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# Potential of water-washing of rape straw on thermal properties and interactions during co-combustion with bituminous coal

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## HIGHLIGHTS

- Serial experiments were performed to investigate co-combustion of rape straw and coal.
- Alkali metals affect the extent of fuel interactions during co-combustion.
- Activation energy for washed fuel was lower than that for unwashed rape straw.
- Water-washing was proposed as pretreatment option for rape straw co-combustion.

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## ABSTRACT

The aim of this work was to study the thermal properties and interactions during co-combustion of rape straw (RS) before and after water-washing with bituminous coal. A series of experiments was conducted to investigate the properties and interactions during co-combustion of RS with bituminous coal (at 10, 20, 40 and 60% RS). The feasibility and potential of water-washing as an RS pre-treatment was also explored. Reactivity and the amount of heat released followed a quadratic trend, while changes to the degree of interactions between the fuels conformed to a cosine curve. Water-washing increased the ignition and burn-out temperatures and slightly decreased reactivity. Demineralization negatively affected the previously synergistic co-firing relationship, nevertheless, the amount of heat released increased by 10.28% and the average activation energy (146 kJ/mol) was lower than that of the unwashed blend (186 kJ/mol). Overall, water-washing of RS could prove a useful pre-treatment before co-combustion with bituminous coal.



## 1. Introduction

The use of biomass in waste-to-energy power generation processes is increasingly gaining importance because of its renewable and carbon-neutral characteristics (Hupa et al., 2016; Liu et al., 2013; Tamura et al., 2014). At a global level, the amount of electricity produced from burning biomass increased by an average of 13 TWh per year between 2000 and 2008 (Evans et al., 2010). China's National Energy Administration's 13th Five-year Plan targets increasing the share of biomass-based energy in China's power supply to 4% to decrease the country's reliance on coal and to help mitigate the haze crisis. Co-combustion of biomass blended with coal could not only help to dispose of abundant biomass resources in a more efficient manner, but could also substitute less environmentally friendly methods of power generation. During the current transition period, co-combustion is a viable option that is gaining momentum because of its ability to combat both the environmental burden and the energy crisis (Demirbas, 2003; Sahu et al., 2014). In 2015, the National Bureau of Statistics reported that the rapeseed yield in China was 15 million tons, which, using a product–residue coefficient of 2 (Zhou et al., 2011), meant that approximately 30 million tons of rape straw (RS) was also produced in that year. This suggests that RS offers a tremendous energy potential in China, approximately 226 TWh in the year 2015 based on the calculation derived from Niu et al. (2016a). However, the differences between the combustion characteristics of biomass and coal cannot be ignored; especially those that might limit biomass' use in conventional boilers, such as its low heating value and its ash components. Especially the slagging and fouling problems deduced from ash component in biomass, which would negatively affect the boiler, can't be ignored (Niu et al., 2016b; Nunes et al., 2016). To understand how co-combustion can better achieve a more effective and cleaner use of China's abundant RS

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resource, it is essential to take the fundamental thermal properties of the material into account.

Thermogravimetric analysis (TGA) has been extensively applied to analyze the combustion properties of a wide range of fuels (Wang et al., 2016; Xie and Ma, 2013). This method involves a small-scale simulation of the combustion process and yields characteristic combustion parameters, such as the ignition and burnout temperatures and kinetic parameters. TGA was used by Liu et al. (2016) to analyze the co-combustion properties and interactions of oil shale semi-coke with torrified cornstalk. Activation energy calculations showed that co-firing yielded a synergetic effect. Wang et al. (2011) had also previously identified interactions, especially at high temperatures, between oil shale semi-coke and cornstalk using an interaction index. However, in other TGA work researchers found no evidence of interaction between coal and biomass (Vhathvarothai et al., 2014). Recently, Zhang et al. (2016b) used TGA to study the combustion of coal gangue blended with pine sawdust and concluded that the thermal effect dominated the interaction within blends. According to Zhang et al. (2016b), the heat transfer from pine sawdust to coal gangue during blends combustion was greatly influenced by the thermal inertia of coal gangue. As a result, the thermal behavior between the blends was affected and the interaction emerged with primarily dominated by the aforementioned influence rather than the structural changes. Such diversity in the results suggests that the co-combustion behavior of biomass and coal depends on the fuels being used, which is of great importance to the design of equipment and operating parameters. However, investigations focusing on the co-combustion of RS and bituminous coal (BC) are lacking in the literature and thus required for the development of this technology option.

