

Investigation into the removal of sulfur from tire derived fuel by pyrolysis

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Abstract

There is growing interest in the use of scrap tires as both a fuel and a feed material for petroleum feedstocks due to their abundance and their chemical composition. However, the sulfur content of scrap tires is a potential obstacle to scrap tires utilization as a fuel. In this paper, the partitioning of sulfur was investigated from the two major pyrolytic products from passenger car tires, liquid oils and solid chars, and the potential of producing a low sulfur char for fuel applications. The removal of sulfur during tire pyrolysis offers the greatest potential for the separation of sulfur products from the evolved gases and vapors. The influences of heating rate and pyrolysis temperature were investigated from 325 to 1000 °C, a range where substantial devolatilization occurs. The pyrolysis char and derived oil were analyzed for sulfur, and compared to the original parent sulfur content in tire derived fuel (TDF) samples. The results of sulfur determination verify that the overall desulfurization from the pyrolysis reaction is essentially unaffected by the heating rate but is affected by the ultimate pyrolysis temperature.

Keywords: Tire derived fuels (TDF); Pyrolysis; Desulfurization; Devolatilization; Sulfur

1. Introduction

Since the 1970s, a number of studies have investigated available technologies to combust used tires in industrial applications that are related to the use of tires as a supplemental fuel. Questions concerning air emissions from burning tire derived fuels (TDF) have arisen due to pollutant emissions. Sulfur is present in tires at varying concentrations [1] and when oxidized to sulfur dioxide (SO₂) during combustion can be an emission problem because it is a regulated air pollutant. The combustion of a combination of TDF and coal will potentially result in an increase in SO₂ emissions if the sulfur content of the TDF is greater than that of the coal being burned.

Attempts to answer these air pollution related questions create the basis for much research. The pyrolysis of solid fuels has been generally recognized as an economical and

technically feasible method of desulfurization [2,3]. During pyrolysis, the solid partially decomposes and produces gaseous, liquid and solid residuals as pyrolysis products. The majority of trace metals in the solid fuel are retained in the solid residue, but volatile elements are released in vapor form [2]. The release of sulfur from the tire structure before combustion by pyrolysis may offer the greatest potential for the separation of sulfur, and its compounds, from the resulting char. Different pyrolysis conditions may have a great effect on the yield and composition of the three pyrolysis products. Temperature and heating rate are two of the most important parameters affecting the yield and composition of the volatile fraction [3] and would therefore be expected to affect the degree of sulfur removal from the char.

The growing interest in pyrolysis of tires has been due mainly with the study of TDF combustion. However, not many studies have focused on the influence of heating rate and pyrolysis temperature on the release of other pyrolysis by-products such as sulfur products and volatile

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hydrocarbons. This study focuses on an understanding of the influences of heating rate and pyrolysis temperature in relation to the recovery of pyrolysis products and the removal of sulfur from TDF during pyrolysis.

2. Experimental method

The TDF samples were supplied by two commercial sources and are a mixture of different kinds of tires. The samples were shredded and sieved to the sizes of 1.00–2.00 mm. The major composition include 80.7% carbon, 7.4% hydrogen and 6.7% ash, with minor quantities of oxygen, sulfur, nitrogen and chlorine [4]. Details of the experimental system and the design of the laboratory scale pyrolysis reactor have been discussed elsewhere [4–6] and are briefly discussed here. A series of experiments was performed with heating rates of 1, 5 and 10 °C/min in the laboratory scale pyrolysis reactor. The average TDF quantity is 3–4 g and is steel wire free. Derived gases and vapors were continuously removed from the hot zone by a vacuum pump at the flow rate of 0.47 L/min. At the end of each pyrolysis experiment, the condensed oil, residual ash, and filter paper were removed. The mass of the residual ash, soot and condensed oil were determined gravitationally. The mass of the gases was calculated by difference between residual ash, soot, condensed oil, and initial weight of the TDF sample. The solid char was analyzed for sulfur and compared to the original parent sulfur content in the TDF using the ASTM D3176, standard practice for ultimate analysis of coal and coke. The ASTM method was written specifically for the determination of sulfur in coal and coke, and is also applicable to the same analysis of TDF and TDF char products. The analyses were performed by OKI Analytical Company, a certified commercial laboratory in Cincinnati.

