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In-situ removal of sulfur from high sulfur solid waste during molten salt pyrolysis

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ABSTRACT

In order to address the adverse effects of high sulfur content on the subsequent use of pyrolysis char, the removal of sulfur from high sulfur solid waste during molten salts pyrolysis was studied in this work. The results show that sulfur content of molten salts pyrolysis char was significantly lower than that of general pyrolysis char because molten salts catalyzed the decomposition of organic sulfur. Moreover, the removal efficiency of sulfur in molten salts pyrolysis char was obviously enhanced with the increase of temperature and time. Especially under the condition of 850 °C and 2 h, more than 33 wt% of the sulfur in molten salts pyrolysis char was successfully removed compared with ordinary pyrolysis char. Molten salts, which provided a larger contact area between char and volatiles, promoted a large amount of easily decomposed organic sulfur-containing compounds production by the cyclization reactions between char and hydrogen sulfide at higher temperatures. Due to the adsorption of H_2S by molten salt, the ·SH radical was released more into the molten salt in the form of H_2S rather than reacting with zinc oxide to form thermal stable zinc sulfide. Both of these reasons contributed to the removal of sulfur in the molten salt pyrolysis char.

1. Introduction

A large amount of solid wastes is produced every year in China. Statistics show that China produced up to 3,270,790,000 tons of solid waste in 2015 alone [1]. The storage of the solid waste occupies a lot of land and potential environmental pollution caused by the unreasonable disposal of solid waste becomes more serious [2]. Heat treatment technology offers a promising method for most solid waste treatment, which could fast reduce the volume of the waste and recover energy and resources at the same time [3]. Considered to be a very important heat treatment technology, pyrolysis can transform solid waste into useful gases, tar and char. So far, pyrolysis of solid waste has been broadly studied by using different kinds of reactors such as fixed bed, fluidized bed, rotary kiln and closed batch reactor [4–8].

Compared with general pyrolysis process, molten salts pyrolysis have several advantages: molten salts are excellent heat transfer media, the reactions are very fast, and there is good contact between the liquid and the samples [9]. These advantages have been confirmed in our previous study of Zhundong coal molten salt gasification [10]. So far, molten salt pyrolysis technology has been extensively studied in the field of solid waste treatment [11–14]. Yin et al. [15] harvested capacitive carbon by carbonization of waste biomass in molten salts. Studies have shown that alkaline metal-based molten salts can help catalyze the pyrolysis process [16]. Jin et al. [17] further found intermixtures of Li_2CO_3, Na_2CO_3 and K_2CO_3 exhibited higher catalytic activity to the aimed reaction than the any simple ones by using molten carbonate salts catalyst for the wastepaper gasification. Therefore, it is feasible to use molten salt for catalytic pyrolysis of solid waste.

Moreover, molten salt pyrolysis can reduce the release of acid gases [18]. Siefert et al. [19] found alkali metal salt could capture acid gases such as H_2S by using alkali metal hydroxide to catalyze coal gasification. This property of molten salt is very important for the treatment of high-sulfur solid waste, such as waste tires and petroleum coke. Because sulfur-containing gases that will cause serious environmental pollution during the pyrolysis of high-sulfur solid waste will be captured by molten salt. Besides, the sulfur remained in the char would have a bad effect on the subsequent use of the solid products [20]. Therefore, the knowledge of sulfur removal and transformation is very important for the utilization of high-sulfur solid waste including waste tires by molten salt pyrolysis.

Recently, many studies focus on the behavior of sulfur in the pyrolysis process of waste tires. Unapumnuk et al. [21] found that half of the original sulfur was remained in the char rather than released as gases or condensed in the tar within the range of 350–850 °C during waste tires pyrolysis. According to our previous study, the sulfur in the char was mainly present in the form of sulfides during rapid pyrolysis of

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