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Characteristics and reaction mechanisms of sludge-derived bio-oil produced through microwave pyrolysis at different temperatures

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ABSTRACT

Based on the study of the effect of different final pyrolysis temperatures on the production of bio-oil by catalytic microwave pyrolysis of sludge, a mathematical model has been used to accurately calculate the calorific value of each component in the bio-oil mixture, making it enable to study the variations in the calorific value of bio-oil at a final pyrolysis temperature from a single-component perspective. Results showed that the yield and calorific value of bio-oil reached the maximum at 22.60% and 35.47 MJ kg^{-1}, respectively, with iron oxide as a catalyst, increasing by 5.16% and 16.83% compared with those without a catalyst. The calculation model based on Huggett's oxygen consumption method realized the accurate calculation of the calorific value of a single component in the bio-oil, which could explain why the calorific value of the bio-oil mixture varies with the final pyrolysis temperature. The relative deviation between the model calculating value and the measured value of the component was lower than 5%. The content of fatty hydrocarbons and high-carbon compounds gradually decreased with temperature increased. Increasing temperature leaded to the breakage of chemical bonds of the high-carbon compounds and the formation of low-carbon compounds, which resulted in a decrease in the calorific value of bio-oil. The content of high-calorific value components, such as octadecane and docosane, reached a maximum of 35.78% in the bio-oil mixture at 550 °C, which was significantly higher than the contents at 650 °C and 750 °C. This result may explain why the calorific value of the bio-oil mixture was obviously higher at 550 °C.

1. Introduction

The shortage of nonrenewable energy resources has become increasingly severe with the development of industry rapidly, therefore, searching for new energy resources has become an urgent societal challenge [1]. In this regard, efficient, stable, and cheap energy have become the focus of people's attention and numerous studies [2]. Meanwhile, increases in the economy and population have caused sharp increases in the excess of sludge. Some traditional sludge treatment methods as landfill and incineration can basically meet current requirements to control water and air pollution [3]. However, Peccia and Westerhoff [4] has pointed out that these traditional methods have significant defects in the resource reclamation from sludge. The pyrolysis treatment of sludge can convert the organic matters into biofuel, which can realize both the harmless treatment and resource reclamation of sludge [5]. Nevertheless, the low yield efficiency of biofuel is the key problems [6]. At the meanwhile, the big consumption of energy during the pyrolysis should not be neglected [7]. Given this situation, the microwave pyrolysis of sludge, as a new sludge treatment technology, realizes a highly efficient reduction of sludge and also transforms the sludge into bio-gas and bio-oil [8]. Bio-oil, as a kind of energy substance, has been proven to have certain potential and value for reclamation [9]. Moreover, the microwave pyrolysis of sludge technology has the advantages of easy operation, uniform heating, and low cost [10]. Hence, it is regarded as one of the promising sludge treatment technologies and has attracted the increasing attention of scholars [11].

In spite of these advantages, however, the microwave pyrolysis of sludge has shown the defects of low yield and poor oil quality in the

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generation of bio-oil [12]. Therefore, people have begun to explore various approaches to increase the yield and the quality of bio-oil. The main factors that influence the production of bio-oil from the microwave pyrolysis of sludge include microwave-absorbing materials, catalysts, and final pyrolysis temperature. Domínguez et al. [13] pointed out that adding microwave absorbing materials could enhance the ability of microwave absorption. But Zuo et al. [14] indicated that the increasing of heating rate and the reduction of pyrolysis time caused by adding microwave absorbing materials had little effect on the yield of bio-oil. Compared with microwave-absorbing materials, the catalysts had certain effects on the distribution of components as well as the yield of bio-oil [15]. At the meanwhile, the experimental results of Shao et al. [16] showed that adding catalysts could promote the degradation of organic matters to produce less solid residues. Lin et al. [17] pointed out that the basic catalysts were good for the generation of alkane and polyaromatic hydrocarbons, while the acid catalysts were beneficial to the generation of heterocycles, ketones, alcohols, and nitriles. Yu et al. [18] found that adding different metal oxides as catalysts not only rendered the organic matters in the sludge to decompose more easily but also significantly increased the yield of the bio-oil. On one hand, Aluminum oxide (Al_2O_3) had high selectivity toward the hydrocarbons in the bio-oil [19], which could improve the production of hydrocarbons. On the other hand, Al_2O_3 could also reduce the content of oxygen element, which enhanced the calorific value of the bio-oil [20]. Iron oxide (Fe_2O_3) could mainly facilitate the oxidation reaction of organic matters in the sludge [21], which could increase the production of bio-oil. Besides, Kastner et al. [22] pointed out that, adding Fe_2O_3 as the catalyst during the pyrolysis of red mud could simultaneously reduce acidity and generate upgradable intermediates from the aqueous fraction, which greatly improved the quality of bio-oil. Therefore, the appropriate catalysts used to catalyze the pyrolysis of sludge not only increased the yield of bio-oil and improved the qualities of bio-oil but also increased the stability of bio-oil, reduced the industrial costs and hazards to the environment. Additionally, the final pyrolysis temperature also has large effects on the yield, composition, and characteristics of bio-oil [23]. Some studies showed that, under the medium temperature from 200 °C to 700 °C, the yield of bio-oil increased first and then decreased with the increase of final pyrolysis temperature. Fan et al. [24] found that the yield of bio-oil was the largest at 500 °C. However, Gao et al. [25] indicated that the maximum yield of bio-oil was realized at 650 °C. Thus, it could be concluded that the yield of bio-oil reached the maximum between 500 °C and 700 °C. When the final pyrolysis temperature was too high (above 700 °C), the yield of bio-oil decreased significantly. Temperature increase also was beneficial to the breakage of the chemical bond of the organic compounds in the sludge, which led to the formation of bio-oil. When the temperature was too high, however, it would cause the second decomposition of the products, which caused a decrease in the yield of bio-oil. The change of final pyrolysis temperature not only affected the yield of bio-oil but also caused changes of components in the bio-oil [26]. The main reason for changes in the bio-oil components was that the temperature increase promoted the decomposition and recombination of organic molecules in the sludge, thereby causing changes in the bio-oil components [27]. And the increase in the content of the components of high calorific value would enhance the calorific value of the bio-oil. Therefore, the selection of the optimum final pyrolysis temperature is also vital to an increase in the yield and calorific value of the bio-oil.

