



# Physicochemical, kinetic and energetic investigation of coal–biomass mixture pyrolysis

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## ABSTRACT

The pyrolyzing behavior of solid fuel mixtures was quantified from the physicochemical, kinetic and energetic perspectives using scanning electron microscope and simultaneous thermogravimetric analyzer. The effects of water leaching on biomass pyrolysis and coal–biomass co-pyrolysis were investigated simultaneously from all three perspectives and the behaviors were cross-examined. The water leaching of the biomass significantly decreased the inorganic content and reduced its char yield. The activation energy for the leached biomass was calculated to be higher than the untreated counterparts, and the heat of pyrolysis of biomass increased on water leaching due to mitigation of secondary reactions. The co-pyrolysis of coal and biomass fuel mixtures exhibited a weighted additive physicochemical, kinetic and energetic behavior for the conditions tested in this study. It was shown that the interactions between leached biomass and coal during co-pyrolysis were minimal by successful simulation of co-pyrolysis kinetics using the individual kinetic parameters of coal and biomass pyrolysis reactions. The energetic properties of the fuel samples, viz. heat of pyrolysis and heat of gasification, were calculated on per unit volatile mass basis using a pyrolysis mathematical model. It was demonstrated that these energetic properties were additive in nature for coal and leached biomass co-pyrolysis.

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## 1. Introduction

Questions about the long-term availability of traditional fossil fuels, their geopolitical availability, and the tightening environmental restrictions have resuscitated the need to explore renewable and clean sources of energy to alleviate the concerns of ever increasing energy demand. Biomass is regarded as a carbon neutral and renewable source of energy, and carries high potential for sustainable development in the future [1–3]. Lignocellulosic biomass feedstocks can be converted into liquid (bio-oil), gaseous (bio-gas) and solid (bio-char) forms of fuels using various thermochemical conversion techniques [4].

The co-firing of coal and biomass mixture samples is an alternative fuel route to improve the economics and performance of gasifiers/reactors. Significant efforts have been directed in the literature towards realizing efficient coal–biomass co-firing from the existing scaled-up plants [5–11]. However, predicting the performance of scaled-up plants from laboratory based experiments is not straightforward. This is primarily due to the intricate co-pyrolysis behavior of coal and biomass fuel mixtures. The chemical composition of biomass is substantially different than coal, and unlike coal this composition varies widely among

different sources of biomass feedstocks [12,13]. Thus, an organized methodology is required to qualitatively and quantitatively characterize the co-pyrolysis of coal and biomass fuel mixtures.

Biomass feedstocks contain a substantial amount of alkali compounds, which significantly affects the operation of gasifiers [3,14–16]. Alkali compounds interact with the fuel samples to help catalyze the primary pyrolysis reactions [14,16–18]. However, the failure to remove condensed alkali compounds from downstream gases results in corrosion problems and gas/tar quality deterioration [3]. The knowledge of alkali composition is also necessary to avoid ash related problems in plants, including slagging, fouling and corrosion. Failure to predict these factors may lead to problems such as unplanned outages and higher operational costs in gasifiers [19,20]. Accordingly, usage of small proportion of biomass with coal mixtures in co-firing applications dissipates such negative effects [18]. Another way of reducing the influence of inorganic salts on biomass pyrolysis is to leach the feedstocks with water [21–26]. This process also reduces the nitrogen-oxide content in the resultant chars [18]. The removal of inorganic salts (ash) increases the fixed carbon percentage, and thus increases the energy density of the fuel. All these factors together produce a desirable effect for the plant operation [25]. However, the co-pyrolysis behavior of leached biomass with coal has not been thoroughly investigated in the literature [18].

To exploit the full potential of biomass energy, an improved understanding of coal–biomass co-pyrolysis process needs to be developed.

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Also, the effect of water leaching, and its benefits thereof on the co-pyrolysis process, needs to be investigated. For this reason, a systematic methodology needs to be developed for the complete characterization of different fuel mixtures undergoing thermochemical conversion processes. Thus, the current study characterizes physical, chemical, kinetic and energetic properties of solid fuels and their mixtures undergoing pyrolysis. There are instances of such characterization studies in the literature, viz. physicochemical [12,19,27–30], kinetic [31–38] and energetic [39–43]; however, previous studies have not considered all of the behaviors simultaneously in a single study nor has their impact on each other been documented. This study provides the properties of individual coal and biomass fuels and investigates the effects of water leaching and coal–biomass co-pyrolysis on the pyrolysis behavior.

## 2. Experimental

### 2.1. Materials and preparation

Samples used in this study included corn stover (CS) and switchgrass (SG) biomass feedstocks as well as bituminous US eastern steam coal (EC), namely, McClure River. The proximate and ultimate analyses for these samples are provided in Tables 1 and 2, respectively.

Biomass feedstocks were milled to produce finely grinded samples. The finely grinded biomass particles were sieved through calibrated sieves within 400–500  $\mu\text{m}$  range. To examine the influence of inorganic salts, the biomass samples were tested in both untreated (Raw) and distilled water washed (Leached) states, as mentioned in the literature [21–26]. For this purpose, sieved biomass samples were leached in a well stirred heated container (non-boiling water, temperature around 100 °C) for 2 h before air drying them at 110 °C. All four biomass samples were dried at 110 °C in air before testing in the STA, and the absence of moisture from samples was validated through negligible mass drop during separate TGA measurements from room temperature up to 150 °C.

