



## Technical Note

## The fate of sulfur during rapid pyrolysis of scrap tires



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## HIGHLIGHTS

- Sulfur species in pyrolysis char, tar and gases from scrap tires were investigated.
- Sulfur was mostly in the form of thermally unstable thiophenic in scrap tires.
- Besides H<sub>2</sub>S, CH<sub>3</sub>SH, COS and SO<sub>2</sub> were formed during rapid pyrolysis of scrap tires.
- Interactions between volatiles and char promoted thiophenic and sulfones formation.

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## ABSTRACT

The fate of sulfur during rapid pyrolysis of scrap tires at temperatures from 673 to 1073 K was investigated. Sulfur was predominant in the forms of thiophenic and inorganic sulfides in raw scrap tires. In the pyrolysis process, sulfur in organic forms was unstable and decomposed, leading to the sulfur release into tar and gases. At 673 and 773 K, a considerable amount of sulfur was distributed in tar. Temperature increasing from 773 to 973 K promoted tar decomposition and facilitated sulfur release into gases. At 1073 K, the interactions between volatiles and char stimulated the formation of high-molecular-weight sulfur-containing compounds. After pyrolysis, almost half of the total content of sulfur in raw scrap tires still remained in the char and was mostly in the form of sulfides. Moreover, at temperatures higher than 873 K, part of sulfur in the char was immobilized in the sulfates. In the pyrolysis gases, H<sub>2</sub>S was the main sulfur-containing gas. Increasing temperature stimulated the decomposition of organic polymers in scrap tires and more H<sub>2</sub>S was formed. Besides H<sub>2</sub>S, other sulfur-containing gases such as CH<sub>3</sub>SH, COS and SO<sub>2</sub> were produced during the rapid pyrolysis of scrap tires.

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## 1. Introduction

Recently, a large number of scrap tires are continuously generated in China. The disposal and treatment of scrap tires have drawn much attention for both environmental concern and resources recovery (Llompert et al., 2013). The pyrolysis technology has been broadly applied for the utilization of scrap tires by using different types of reactors such as fluidized bed, spound bed, rotary kiln and fixed bed (Li et al., 2004; Kaminsky et al., 2009; López et al., 2010, 2011). Useful products such as gases, tar and char can be obtained through the pyrolysis process (Ucar et al., 2005; Mui et al., 2010; Doğan et al., 2012). However, sulfur is widely presented in tires and the release of the sulfur-containing gases during scrap tires pyrolysis could cause seriously environmental pollution. Moreover, sulfur remained in the solid products or transformed into pyrolysis tar would raise some safety and quality problems for the consequent use of these products (Rodriguez et al., 2001). As a result,

knowledge of sulfur transformation is essential for the utilization of scrap tires through pyrolysis process.

So far, a few research findings have been focused on the fate of sulfur during the pyrolysis of scrap tires. Murena (2000) reported that sulfur compounds tended to release into gases at low temperatures. H<sub>2</sub>S was found as the main sulfur-containing component in gaseous products during flash pyrolysis of used tires by using a thermal plasma reactor (Tang and Huang, 2004). The initial temperature for the decomposition of scrap tires increased with the increasing of heating rate from 1 to 100 K min<sup>-1</sup> (Unapumnuak et al., 2006). At temperatures from 623 to 1123 K, most of sulfur was remained in the char rather than released into gases or condensed in the tar (Unapumnuak et al., 2008).

In addition to the reaction conditions, the fate of sulfur during thermal conversions of coal was found to be significantly affected by the sulfur speciation and inorganic matters in the raw material (Liu et al., 2010; Zhang and Yani, 2011). Compared with coal, scrap tires are rich in carbon and hydrogen and mainly consist of organic compounds of high molecular weight. For the quality modification of rubber used for tires production, sulfur is usually used. According to previous studies, sulfur was mostly in the form of C–S bonds

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in scrap tires (Modrow et al., 2001; Quek and Balasubramanian, 2013). The investigation of the fate of organic sulfur during the pyrolysis of coal char indicated that ‘SH radical was the key intermediate interacting with char to form secondary sulfur compounds in the pyrolysis products (Yan et al., 2005). The formation of the ‘SH radical and its thermal behavior depended on the thermal stability of sulfur-containing organic compounds which might be particularly important during the pyrolysis of scrap tires due to the polymer characteristics. On the other hand, scrap tires were of high contents of Ca and Zn (Gieré et al., 2006; Alexandre-Franco et al., 2010). Compounds of these elements could enhance sulfur immobilization by forming thermal stable sulfates and/or sulfides (Hu et al., 2006; Ling et al., 2013). Nevertheless, no detailed information had been reported to further illuminate the mechanism of sulfur transformation during the pyrolysis of scrap tires.

In this study, rapid pyrolysis of scrap tires was conducted at temperatures ranging from 673 to 1073 K. The pyrolysis product yields as well as the sulfur distribution in these products were observed. To forward the understanding of the mechanism of sulfur transformation, sulfur speciation in char, tar and pyrolysis gases were investigated by using a X-ray photoelectron spectrometer, GC–MS and a trace sulfur analyzer. The thermal behavior of inorganic materials was concerned for their effects on the sulfur immobilization.

