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Effect of temperature on the enrichment and volatility of 18 elements during pyrolysis of biomass, coal, and tires

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ABSTRACT

The effect of temperature on the enrichment and volatility of elements during pyrolysis of brown coal, biomass pellets, and used tires was evaluated. The elements investigated included barium (Ba), bromine (Br), calcium (Ca), chlorine (Cl), chromium (Cr), copper (Cu), iron (Fe), potassium (K), manganese (Mn), phosphorus (P), lead (Pb), rubidium (Rb), sulfur (S), silicon (Si), strontium (Sr), titanium (Ti), yttrium (Y), and zinc (Zn). The pyrolysis experiments were conducted in a semi-continuously operated triple-screw reactor at four temperatures: 500, 550, 600, and 650 °C. An enhancement in the total contents of elements was observed in all materials due to pyrolysis. The highest enrichment of elements was observed in char from pyrolysis of coal, followed by biochar, and char from pyrolysis of tires. Differences between investigated materials were also observed regarding volatility of elements and they were attributed primarily to (i) discrepancies in the composition of raw materials, (ii) secondary reactions of chars, and (iii) the affinity and occurrence of elements.

1. Introduction

Coal is the second largest source of energy in the world relative to petroleum and other liquid fuels [1]. Its utilization, however, is expected to decline after 2025 due to the policies and investment decisions giving preferentiality to cleaner and increasingly competitive energy sources such as renewable energy sources [2]. Biomass and wastes, with biomass being the number one renewable source of energy worldwide, are predicted to deliver up to 13% of the world's total energy consumption by 2040 [1,2]. The importance of utilization of biomass and waste (e.g., tires) as an energy source is associated primarily with their increased production and environmental concerns related to their disposal [3,4]. It is not however exempt from problems as biomass and tires, as well as coal, contain elements that can be potentially hazardous. These elements are then distributed diversely among the products of thermal conversion processes and may (i) result in severe harm to the ecosystem and human health [5], (ii) lead to serious problems such as slagging, agglomeration, deposition and heated side corrosion in the thermal utilization process [6], and/or (iii) act as a catalyst [7].

The majority of prior research has been focused on the behavior of elements during thermal utilization processes of coal such as combustion and gasification. It has been found that the release of elements depends on the temperature of their volatility. Contingent on this volatility, elements can be grouped into three categories: non/low/semi-volatile, volatile, and highly volatile [5]. Volatility on the other hand may be related to (i) the affinities, concentrations, and modes of occurrence of elements; (ii) the interaction between elements; (iii) physical changes and chemical reactions of elements during thermal conversion processes; and (iv) operating parameters of thermal conversion processes such as temperature [5,8].

The number of studies investigating the effect of temperature on the release, distribution and/or volatility of elements during pyrolysis of coal is fairly limited. Yiwei et al. [9] investigated the release and enrichment of 44 elements during pyrolysis of coal and concluded that as the pyrolysis temperatures increased, the release ratio of elements increased as well. The effect of pyrolysis temperature was further confirmed by Yiwei et al. [10] in their following study on the occurrence and transformation behaviors of 12 elements. In addition, it was found that the presence of these elements was associated with organic material and residue [10]. Similar findings were reported by Wei et al. [8] who studied the volatilization of elements during oxidative pyrolysis of coal. It was found that the increase in volatility of elements with an enhancement of pyrolysis temperature was vastly attributed to silicates [8]. Arsenic (As) was found to be the most volatile, and antimony (Sb), lead (Pb), zinc (Zn), cadmium (Cd) and chromium (Cr) were found to be moderately volatile [8].

In the case of biomass, the majority of prior research has been focused on the behavior of alkali and alkaline metals during pyrolysis, while the behavior of the other elements has yet to be adequately

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examined. Koewn et al. [11] pointed out that the behavior of alkali and alkaline metals during pyrolysis of biomass may be different from the behavior of these metals in coal, particularly at a temperature <900 °C. The variation in the behavior was likely due to the differences in the structure and composition between both materials [11]. It was also found that the volatilization of alkali and alkaline metals depended on biomass properties, valence of metal species, heating rate, and temperature [6,7], wherein the bulk of release took place at a temperature >500 °C and was attributable to the evaporation of inorganic salts [12,13]. The release of alkali metals <500 °C was primarily associated with decomposition of the organic structure [12,13].

Similar to biomass, the behavior of elements during pyrolysis of waste tires has not been broadly investigated as the information available typically centers on leaching of heavy metals. The information that is lacking is with regard to either the evaluation of the enrichment and volatility of elements or the effect of pyrolysis temperature on these parameters. Since tires can contain significantly high amounts of some elements (e.g., Zn and Fe) [14], more detailed knowledge about the behavior of these elements during pyrolysis would be beneficial from a technological, environmental, and economic vantage point.

Therefore, the purpose of this study was to compare and more comprehensively understand the effect of temperature on the enrichment and volatility of 18 elements during pyrolysis of three diverse materials. Specifically, coal, biomass, and tires were selected for evaluation due to (i) their greatest utilization in the production of energy, among fossil fuels (coal) and renewable energy sources (biomass), and (ii) their increased production (i.e., biomass and tires). To accomplish this task four pyrolysis temperatures were chosen: 500, 550, 600, and 650 °C. The effect of pyrolysis temperature on basic characteristics of chars has been investigated, as well as their yields and discrepancies.