Domestic and foreign scholars have conducted many studies about how to improve the yield and quality of bio-oil from the microwave pyrolysis of sludge. Two problems should not be neglected: (1) The generation mechanisms of the key components with high calorific value in the bio-oil under different pyrolysis conditions (including the breakage and recombination of the carbon chains of compounds and the changes of the carbon's atomic number) are not clear, which will have significant effects on increases in the quality of bio-oil from microwave pyrolysis through the optimization of operation parameters. (2) Bio-oil is a complex mixture, and its calorific value can be measured only by the oxygen bomb calorimeter. Such a calorific value can reflect only the calorific value of the mixture but not the calorific values of the key components that cause changes in the calorific value of the mixture. Thus, the reasons for changes in the calorific value of the bio-oil under different pyrolysis conditions cannot be explained, and a deep analysis of the generation mechanisms of the bio-oil also can't be made. To solve these bottleneck problems, the calorific values of the components of bio-oil can be calculated by means of a mathematical model. So far, however, no method for the direct calculation of the calorific value of the bio-oil from the microwave pyrolysis of sludge has been found, the only method available in use is the calculation of the heat release rates of biomass combusted, which is used in the fire research field. Theories for this calculation suggest that the amount of heat generated from the oxygen of each unit mass consumed is 13.1 $MJ\,kg^{-1}$ when the organic matter of 1 mol is completely combusted, and for most of the substances combusted, the deviation is within 5% [28]. Therefore, the amount of oxygen (O_2) required for the complete combustion of certain organic components in the bio-oil from the microwave pyrolysis of sludge can be calculated first, and then the calorific values of certain organic components in the bio-oil can be calculated. If such a method can be used to calculate the calorific value of specific component in the bio-oil from the microwave pyrolysis of sludge at different final pyrolysis temperatures, the reasons for these changes in the calorific value of the bio-oil can be verified, thus, providing a basis for the subsequent analysis of the generation mechanism of bio-oil.

Because current technology can determine only the calorific value of the bio-oil mixture but cannot reveal variations in single components of the bio-oil with the different final pyrolysis temperatures, it fails to explain why the calorific value of the bio-oil mixture varies with temperature. Therefore, to study the variations of the calorific value of bio-oil with different final pyrolysis temperatures from the perspective of a single component. This work introduces a calorific value mathematical model based on the oxygen consumption method to calculate the calorific value and the changes in each component in the bio-oil mixture, basing on the study of the influence of different final pyrolysis temperatures on the bio-oil. Additionally, this work also explores the change rule of different kinds of compounds and the number of carbon atoms in bio-oil in order to reveal the reaction mechanisms of bio-oil.

2. Materials and methods

This section briefly introduces the main characteristics of sludge samples used in this work, focusing on the experimental process of microwave pyrolysis and the analysis methods of products. Moreover, a mathematical model newly established is detailed here in order to accurately calculate the lower heating value of a single component in the bio-oil.

2.1. Materials

The sludge sample with a moisture content of 86.65%, an ash content of 31.31%, and volatile matter content of 69.69% used in these experiments was collected from a municipal wastewater treatment plant in Shenzhen, China. The raw sludge was analyzed by an elemental analyzer (vario EL cube, Elementar, Germany) based on the ash-free basis, and the content of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) were 36.34%, 6.61%, 49.41%, 6.6%, and 1.04%, respectively. The sludge sample was placed in an oven (SX2-2.5-10, Rongfeng, Shanghai, China) for drying at 105 °C for 12 h until the mass of the sludge became stable, and then the sludge was grinded with an agate mortar (130 mm, Leigu, Shanghai, China) to make the particle size of the sludge sample about 1 mm. To increase the yield of bio-oil from the microwave pyrolysis of sludge, this work used Al_2O_3 (Macklin, AR) and Fe_2O_3 (Macklin, AR) as catalysts. In order to achieve the high temperature required for complete pyrolysis, the silicon carbide (SiC,