## 2. Material and methods

The scrap tires were sampled from used tires supplied by the nearby residents. The samples were shredded and sieved to the sizes of 0.5 to 1 mm. After drying to constant weight at 378 K, the proximate and ultimate analyses of the scrap tires were carried out by using a TGA2000 proximate analyzer and a Vario Microcube elemental analyzer, respectively. The results are shown in Table 1. The sample has a high content of carbon. The sulfur content in the sample is 2.05%. There is a high content of ash in the scrap tires and the chemical compositions of the ash were performed by X-ray fluorescence spectrometry (XRF). As shown in Table SM-1 in Supplementary material (SM), the major compositions of the ash are CaO, SO<sub>3</sub>, SiO<sub>2</sub>, MgO, ZnO, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

The rapid pyrolysis of scrap tires was conducted in a vertical furnace as shown in Fig. SM-1. At the beginning, 1 g of the sample was placed in the quartz basket which was fixed at the top of the reactor. Then the carrier gas N<sub>2</sub> was input into the reactor at a certain flow rate (0.4 L min<sup>-1</sup>) controlled by a mass flow controller. The reactor was heated by the electric furnace to the set temperatures ranging from 673 to 1073 K. When the furnace was stable at the set temperature, the quartz basket was put into the reaction zone rapidly. The pyrolysis gases were carried out by the N<sub>2</sub> and were cooled down by the ice bath. The tar and gaseous products were separated and collected for the subsequent analysis. After pyrolysis, the char was pulled out and cooled down to room temperature under N<sub>2</sub>. Meanwhile, the tar were washed with dichloromethane and collected. The collected tar were dried at 313 K to remove the dichloromethane for subsequent analysis. The total content of sulfur in the tar was detected using a Vario Microcube elemental analyzer. The sulfur-containing compounds in the tar were identified by GC–MS (Agilent 7890 A/5975 C). The operating

conditions were similar to that in the literature (Chen et al., 2010). A fused-silica capillary HP-5 ms column (30 m × 0.25 mm id) with 0.25 μm film thickness was used (J & W Scientific, Folsom, CA, USA). The column temperature program was firstly retained at 40 °C for 3 min and then heated at an increasing rate of 6 °C min<sup>-1</sup> to 300 °C, after which it was kept at 300 °C for 5 min. The sulfur-containing gases in pyrolysis gases were measured by a HC-5 trace sulfur analyzer. All the experiments were repeated more than 3 times and the mass balance of sulfur was between 85% and 115%. Other gases like CH<sub>4</sub>, H<sub>2</sub> and CO was determined by GC (Agilent 3000A micro-GC). In the process, N<sub>2</sub> acted as the balance gas and the production of other types of gases were calculated on the basis of the determined concentrations and relative volume fraction in the gas.

Furthermore, X-ray powder diffraction (XRD) was employed to provide detailed information about mineralogical characteristics of the char. And the sulfur speciation in scrap tires and char were investigated by using a VG Multilab 2000 X-ray photoelectron spectrometer (XPS). The relative concentrations of different sulfur forms were calculated according to the corresponding peak values fixed at 162.2 ± 0.6, 163.3 ± 0.4, 164.1 ± 0.2, 168.2 ± 0.2 and 170.0 ± 1.0 eV of binding energy for inorganic sulfides, aliphatic sulfur, thiophenic, sulfones, and sulfates, respectively (Kozłowski, 2004; Marinov et al., 2004; Ko et al., 2006; Liu et al., 2007, 2012).

## 3. Results and discussion

### 3.1. Sulfur contents in scrap tires pyrolysis products

The yields of the products from the pyrolysis of scrap tires are shown in Fig. 1a. Scrap tires mainly consists of organic polymers, the cleavage of which was strongly affected by the operating temperature (Leung et al., 2002). The results drawn from this work were similar to these in previous studies (Rodriguez et al., 2001; López et al., 2010). With the temperature increasing from 673 to 773 K, char yields underwent remarkable decrease. At temperatures high than 773 K, the char yields slightly decreased. In the present study, the tar yields (as well as sulfur contents in tar which were discussed in the next paragraph) were calculated as the difference between total and the sum of char yields and gas yields. With the decomposition of scrap tires, the production of gases and tar were facilitated. The further decomposition of char enhanced the tar production at 773 K. Compared with the gas and tar yields at 873 K, the gas yields increased notably while the tar yields decreased at 973 and 1073 K. Therefore, at these temperatures, the formation of small molecular gases was attributed to the cracking of high molecular-weight tar.

Fig. 1b shows the sulfur distribution in the pyrolysis products of scrap tires. Most of sulfur was found in the char which was mainly due to the great thermal stability of sulfur-containing organic and/or inorganic compounds formed during the pyrolysis process. However, a large amount of sulfur was transformed into gases. At 673 K, although the gas yields were quite low, a considerable amount of sulfur was found in the pyrolysis gases. The results indicated that some sulfur-containing compounds were unstable and easily decomposed at low temperatures. The decomposition of these compounds was facilitated at 773 K. As a result, the sulfur

**Table 1**  
Properties of scrap tires.

Proximate analysis (%)				Ultimate analysis (%)				
Moisture	Volatile matter	Fixed carbon	Ash	C	H	O*	N	S
0.4	62.9	18.1	18.6	68.8	5.9	3.3	0.9	2.1

\* Calculated by difference.

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