Catalytic and non-catalytic synergistic effects and their individual contributions to improved combustion performance of coal/biomass blends

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HIGHLIGHTS

- Catalytic and non-catalytic synergistic effects on co-firing were distinguished.
- Extent of synergistic effects were found dependent on coal constituents and rank.
- Non-catalytic synergistic effect was found more pronounced in fuel blends.
- Synergistic inhibition might occur as a result of competing synergistic effects.
- Individual contribution of catalytic and non-catalytic synergy was quantified.

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ABSTRACT

This study focuses on the synergistic properties of three types of coal when co-fired with oat straw at different blending ratios. The results demonstrated non-additive interaction between oat straw and coal samples. The catalytic effect of oat straw ash and the non-catalytic effect of its organic constituents on these coal samples were isolated and analysed to measure their contribution to the confirmed synergistic effects during co-firing. The results showed a level of synergy suppression between catalytic and non-catalytic effects due to the overlapping function of the catalytic AAEMs and the radical propagation promoted by organic content of biomass. A novel index, i.e., synergy combination efficiency, was therefore proposed and used to quantify the level of synergistic promotion or synergistic inhibition occurring during the co-firing of these fuel blends. It was found that at a blending ratio of 30 wt% oat straw, the Guizhou coal achieved a synergy factor (S.F) of 1.50, with non-catalytic and catalytic synergy contributing 69.1% and 30.9% respectively. This coal blend showed the highest synergistic promotion with a combined efficiency of 194%, which demonstrated the potential of the use of co-firing synergy to improve combustion performance of poor quality coals.

1. Introduction

Despite the damaging effects of coal utilization on the environment, there is a forecasted increase in coal consumption, particularly in China, with power generation expected to increase from 900 GW in 2015 to 1775 GW by 2030 [1]. The reserve of China's low rank coal (LRC) is estimated at about 46% of the total proven coal reserves [2]. Most of these LRCs are found in south-western provinces and north-eastern provinces and are considered low grade coals due to the high content of ash, sulphur and/or moisture. Almost three-quarters of China's electricity is generated from coal-fired power plants but the contribution of LRCs to this electricity generation remains inconsequential [3]. This is mainly due to several problems associated with the utilization of LRCs such as lower conversion efficiency, higher SO_2 & CO_2 emissions, the release of volatile organic carbons (VOCs) and particulate matter pollution. Recently, there has been an increase in the localised utilization of these low rank coals especially in the north-eastern provinces of China due to the low costs [4,5]. However, there is

a need to develop novel methods to utilize these low rank coals in a more efficient manner. Gani, Morishita [6] suggested that the effective large-scale utilization of LRC would require the improvement in ignition and burnout performance of the coal by adding supplementary fuels. Hence, co-firing of LRC with biomass can be advantageous due to the higher volatile matter content of biomass which is expected to lead to such improvements. The co-firing of coal with biomass is a simple but cost-effective approach to large-scale deployment of biomass in pulverized fuel utility boilers. However, owing to the significant difference in the combustion characteristics of biomass and coal, only partial substitution of coal is acceptable in order to reduce the degree of performance incompatibility to an acceptable level in utility boilers [7–9].

This partial substitution of coal with biomass offers benefits such as reduced emissions of NO_x, SO_x and greenhouse gases due to the low sulphur, low nitrogen and carbon lean nature of biomass compared with coal [10,11]. This will also improve energy conversion efficiency and economics of biomass utilization as well as its energy conversion efficiency since large-scale fossil-fired plants are more efficient than small-scale biomass plants. Furthermore, partial substitution can lead to the improvement in the efficiency power plants with minimal technical risks on implementation [10,12,13]. It also allows the usage of a wider range of fuels including low grade coals that are cheaper, hence providing cost incentives. Normally, ignition temperature, fuel reactivity, burnout and ash deposition behaviour are crucial characteristics for the determination of the suitability of solid fuels for co-firing [8,14–18]. However, inconsistent results were reported due to the conflicting influences (additive and synergy observations) of the biomass on the fuel blends. Some of the studies showed synergistic nature that resulted in improvement in combustion performance [19,20] while the others demonstrated additive behaviours that suggested insignificant change in combustion performance [20,21]. It is reported that alkali and alkaline earth metals (AAEMs) in biomass were found to enhance coal char reactivity in some cases [22] while differing significantly in others [23].