Alongside the combustion characteristics, another noticeable difference between the fuels is the straw's alkali metal content, which could be an obstacle to its clean use given its potential to damage the furnace (Niu et al., 2016b). Issues mainly arise because at high temperatures potassium in the straw can form KCl and $KSO_4$, which have low melting temperatures and so tend to condense at the surface of heat exchanger (Tortosa Masiá et al., 2007). Although co-combustion may offer a solution to mitigate alkali-related issues of straw combustion, the slagging hazard remains more serious than in the combustion of coal (Said et al., 2013).

Water-washing has been promoted as an environmentally acceptable, effective pre-treatment to eliminate alkali metals, with the amount of work published in this area steadily growing (Chen et al., 2017; Madanayake et al., 2017; Gudka et al., 2016; Chin et al., 2015; Teng and Wei, 1998). The pre-treatment of leaching as well as torrefaction were reviewed and appraised by Madanayake et al. (2017) The effect of water-washing on the thermal properties of rice straw (Said et al., 2013) and sorghum (Carrillo et al., 2014) have been reported, while Liu et al. (2015) showed that water-washing could improve the combustion characteristics of biochar. Considerable work has also been carried out to investigate the influence of water-washing on the pyrolysis and combustion properties of wheat straw, cornstalk, rice stalk, cotton stalk (Deng et al., 2013) and grasses (Fahmi et al., 2007). Despite this, to our knowledge, little work has investigated the characteristics and interactions of water-washed biomass that is then co-combusted with coal.

To address current gaps in the literature, the current work reports on a series of experiments that were designed to study the thermal properties and interactions for various RS–BC blends. The fuels, which are commonly used in China, are also studied individually. A second part of the work analyzes the feasibility and potential of applying water-washing treatment to the energy production process.

## 2. Materials and methods

### 2.1. Raw materials and water-washing

The RS used for this study was collected from Handan, Hebei Province, China. The BC was derived from Shenmu, Shanxi Province, China. BC samples were crushed until they passed through a 200-μm sieve, while RS samples were oven-dried at 45 °C for 48 h and then ground until they passed through a 20 mesh. The moisture content for BC was 2.71% with a particle size of 200 μm and the RS sample was 6.17% with 0.9 mm. Samples were then dried in an oven for 12 h at 105 °C for the following analyses.

As well as analyzing the materials individually, four RS–BC blends were also investigated. Blends with an RS mass fraction of 10, 20, 40 and 60% were formulated (denoted 10RS90BC, 20RS80BC, 40RS60BC and 60RS40BC, respectively).

Water-washing experiments were conducted using electromagnetic stirrer at room temperature following the set-up described by Liu et al. (2015). A total of 10 g RS was soaked and continuously agitated in 500 mL of deionized water for 6 h. The mixture was then separated by a suction filter with the solid residues of water-washed rape straw (WWRS) then dried and prepared as above.

### 2.2. Sample characterization

The composition of a given fuel can determine its properties and the combustion performance and associated potential environmental problems that may arise during the thermal conversion process (Vassilev et al., 2010). Thus, proximate, ultimate, alkali metal analyses and higher heating value determination were performed and the methods were listed in Table 1. The proximate analysis was carried out according to the ASTM E1131-08 standard for coal and using the procedure suggested by Munir et al. (2009) for RS using a SDT Q600 Thermogravimetric Analyzer (TA Instruments, New Castle, Pennsylvania, USA). For the ultimate analysis, the carbon, hydrogen, nitrogen and sulfur content were determined by a Vario Macro Elemental Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Deutschland), with oxygen then calculated by difference. The dry-ashing method was adopted for the analysis of alkali metals with the ash of each fuel produced according to the Chinese National Standards GB/T 28731-2012 and GB/T 212-2008. Subsequently, a chemical component analysis was performed by ARL DVAN'XP+ X-ray Fluorescence (Thermo Fisher Scientific, Waltham, Massachusetts, USA) (Karampinis

**Table 1**
The methods of proximate, ultimate, alkali metal analyses and higher heating value determination.

| | Standard methods/References | Test equipment/Equations |
|---|---|---|
| Proximate analysis | ASTM E1131-08 (Coal)<br>Munir et al. (2009) (Straw) | SDT Q600 Thermogravimetric Analyzer (TA Instruments, New Castle, Pennsylvania, USA) |
| Ultimate analysis | BS EN 15104:2011 | Vario Macro Elemental Analyzer (Elementar Analysensysteme GmbH, Langenselbold, Deutschland) |
| Alkali metal analysis | Karampinis et al. (2012) | ARL DVAN'XP+ X-ray Fluorescence (Thermo Fisher Scientific, Waltham, Massachusetts, USA) |
| Higher heating value | Smith et al. (2016) | HHV = (0.3383•Carbon%) + (1.422•Hydrogen%) − (Oxygen%/8) |