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## **Applied Energy**

journal homepage: www.elsevier.com/locate/apenergy



# Effect of minerals and binders on particulate matter emission from biomass pellets combustion



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#### HIGHLIGHTS

- The effects of minerals/binders on PM emissions from biomass combustion were studied.
- Diatomite can effectively reduce the emission of PM<sub>1</sub>.
- All the binders have no inhibitory effect on the PM emissions.
- Composite additives showed positive synergistic effect in reducing PM1 emissions.

#### ARTICLE INFO

#### Keywords: Minerals Binders Particulate matter Emission Pellets

#### ABSTRACT

In this study, the effect of minerals and binders on the emission characteristics of particulate matter (PM) from biomass pellets combustion is investigated using a fixed bed combustor combined with a Dekati low pressure impactor (DLPI). It was found that densification reduced PM emission as the pellets hindered the release of alkali metals in comparison to the bulk biomass. The generation of PM<sub>1</sub> was mainly due to the homogeneous condensation and heterogeneous coagulation of alkali chlorides and sulfates. Alkaline earth metals and Si played a dominant role in the formation of PM<sub>10</sub>. Diatomite in mineral additives could effectively reduce the emission of PM<sub>1</sub>, while the binders showed no inhibitory effect on the PM emission. Composite additives prepared with carboxymethyl cellulose (CMC) and diatomite showed a positive synergistic effect in reducing the emissions of PM<sub>1</sub> with the optimum CMC/diatomite ratio of 1:4. The results showed that composite additives of minerals and binders are excellent choices for the industrial production of biomass pellets from the view of increasing pellet quality and reducing PM emission.

#### 1. Introduction

Utilization of biomass resources can contribute to solving the energy crisis due to their abundance and renewable characteristics [1–4]. However, biomass resources generally have a low bulk and energy density, and are strongly dependent on seasonal and geographical conditions [5]. These disadvantages cause transport issues and block its efficient and large-scale utilization [6,7]. Fortunately, these difficulties can be solved with biomass densification technology [8]. The cost of storage and transportation can be greatly reduced after densification with an increased bulk and energy density [9]. Furthermore, densified biomass exhibits a uniform performance with controlled moisture content, which is advantageous for large scale utilization [5,10,11]. Therefore, over the last decades, biomass densification technology has

received increasing attention.

Densified biomass has the potential to replace the fossil fuels across all energy utilization fields [12,13], e.g. heat and electricity production [14,15], and chemical and liquid fuel synthesis [13]. Currently its utilization concentrates mainly on heat and electricity production with combustion technology. During the combustion process, volatile species tend to release to the gas phase and form fine particles with a aerodynamic diameters less than  $10\,\mu\text{m}$  (PM<sub>10</sub>). Roy and Corscadden [15] found that particulate emission from biomass briquettes combustion in a domestic stove varies significantly from 30 to 47 mg/Nm³ for maple and birch to 300–800 mg/Nm³ for Northland, Crackling and Envirolog. Combustion tests with agro-pellets, wood and peat were conducted in a pellet boiler (40 kW) and the results showed that dust emissions from citrus shell, wheat straw and sunflower husk pellets were higher than

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Table 1
Fuel Properties and inorganic components of the raw cotton stalk ash.

	Proximate analysis (wt%)				Ultimate analysis (wt%)					
Sample	$M_{ad}$	A <sub>db</sub>	$V_{db}$	FC <sub>db</sub>	$C_{db}$	$H_{db}$	$N_{db}$	S <sub>db</sub>	O <sub>db</sub>	LHV (MJ/kg)
Cotton stalk	4.55	2.74	78.61	18.65	45.72	5.43	1.09	0.24	44.77	15.97
Inorganic components wt%	MgO 9.06	$Al_2O_3$ 2.24	$SiO_2$ 3.87	P <sub>2</sub> O <sub>5</sub> 11.59	SO <sub>3</sub> 11.74	Cl <sub>2</sub> O 2.37	K <sub>2</sub> O 30.51	CaO 27.94	$\begin{array}{c} \mathrm{Fe_2O_3} \\ \mathrm{0.58} \end{array}$	Na <sub>2</sub> O -

Note: M: moisture, A: ash, V: volatile, FC: fixed carbon, ad: air dried basis, ab: dried basis, "-" means not detected.

emissions from peat combustion [16]. The emitted particulate matter is a major cause of atmospheric pollution especially in China, which also poses a hazard to human health. Research indicates that long term exposure to particulate matters increases the risk of asthma attacks, cardiopulmonary, and lung cancer [17,18]. With the rapid growth of biomass pellets utilization, PM emission form biomass pellets combustion can no longer be ignored and related researches are needed.

