and  $6.68 \pm 0.15$  for the latter. The increase of phenolics EFs for high-sodium coal compared with Jinyu coal also demonstrates that less NOx engaged with phenolics (see Figure 1).



Figure 4. EFs of NO<sub>x</sub>, SO<sub>2</sub>, CO and CO<sub>2</sub> for tested coal samples.

Our research revealed that the following aspects probably minimized NOx generation of high-sodium coal. Firstly, less N in high-sodium coal (see Table 1) was the direct reason for the decrease of NOx. It was noteworthy that during residential combustion with limited oxygen, N elements requiring higher activation energy were less likely to engage with oxygen when the three elements of N, C, and H compete for the O element [37]. Consequently, less NOx was produced. Secondly, Na played a catalytic role in the combustion of high-sodium coal, and more organic precursors that could otherwise produce nitrated phenols in PM were combusted [38]. Thirdly, Na catalysis significantly decreased the ignition temperature and peak temperature for PM oxidation [39]. More coke nitrogen, such as pyrrole nitrogen and pyridine nitrogen, which should have been burnt at a higher temperature, was not combusted and left in PM. This reduced the NOx formation, too. Fourthly, Na increased the activity of coke and promoted the heterogeneous reduction reaction of coke to NO. This promoted the conversion of fuel nitrogen to N<sub>2</sub> instead of NOx [37].

The PM EFs increase can be explained by nuclei development from high-sodium coal. Sodium chloride (NaCl) is a volatile component with high content in high-sodium coal. Most Na elements in NaCl are released into gas phase as a simple substance, form nanosized particles at the early stage of coal combustion and serve as effective nuclei [38,40,41]. The nuclei formed from Na then react chemically and condense with those suspended pollutants, such as NO<sub>2</sub>, SO<sub>2</sub> and hydrocarbons, leading to more PM being generated [28,42–44].

According to the previous literature, the emission of NO*x* is diminished by ash over wide temperature ranges [45]. Moreover, the adsorption effect of diatomite plays an important role in the reduction effect on PM EFs and nitrated phenols EFs. Phenolics and nitrated phenols are adsorbed onto diatomite, which has a large specific surface area, excellent adsorption performance and macropores [46,47]. The macropores are beneficial for the adsorption of bulky molecules and mass transportation [48]. The retention time of nitrated phenols and phenolics is prolonged, which consequently promotes complete combustion and inhibits early release. Other precursors of nitrated phenols are also burnt more completely. Therefore, the EFs of nitrated phenols and phenolics exhibited a marked reduction trend in the high-sodium sample mixed with 5% diatomite as shown in Figure 1. Furthermore, diatomite, rich in Si and Al, showed excellent capture performance for Na in

NaCl to produce infusible Na compounds. They were transformed into aluminosilicates with increasing temperature [40,49]. Hence, the reduced nuclei of Na led to the decrease of PM. This was further illustrated by the value of Na EFs in PM<sub>2.5</sub>. As shown in Figure 5 (details in Table S6), Na EFs of high-sodium coal in PM<sub>2.5</sub> dropped from  $8.06 \pm 0.31$  ug/kJ to  $5.03 \pm 0.10$  ug/kJ in the diatomite-added sample. Meanwhile, its EFs of Al and Si from diatomite in PM<sub>2.5</sub> rose significantly. This demonstrates that some Na reacted with gasified Si and Al in diatomite and formed aluminosilicates, which was left in the ash instead of being released. There were hence fewer nuclei for PM formation.



