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# Effect of high heating rates on products distribution and sulfur transformation during the pyrolysis of waste tires



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#### ABSTRACT

Fast pyrolysis offers a promising efficient way for the resourceful disposal of waste tires and heating rate was a key influence factor on products properties. However, the heating rates of the widely used experimental apparatus (like thermogravimetric) were generally outside the scope of most fast pyrolysis devices. To better guide actual pyrolysis process, the present study focused on the effects of high heating rates (ranged from 60 to 6000 °C/min) on products distribution and sulfur transformation during waste tires pyrolysis. And experiments were conducted at temperatures from 425 °C to 575 °C by using a self-designed photothermal reactor. The results showed that increasing heating rates posed slight effect on the products yields at 425 °C while obviously decreased char yield by forming more gases at higher temperatures. Moreover, high heating rates promoted the fast cracking of tires to form more radical fragments, leading to the formation of numerous small-molecule  $H_2$ ,  $CH_4$  and  $H_2S$ . Meanwhile, secondary reactions among nascent volatiles remarkably increased the fraction or aromatic compounds in the pyrolytic tar especially at 500 °C and 575 °C. Although high heating rates hardly changed the carbon distribution characteristics in the char, increasing heating rate from 60 to 600 °C/min significantly reduced sulfur content in the char, regardless of the final pyrolysis temperature. These findings were believed to well support the application of fast pyrolysis technique for the disposal of waste tires.

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### 1. Introduction

Waste tires, as a type of hydrocarbon-rich polymer, are difficult to be naturally degraded and might cause potential environmental risks (Iraola-Arregui et al., 2018). In China, the continuous generation of large amounts of the waste tires drew great attention and several techniques had been attempted for the harmless and resourceful disposal of the waste tires (Paul Williams, 2013; Kordoghli et al., 2017). Among the utilization methods, pyrolysis has been recently applied on a large scale (of disposal capacity above 100,000 tons per year) in several provinces of China, which is believed to efficiently transfer waste tires into useful products like tar, char and gases (Martínez et al., 2013). However, the practical operation experience shows that the low thermal conductivity of the waste tires were adverse for their fast cracking at pyrolysis, inhibiting the increase of the disposal capacity (Lah et al., 2013). Besides, the widely distributed sulfur in the waste tires not only remarkably affected the properties of the pyrolysis products, but also put forward high requirements for pollution control in the

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pyrolysis as well as products utilization process (Antoniou and Zorpas, 2019; Tang et al., 2018; Choi et al., 2016).

The thermogravimetric analysis coupled with Fourier Transform Infrared spectrometer and the analytical pyrolyzer coupled with gas chromatography/mass spectrometry (Py-GC/MS) were mostly used in the published studies, to investigate the effects of heating rates on the pyrolysis behavior of waste tires (Liang et al., 2019). And the performed heating rates in Py-GC/MS experiments were usually higher than  $10^3$  °C/s and no significant effect of heating rates was found on the products formation (Xu et al., 2018a, 2018b). In contrast, heating rates in TG analysis were much lower, probably ranged from 5 °C/min to 30 °C/min and remarkable promotion influence was widely identified in the syngas generation by increasing the pyrolysis heating rate of scrap tires (Ding et al., 2015). And Han et al. (2018) reported char yield was almost maintained the same by rising the heating rate from 5 °C/min to 30 °C/min in the pyrolysis of waste tires. However, the different conclusion drawn by Akkouche et al. (2017) that char yield was slightly increased with the same change of heating rate during the pyrolysis of scrap truck tire powder in a lab-scale fixed bed. The amount of the sample in TGA test was far below that used in the lab-scale experiments and the discrepancy might cause the

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