This study focuses on understanding the thermal decomposition characteristics of different coal types when cofired with oat straw. The interactions between the main biomass constituents and the coal were studied to differentiate catalytic and non-catalytic synergetic interactions and their implications on practical applications.

2. Material and methods

2.1. Samples

Three coal samples, i.e., an Australian coal (ATC), a Guizhou coal (GZC) and a Yunnan coal (YNC), and oat straw (OS) were used for this research. The preparation of samples for experimental study was conducted following the British standard BS EN 14780 and ISO 13909 [24,25]. All the fuel samples were milled using a Retsch SM 200 mill (Retsch, Germany) and then were sieved to a size of ≤106 μm. Oat straw was blended with the coal samples in two mass fractions, i.e. 10 and 30 wt%. The blending ratio corresponds to the typical co-blending conditions utilised in practice [19].

2.2. Fuel properties

2.2.1. Proximate and Ultimate analysis

Proximate analysis was performed using a thermogravimetric analyser (TGA) (STA 449 F3 Netzsch, Germany) using approximately 5–10 mg of a sample following the procedures described elsewhere [26]. The higher heating values (HHV) of samples were measured using an IKA Calorimeter C200 (IKA, USA), which was performed with approximately 1.0 g of each sample [27]. All experiments were repeated at least twice and the obtained results from these analyses were averaged. The ultimate analysis (CHNS/O) of the parent fuels was

conducted using a PE 2400 Series II CHNS/O Analyzer (PerkinElmer, USA) while the oxygen content was obtained by finding the difference [26].

2.2.2. Mineral composition

Mineral composition of ash samples of the unblended fuels was determined by using an X-ray Fluorescence (XRF) spectrometer and followed the procedure described elsewhere [26]. Mineral composition of the raw oat straw and the water leached sample was also obtained using the XL3t X-ray Fluorescence (XRF) spectrometer (ThermoFisher Scientific, USA).

2.3. Combustion characteristics

2.3.1. Thermal analysis

The combustion characteristics of individual fuels and their blends were investigated using a non-isothermal technique which was also adopted by other researchers [28,29]. The sample was heated in air (80 vol% Nitrogen and 20 vol% Oxygen) from 50 to 900 °C at a heating rate of 20 °C min^{-1} and a gas flow rate of 50 ml min^{-1}. Peak temperature (PT) was determined as the temperature at which the weight loss ($\frac{dw}{dt}$) of the sample reached its maximum. Burnout temperature (BT) was defined as the temperature at which the rate of burnout (mass loss rate) decreased to less than 1 wt% min^{-1} on weight basis.

2.3.2. Kinetic study

The kinetic parameters of the combustion process of coal and biomass blends can be well described by a first order reaction [30–32], which is the most effective solid-state mechanism responsible for co-combustion. Therefore, the activation energy are well represented by a first order Arrhenius plot, which can be calculated using TGA data collected for non-isothermal kinetics detailed elsewhere [33,34].

The degree of thermal conversion, α, can be defined as

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \tag{1}$$

where w_0 is the initial mass in mg, w is the mass of sample at time, t, while w_∞ is the final mass of the sample in mg. The reaction rate constant, k is expressed as:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{2}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is temperature (K), A is pre-exponential factor (min^{-1}), and E is activation energy (kJ mol^{-1}).

Using the differentiated law of conservation of mass, kinetic equation can be expressed as:

$$\frac{d\alpha}{t} / (1 - \alpha) = A\left(\exp\left(-\frac{E}{RT}\right)\right) \tag{3}$$

where α is conversion over a time span.

The kinetic parameters were then calculated based on conversions between 1% and 30%, which is the best region to measure reaction kinetics [35].

2.3.3. Catalytic effect of biomass ash

In order to determine the influence of catalytic minerals in biomass-derived ash on combustion process, organic compounds of oat straw was burnt out at a temperature below 150 °C using a plasma cleaner (PR300, Yamato Scientific, Japan) to prepare low temperature ash of oat straw (OS_LTA). The OS_LTA was then blended with all coal samples at 0.8 and 2.8 wt% on a weight basis and the thermal analysis of these blends was then carried out. Blending ratio of the ash was chosen based on ash content of the 10 and 30 wt% oat straw blends (0.7 and 2 wt%). Hence, 97.2 wt% coal + 2.8 wt% OS_LTA can be used to mimic the thermal behaviour of 70 wt% coal + 2 wt% OS_LTA. This will help in