**Figure 5.** EFs of Na, Al and Si in PM<sub>2.5</sub> for different coal samples.

In addition, as shown in Table S3, the average modified combustion efficiencies (MCE) were 79.25  $\pm$  1.20, 77.70  $\pm$  1.20 and 90.89  $\pm$  2.40% for Jingyu coal, high-sodium coal and high-sodium coal with 5% diatomite, respectively. The values of carbon content in the bottom ash (C<sub>ad(bot)</sub>) were 26.89  $\pm$  1.78%, 31.26  $\pm$  2.20% and 24.58  $\pm$  1.68%, respectively (see Table S3). All of this suggests that diatomite remedies the defect of high-sodium coal and a higher MCE and a higher burnout rate of carbon was obtained. Our findings also agreed with previous research showing that the removal of Na improves the combustion performance of high-sodium coal [33,50,51]. This is closely related to the absorption ability of diatomite, which also captures PM precursor volatile matters and enables them to be combusted completely. The TE values of the three samples (7.8  $\pm$  0.5%, 7.5  $\pm$  0.3% and 10.6  $\pm$  0.3%, respectively) further verified this conclusion. The figure surged by 41.3% when the sample with 5% diatomite was compared with that without diatomite (see Figure 2).

The optical characteristics performance of methanol soluble organic in  $PM_{2.5}$  consisted of the EFs of phenolics and nitrated phenols in  $PM_{2.5}$ . Hence, coal generating fewer nitrated phenols presented lower AAE, Abs<sub>365</sub> and MAE<sub>365</sub>.

# 5. Conclusions

In this study, high-sodium coal mixed with diatomite was innovatively proposed for residential combustion. It can solve slag fouling simply by releasing the ash and slag downward. Some conclusions can be drawn as follows:

 High-sodium coal discharged fewer nitrated phenols but higher PM EFs compared with Jinyu coal with less Na content. However, the PM of high-sodium coal was substantially promoted because the more easily vaporized component of Na became more condensation nuclei of particles.

- (2) Diatomite can dramatically decrease the PM emission caused by Na and improve the combustion performance of high-sodium coal. After 5% diatomite was added into the high-sodium coal, PM<sub>2.5</sub> EF<sub>S</sub> sank to as low as 46.7%, and its EFs of phenolics and nitrated phenols also dropped significantly compared with high-sodium coal. The new mixture has therefore a superior combustion performance over Jingyu coal and high-sodium coal.
- (3) High-sodium coal with 5% diatomite is indeed an ideal solid fuel due to its advantages in nitrated phenols and PM reduction compared with Jingyu coal. Therefore, highsodium coal is not only a conventional energy source in power plants, but also an environmentally friendly and promising fuel for residential combustion when mixed with 5% diatomite.

**Supplementary Materials:** The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/fire6030089/s1, Table S1: Delivered energy-based EFs for phenolics and nitrated phenols in PM2.5, PM2.5 and TSP of high-sodium coal with different diatomite content. Table S2: Delivered energy-based EFs (average  $\pm$  standard deviation, mg MJ<sup>-1</sup>) of phenolics and nitrated phenols in PM2.5, TSP and gas phase; Table S3: PM EFs, MCE, TE and Cad(bot) for tested coal samples; Table S4: Optical characteristics and OC concentration for PM2.5 in flue gas from different coal combustion; Table S5: EFs of NOx, SO2, CO and CO2 for tested coal samples; Table S6: EFs of Na, Al, and Si in PM2.5 for different coal samples; Table S7: Received mass-based EFs (average  $\pm$  standard deviation, mg kg<sup>-1</sup>) of phenolics and nitrated phenols in PM2.5, TSP and gas phase.

**Author Contributions:** Conceptualization, J.W.; Data curation, J.Q.; Formal analysis, J.Q.; Funding acquisition, J.W.; Investigation, J.Q.; Methodology, J.Q. and J.W.; Project administration, J.W.; Resources, J.Q. and J.W.; Software, J.Q.; Supervision, J.Q. and J.W.; Validation, J.W.; Visualization, J.W.; Writing—original draft, J.Q.; Writing—review and editing J.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was founded by the National Natural Science Foundation of China (No. 51974311), the Doctoral Specialty Foundation of Xuzhou College of Industrial Technology (XGY2022EA05) and the Industrial R&D projects of Xuzhou College of Industrial Technology (XGY2022CXY05).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

**Acknowledgments:** We thank Guan, Meng from China University of Mining and Technology for her linguistic assistance during the preparation of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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