Research on PM formation during the coal combustion process has been extensively studied over the last decades [19–22]. Liu [19] and Yu [20] indicated that  $PM_{1-10}$  (particles of aerodynamic diameters between 1 and  $10\,\mu m$ ) generated from coal combustion is mainly composed of refractory elements (Si, Al, Fe), while Na and S are the dominant elements in  $PM_1$  (particles of aerodynamic diameters less than  $1\,\mu m$ ). The introduction of extrinsic minerals is a feasible method for reducing the transformation of alkali metals into PM by fixing these elements in the coarse ash particles via complex physical and chemical reactions [21,22]. Xu et al. [23] studied the effects of eight kinds of mineral additives on PM emission, and found that anatase was most effectively at reducing  $PM_{0.2}$  (particles of aerodynamic diameters less than  $0.2\,\mu m$ ) emission, while kaolin was conducive at reducing  $PM_{2.5}$  (particles of aerodynamic diameters less than  $2.5\,\mu m$ ) emission.

The main inorganic compositions of PM<sub>10</sub>, especially PM<sub>1</sub>, formed from biomass combustion are significantly different to those generated during coal combustion [24]. For biomass combustion, alkaline earth metals (Ca and Mg) play an important role in the formation of PM<sub>1-10</sub>, while K and Cl are abundant in PM1 [25]. Similar to coal, mineral additives have been employed in biomass combustion in order to mitigate PM emissions [17,26]. Bäfver et al. [26] investigated the influence of limestone and kaolin on the PM emission characteristics of oat grain combustion and found that kaolin addition reduced the PM emission, while no obvious influence was observed for limestone. Previous studies [17,26] showed that kaolin effectively reduces the concentration of coarse particles at the cost of increasing the fine particles emission. However, little attention has been given to investigating the effects of the addition of binders on PM emission. During the pelletization process, binders are commonly used to enhance the quality of the pellets [27-29]. Si et al. [9] found that the addition of carboxymethyl cellulose into wheat straw and cotton stalk pellets could effectively improve the durability, compressive strength and relaxed density. It can be expected, in light of the different compositions, that the introduction of binder will change the PM emission behavior. Previous research [15] found that the PM emission from waxed briquettes of Northland, Crackling and Envirolog is higher than from other non-waxed briquettes. Unfortunately, related studies are rare and the influence mechanisms of binders are not clear. Furthermore, composite additives with binders and minerals have been proposed with the aim of improving pellet quality and reducing ash-related problems [30-32].

However, PM emission characteristics for pellets with composite additives are still unknown and related studies are urgently required.

In this work, three kinds of mineral additives (kaolin, diatomite, and calcium hydroxide) and three kinds of binders (bentonite, calcium lignosulfonate, and carboxymethyl cellulose (CMC)) were introduced into biomass pellets to investigate the effect of these minerals and binders on PM emission. Based on the experimental results, composite additives with different mixing ratios of CMC and diatomite were selected to achieve a high performance of pellet with reduced PM emissions. This study provides scientific guidance for the industrial application of biomass pellets with an emphasis on the reduction of PM emissions.

#### 2. Experiments and methods

#### 2.1. Materials

Cotton stalk is an abundant biomass resource in China with the estimated amount produced being between 14 and 20 million tons per year [33-35]. In this work, a cotton stalk, that was collected in the Wuhan, Hubei province, was used. The as received fuel was ground and sieved to a particle size of less than 0.2 mm and then dried in an oven (105 °C) for 24 h. The proximate analysis, ultimate analysis and heating value of the fuel were measured using a SDTGA-2000 industrial analyzer (Las Navas, Spain), EL-2-type elemental analyzer (Vario, Germany), and automatic calorimeter (model 6300, Parr Instrument Company, Moline, IL, USA), respectively. The ash elemental composition of the fuel was measured by a X-ray fluorescence spectrometer (XRF, EAGLE III, EDAX Inc. USA). Results are shown in Table 1. The minerals then used were kaolin, diatomite, and calcium hydroxide and the binders were bentonite, calcium lignosulfonate, and CMC. All the chemicals were of analytical purity and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. The main compositions of the minerals and binders are shown in Table 2.

#### 2.2. Densification process

Pellets were prepared using an universal material testing machine (CMT5205, MTS, China). Minerals/binders (5 g, dry basis) and raw materials (95 g, dry basis) were first mixed in a beaker. Then, 15 wt% deionized water was added and stirred for half an hour by an electric stirrer (DJ1C-40) to ensure complete mixing. Approximately 1 g mixed fuel was weighed and placed in the empty slots of a mold. The pelletization was carried out at a pressure of 120 MPa with a 180 s holding time. Detailed information about the instrument can be found in the previous works [36].

**Table 2**The main composition of minerals and binders.

Minerals/binders	Kaolin	Diatomite	Calcium hydroxide	Bentonite	Calcium lignosulfnate	CMC
Composition	$\mathrm{Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O}$	${ m SiO}_2$	Ca(OH) <sub>2</sub>	$Al_2O_3\cdot 4(SiO_2)\cdot H_2O$	$C_{20}H_{24}CaO_{10}S_2$	[C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> (OH) <sub>2</sub> OCH <sub>2</sub> COONa]n

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