



# A novel index for the study of synergistic effects during the co-processing of coal and biomass



Jumoke M. Oladejo<sup>a</sup>, Stephen Adegbite<sup>a</sup>, Cheng Heng Pang<sup>b</sup>, Hao Liu<sup>c</sup>, Ashak M. Parvez<sup>a</sup>, Tao Wu<sup>b,d,\*</sup>

<sup>a</sup> Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo 315100, China

<sup>b</sup> Municipal Key Laboratory of Clean Energy Conversion Technologies, The University of Nottingham Ningbo China, Ningbo 315100, China

<sup>c</sup> Department of Architecture and Built Environment, The University of Nottingham, Nottingham NG7 2RD, UK

<sup>d</sup> New Materials Institute, The University of Nottingham Ningbo China, Ningbo 315100, China

## HIGHLIGHTS

- A novel indicator was proposed to quantify the extent of synergy in co-processing.
- Synergistic interactions are biomass constituents dependent.
- AAEMs in biomass showed catalytic effect on synergistic interactions.
- High volatile content demonstrated non-catalytic effect on synergistic interactions.
- Synergistic interactions can be used to enhance combustion performance.

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## ABSTRACT

In this study, synergistic interaction between coal and biomass and its intensity were investigated systematically using a low rank coal and its blends with different biomass samples at various blending ratios. The catalytic effects of minerals originated from biomass were also studied. It was found that some of the minerals existing in the ash derived from oat straw catalysed the combustions process and contributed to synergistic interactions. However, for the coal and rice husk blends, minimal improvements were recorded even when the biomass and coal blending ratio was as high as 30 wt%. Biomass volatile also influenced the overall combustion performance of the blends and contributed to synergistic interactions between the two fuels in the blends. Based on these findings, a novel index was formulated to quantify the degree of synergistic interactions. This index was also validated using data extracted from literature and showed satisfactory correlation coefficients. It was found that at a blending ratio of 30 wt% oat straw in the blend, the degree of synergistic interaction between coal and oat straw showed an additional SF value of 0.25 with non-catalytic and catalytic synergistic effect contributing 0.16 (64%) and 0.09 (36%) respectively. This index could be used in the selection of proper biomass and proper blending ratio for co-firing at coal-fired power stations aiming at improving the combustion performance of poor quality coals via enhancing synergistic interactions during co-processing.

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## 1. Introduction

The low cost and carbon lean nature of biomass make it a promising energy alternative for the mitigation of CO<sub>2</sub> emissions [1,2]. However, the technical, economic and socio-ethical issues associated with the large-scale utilization of biomass have hindered its large-scale development [3,4]. One of the feasible solu-

tions to mitigate these issues is to cofire biomass with coal. This approach has become a general practice in western countries as it offers significant social and environmental benefits in terms of energy security, energy sustainability, greenhouse gas emission reduction, and economic developments [1].

In the past few decades, extensive research has been carried out in understanding the suitability of coal/biomass blends in various thermochemical conversion processes [5–7]. Synergistic effect was observed for some blends [1,8] while additive behaviour was also observed for some other blends [9,10]. The synergy observed in coal/biomass blends was mainly attributed to the catalytic and

\* Corresponding author at: Department of Chemical and Environmental Engineering, The University of Nottingham Ningbo China, Ningbo 315100, China.

E-mail address: [tao.wu@nottingham.edu.cn](mailto:tao.wu@nottingham.edu.cn) (T. Wu).

non-catalytic effect of biomass constituents on coal during co-firing. The non-catalytic synergistic effect is mainly associated with the high volatile content in biomass while catalytic synergistic effect is normally dictated by Alkali and Alkali Earth Metals (AAEMs) in biomass which enhances the reactivity of chars derived from coal [11,12]. Nonetheless, even though all biomass have AAEM species, the presence of synergy and its intensity are dependent on the physical/chemical properties of the fuels, especially the AAEM content [13].

To date, much effort has been made to understand the catalytic influence of AAEMs on the co-processing of biomass with coal. Many researchers have studied the catalytic performance of ash derived from high temperature ashing process ( $\geq 550$  °C) or some components of ash, such as K, Ca and Si [14]. However, most AAEM species are normally released at very low temperatures ( $< 500$  °C) [15]. Therefore the use of high temperature ash as catalyst did not show the catalytic effect of AAEMs originated from biomass. So far, not much work has been carried out to show the catalytic effect of minerals in biomass. In addition, although synergistic interactions [1,8] have been studied greatly in the past few decades, there is not much effort being made to distinguish the contribution of catalytic effect and non-catalytic effect on the overall synergistic interactions occurring, needless to say there is a reliable approach to quantify synergistic interactions and the contribution from catalytic and non-catalytic factors.