Eastern coal was received in the form of powder with mean diameter lower than 400  $\mu\text{m}$  sieve. The EC sample was received in a wet state (about 30% moisture by weight), and thus was thoroughly dried in air at 110 °C for 4 h before use. Two more test samples were prepared by mixing EC with leached biomass samples in the ratio of 80:20 by mass to investigate interactions between coal and salt-free biomass samples. The biomass sample weight ratio was restricted to 20% by mass as per the guidelines mentioned in the literature [18,44]. Thus, in total seven test samples were developed and evaluated, including, EC, SG-Raw, CS-Raw, SG-Leached, CS-Leached, EC & SG-Leached mix (80:20 by mass) and EC & CS-Leached mix (80:20 by mass).

### 2.2. Instrumentation and procedure

The characterization of fuel was conducted using two instruments. An Environmental Scanning Electron Microscope (ESEM) was used to conduct the physicochemical characterization of the samples, while a Simultaneous Thermogravimetric Analyzer (STA) was used to characterize the samples based on its kinetic and energetic properties. The STA was also used to produce the pyrolyzed char and char oxidized ash samples from the fuel to conduct their physicochemical analysis.

**Table 1**  
Proximate analysis (dry basis).

Fuel	EC	SG-Raw	CS-Raw
% ash	10.50	2.86	5.01
% volatile	28.28	82.58	82.13
% fixed carbon	61.22	14.56	12.86
Calorific value (kJ/kg)	32734	18873	18778
MAF <sup>a</sup> calorific value (kJ/kg)	36574	19429	19769

<sup>a</sup> Moisture and ash free.

**Table 2**  
Ultimate analysis (dry basis).

Fuel	EC	SG-Raw	CS-Raw
% carbon	82.26	48.81	53.27
% hydrogen	4.75	6.32	5.67
% nitrogen	1.56	0.35	0.62
% sulfur	0.88	0.08	0.10
% ash	10.50	2.86	5.01
% oxygen	0.05	41.58	35.33

These analysis techniques and the sample preparation method are detailed below.

#### 2.2.1. Physicochemical characterization

The physicochemical characterization of the solid fuels, pyrolyzed char and char oxidized ash samples was conducted using a Quanta 600 ESEM. ESEM images provided an enlarged vision of samples with a minor loss in precision, thus enabling the qualitative characterization of the microstructure of fuel, char and ash samples. Multiple images of the samples were collected at 100 $\times$ , 1000 $\times$ , 5000 $\times$  and 10000 $\times$  magnification levels.

The ESEM instrument was further used with an Energy Dispersive X-ray Spectroscopy (EDX) stage to provide the elemental distribution at the surface of the sample. The major elements quantified on the sample surface included C, O, Si, Al, S, P, Na, Ca, K, Cl, Fe and Ti (for EC sample). Any other elements, if found in substantial amount in a sample, were also quantified. The hydrogen element was not quantified due to the limitations of the instrument. A rectangular area, spanning the maximum possible width and height of the particle at a particular magnification, was used to represent the elemental composition of the sample using EDX. The measurements were repeated for several particles of the sample, and an average composition value was used for the analysis ( $\pm 3\%$  variation for C and O element mass fraction measurement from particle to particle). The aforementioned elements were quantified on the basis of mass percentage. The tested fuel, char and ash samples were sputter coated with gold and platinum prior to the ESEM testing to enable imaging. The estimated sputter coated gold and platinum amounts were appropriately deducted from the subsequent elemental analysis of the sample. The preparation of pyrolyzed char and char oxidized ash samples is detailed in Section 2.2.2, along with the methodology for kinetic and energetic analysis of the fuel samples.

#### 2.2.2. Kinetic and energetic characterization

A NETZSCH 449 F1 Jupiter STA was used to characterize the gravimetric (TGA) and energetic (DSC) response of fuels during pyrolysis. Experiments were conducted in an inert atmosphere to avoid oxidation reactions during heating. For this purpose, the furnace was vacuumed and refilled with 99.999% pure nitrogen two times before analysis. Nitrogen flow rate of 80 ml/min was maintained during the analysis. The fuel samples were tested in the mass range of 4.5 to 5.5 mg. The initial and final sample mass was measured with a  $\pm 0.001$  mg accuracy balance. The tests were carried out from 25 °C up to temperatures sufficiently above the pyrolysis temperature of the fuels at atmospheric pressure (800 °C). A five minute residence time at 800 °C was provided to all the experimental and sample preparation (char and ash) runs conducted in this study. The tests were conducted multiple times to ensure repeatability. TGA experiments were found to be repeatable (peak DTG within  $\pm 2\%$ ) and superimposed to check the accuracy of measurements. Temperature measurements were calibrated with melting point of five pure metals and the measurements were accurate within  $\pm 1$  °C. The STA experimental procedure and its calibration methodology have been explained in a previous publication [45].

For pyrolysis energetic analysis, the tests were conducted at a constant heating rate of 20 °C/min in an inert nitrogen atmosphere. A previously developed and validated pyrolysis mathematical model [45] was used in conjunction with the experimental data to quantify

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