2. Materials and methods

2.1. Materials

Three types of feedstock were evaluated: brown coal obtained from the North Bohemian Mines, Czech Republic (CZ); biomass pellets made from sawdust from spruce wood and obtained from AMAR Krby Morava, CZ; and used tires obtained from PRO NORTH® CZECH, CZ.

2.2. Pyrolysis experiments

The pyrolysis experiments were performed in a semi-continuously operated Pyromatic pilot plant unit located in the Technology Center in Ostrava, CZ. The main element of the Pyromatic unit — triple-screw reactor (4 m in length) was heated by five atmospheric gas burners and natural gas was used as a fuel. The temperature of the reactor was sensed by a J-type thermocouple. The solid products of pyrolysis were removed from the reactor by a screw conveyor. A more detailed description of the Pyromatic unit has been described elsewhere [15]. Each test was conducted at a feed flow rate of 20 kg/h for 40 min. The temperatures investigated were: 500, 550, 600, and 650 °C.

2.3. Chemical characterization

2.3.1. Proximate and ultimate analyses

The proximate analyses of raw materials and chars were conducted according to the following standard test methods: ISO 11722 (moisture in coal and tires and their chars), CEN/TS: 15414 (moisture in biomass and biochar), ISO 5071-1 (fixed carbon in coal and its char), ISO 562 (volatile matter in coal and its char), CEN/TS: 15402 (volatile matter and fixed carbon in tires, biomass, and their chars), ISO 602 (ash in coal and its char), CEN/TS: 15403 (ash in tires and their chars), and CEN/TS: 15403 (ash in biomass and biochar). The ultimate analyses of raw materials and chars were carried out according to the ISO TS/12902 (coal and its char), EN 15407 (tires and their chars) and CEN/TS 15407 (biomass and biochar) standard test methods. Finally, the higher heating values (HHVs) of feedstocks and solid products of pyrolysis were determined by a bomb calorimeter according to the EN 15400 standard test method. All analyses were performed in the IGI laboratories (VŠB — Technical University of Ostrava, CZ).

2.3.2. XRF analysis

The X-ray fluorescence (XRF) was used to determine the content of elements in feedstocks and solid products of pyrolysis. The analyses were conducted in the laboratories of the Institute of Public Health in Ostrava, CZ using the SPECTRO X-LAB 2000 (SPECTRO) spectrometer equipped with a 400 W Pd and window X-ray tube.

3. Results and discussion

3.1. Basic characteristics of raw materials and chars

The basic characteristics of raw materials and solid products of pyrolysis such as elemental composition, proximate analysis, and energy content are presented in Table 1. As expected, pyrolysis changed the characteristics of raw materials, wherein biomass and coal exhibited similar patterns and tires exhibited a moderate deviation from these trends. Specifically, enhancements in the contents of ash, fixed carbon, carbon (C), nitrogen (N), sulfur (S), and HHV were observed due to pyrolysis for biomass and coal, whereas reductions were observed in the contents of moisture, volatile matter, hydrogen (H), and oxygen (O). Tires also showed increases in the contents of ash, fixed carbon, C, and S but additionally an increase instead of a decrease was observed in the content of moisture. Decreases due to pyrolysis were, however, observed in the contents of HHV and N apart from volatile matter, H, and O.

The effect of pyrolysis temperature on the basic characteristics of chars was much less pronounced. Biochar (BCh) exhibited consistent trends only for the contents of volatile matter, H (decreases in the content were observed), and C (an increase in the content was observed). Whereas char from pyrolysis of coal (ChPC) showed (i) enhancements in the contents of fixed carbon, C, and moisture, though not until a temperature of 650 °C was reached, and (ii) reductions in the contents of volatile matter, H, N, and O. A number of consistent trends with a pyrolysis temperature increase were observed for tires. That is, enhancements were observed in the contents of fixed carbon, C, N, and H; and reductions were observed in the contents of moisture, ash, and volatile matter. The discrepancy in the effect of pyrolysis temperature between chars obtained during pyrolysis of tires (ChPT) and those obtained during pyrolysis of biomass and coal is expected and it is likely to be related to their different composition. Tires, as opposed to coal and biomass, are made of a complex blend of elastomers, processing oils, carbon black, and a few additives including mineral fillers, vulcanization agents, palticizer, etc. [16]. Biomass is composed primarily of biochemical components such as cellulose, hemicellulose, and lignin [17], whereas coal is a sediment rock (i.e., mixture of organic and mineral matter) [18]. During pyrolysis each material undergoes (i) breaking of different chemical bonds resulting in the formation of volatile compounds, (ii) rearrangement reactions within the matrix of the residue (i.e., primary reactions), and (iii) conversion of unstable volatile products (i.e., secondary reactions) [4,18]. As a result, the composition of produced char is different as well.

3.2. Yields of pyrolysis products

The yields of pyrolysis products at various pyrolysis temperatures are presented in Table 2. All materials resulted in an enhancement in gas yield with an increase of pyrolysis temperature. Biomass and coal exhibited consistent reductions in liquid and solid yields, whereas discrepancies were observed in liquids and ChPT. An increase in the gas fraction and the general decreases in liquid and solid fractions are associated with the occurrence of secondary reactions [4]; a higher