This paper focuses on the synergistic interactions between coal and biomass in the blends. Thermogravimetric analysis (TGA) was conducted to understand the catalytic effects of minerals (AAEMs) from biomass and the non-catalytic effects of volatile matters on the co-processing of biomass with coal. A novel indicator was therefore proposed to evaluate the extent of synergistic interactions as well as to quantify the contribution of catalytic and non-catalytic effects to these interactions.

## 2. Experimental

### 2.1. Coal and biomass samples

One coal and two biomass samples were used in this research. The coal, Yunnan Coal (YC), was obtained from Fuyuan Town (Yunnan Province, China), which is mainly used for industrial process heating especially in wine-making industry. The biomass samples, Oat Straw (OS) and Rice Husk (RH), were chosen to represent agricultural waste and agro-industrial residue respectively due to their abundance globally.

The samples were prepared following standard procedures described elsewhere (BS EN 14780 and ISO 13909) [16,17]. All the samples were initially reduced to a size smaller than 500  $\mu\text{m}$  using a cutting mill (Retsch SM 2000, Germany), and further milled to be smaller than 106  $\mu\text{m}$  using a Retsch SM 200 mill. Each biomass was blended with the coal in three mass fractions, i.e., 10, 30 and 50 wt%.

### 2.2. Proximate, ultimate and heating value analyses

Proximate analysis was performed using a TGA (STA 449 F3 Netzsch, Germany) while ultimate analysis of the samples was conducted using a PE 2400 Series II CHNS/O Analyzer (PerkinElmer, USA). In a TGA test, approximately 5–10 mg of the sample was placed in an alumina crucible following a testing procedure described elsewhere [18,19]. For ultimate analysis, approximately 1.5 mg of sample was placed in a platinum foil pan and tested in the CHNS/O Analyzer. The higher heating value (HHV) of a sample was measured using an IKA Calorimeter C200 (IKA, USA), which utilized approximately 1.0 g of the sample. All experiments were

repeated at least three times with the average value used as the final value.

### 2.3. Mineral composition of fuel

Mineral composition of the unblended fuels was determined by using an X-ray Fluorescence (XRF) spectrometer, the procedure adopted is described elsewhere [20].

### 2.4. Thermal analysis

Combustion characteristics of individual fuels and their blends were measured following a non-isothermal method, which was amended from literature [21,22]. In the test, 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  $\text{min}^{-1}$  and a gas flow rate of 50  $\text{ml min}^{-1}$ . Characterisation of pyrolysis was also conducted using the same technique under pure nitrogen atmosphere ( $> 99.9\%$ ). All experiments were repeated at least three times to ensure repeatability and accuracy.

The initiation temperature (IT) is the temperature at which 0.3 wt% mass loss rate of the sample was achieved after the release of moisture, which is normally used as an indication of the start of fuel decomposition. In fuel characterisation, peak temperature (PT) is inversely proportional to the reactivity/combustibility of the fuel, which was determined as the temperature where the weight loss ( $\frac{dw}{dt}$ ) of the sample reached its maximum. The burnout temperature (BT) represents the end temperature of the burning process, which was determined as the temperature when the rate of burn-out (mass loss rate) decreased to less than 1 wt%  $\text{min}^{-1}$  on weight basis. The ignition temperature at which the fuel burns spontaneously without external heat source was also obtained based on the method adopted by many others [23].

### 2.5. Performance indices

The ignition ( $Z_i$ ) and combustion ( $S$ ) index of the fuels and their blends were calculated based on the Eqs. (1) and (2) [23].

$$Z_i = \frac{\left(\frac{dw}{dt}\right)_{\max}}{t_i t_{\max}} \times 10^2 \quad (1)$$

$$S = \frac{\left(\frac{dw}{dt}\right)_{\max} \left(\frac{dw}{dt}\right)_{\text{av}}}{T_i^2 T_b} \times 10^6 \quad (2)$$

where

$\left(\frac{dw}{dt}\right)_{\max}$  is the maximum rate of mass loss ( $\% \text{ min}^{-1}$ );

$\left(\frac{dw}{dt}\right)_{\text{av}}$  is the average rate of mass loss ( $\% \text{ min}^{-1}$ );

$t_{\max}$  is the time at which the peak mass loss rate is attained (min);

$t_i$  is ignition time (min);

$T_i$  is ignition temperature (°C);

$T_b$  is burnout time (min).

### 2.6. Low temperature ashing

The low temperature ashing of biomass samples was performed using a PR300 Plasma Cleaner (Yamato Scientific, Japan). This device was used to burn off the carbonaceous components of the sample at low temperatures (less than 150 °C) under which the presence of minerals in biomass remains unchanged. The plasma was generated at a power of 200 W. Approximately 0.5 g of a sample was loaded on a glass crucible, placed in the ashing chamber, and exposed to pure oxygen at a flow rate of 100  $\text{ml min}^{-1}$  to

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