The oil produced from pyrolysis was collected in a condenser trap. It had a yellowish color and an unpleasant, petroleum odor. The derived oil was analyzed for total sulfur content using an Agilent (Agilent Technologies, Palo Alto, CA) Model 6890 Series gas chromatography equipped with an Agilent G2350A atomic emission detector (GC-AED). The AED has been well described as an efficient detector for quantification of sulfur and its compound by the selective spectrometric detection technique [7–10]. The sulfur elements were separated on a HP-5MS type capillary column (30 m × 0.25 mm i.d. × 0.25 μm film). Helium was used as a carrier gas at the column flow rate of 1.3 mL/min. The split ratio was 20:1 and an injection volume was 1 μL. The injection temperature and the AED transfer line were controlled at 280 and 310 °C, respectively. The GC oven temperature program was heated from 40 to 300 °C at 10 °C/min and hold for 10 min. A combination of 50 psi oxygen and 45 psi hydrogen was used as a reagent gas with a make up flow rate of 66 mL/min. The detector cavity block was kept at 300 °C. Chromatograms were simultaneously monitored at the emission lines of carbon (179 nm) and sulfur (181 nm).

The percentage of sulfur removed was calculated for each sample by comparing the final total sulfur content of each pyrolyzed sample with the initial total sulfur mass value of the original TDF. TDF does not have a fixed composition and its properties vary, therefore, the sulfur content from one TDF sample may differ from one another. The original parent sulfur content in TDF was 2.5% which was found to be the highest value employed in this study. The desulfurization is the percentage change in the amount of sulfur in the TDF when the TDF is pyrolyzed. The percent desulfurization for each solid char and derived oil can be calculated using the following equation [2,11]:

$$\% \text{desulfurization} = \frac{(S_{\text{TDF}} - S_{\text{pyrolysed}})}{S_{\text{TDF}}} \times 100,$$

where S_{TDF} is the total mass of sulfur content in original TDF sample, g and $S_{\text{pyrolysed}}$ is the total mass of sulfur content in pyrolyzed products, i.e., the pyrolysis char, g.

The initial sulfur value for each sample was calculated by multiplying the weight of the sample prior to pyrolysis by the 2.5% sulfur concentration. In order to determine the relationship between desulfurization and devolatilization, the thermogravimetric (TGA) data from our previous publication [6] was used. The percent devolatilization for each TDF sample was calculated using the TGA data [2,3] as follows:

$$\% \text{devolatilization} = \frac{W_{\text{TDF}} - W_{\text{char}}}{W_{\text{TDF}}} \times 100, \quad (1)$$

where W_{char} is the weight of the solid char or pyrolysed char, g and W_{TDF} is the weight of the original TDF, g.

Desirable heat recovery in the solid char is expressed as following [11]:

$$\% \text{heat recovery} = \frac{\% \text{yield} \times H_{\text{pyrolyzed}}}{H_{\text{TDF}}} \times 100, \quad (2)$$

where yield is the proportion of the total weight of pyrolyzed product to the total weight of the original TDF, H_{TDF} is the heat value of the original TDF, Btu/lb and $H_{\text{pyrolysed}}$ is the heat value of the pyrolyzed product, Btu/lb.

Similar to the heat recovery, the ash recovery was calculated using the same equation but the total weight of residual ash and the percent ash of the original TDF were used instead of the heat value. The repeatability and precision of the entire analysis process was demonstrated by conducting at least three sets of the pyrolysis experiment for each individual condition. The standard derivations for each data set are used to indicate error for that set. The presented results represent the mean value of that data set and the 5% standard error.

3. Results and discussion

TDF samples were subjected to pyrolysis conditions and the percentage removals of sulfur were determined. The analysis results are listed in Table 1. Data in Table 1 indicate that the percent of sulfur removal drops with the

Table 1
Analytical results of TDF samples subjected to pyrolysis conditions

Heating rate, °C/min	Temperature, °C	Desulfurization, %	Devolatilization, %	Heat recovery, %	Solid char recovery, %
1	325	2.3	2.3	NA	NA
	350	49.4	40.1	54.4	52.9
	400	46.1	51.0	38.0	42.0
	500	49.3	55.0	29.7	34.2
	600	53.0	60.1	28.2	33.7
	800	50.1	61.8	27.7	31.4
	1000	52.5	61.2	28.5	32.0
5	325	2.3	2.3	NA	NA
	350	55.5	41.4	45.5	57.7
	400	38.9	37.9	50.4	59.0
	500	45.3	58.2	30.7	34.4
	600	34.5	51.5	34.1	41.7
	800	48.0	60.6	28.1	32.4
	1000	47.7	60.5	29.6	31.9
10	325	6.2	2.3	NA	NA
	350	64.3	40.8	45.6	57.3
	400	36.0	33.6	58.7	59.6
	500	44.8	56.3	31.4	37.0
	600	41.0	53.6	31.3	39.2
	800	48.6	60.1	29.0	32.4
	1000	46.2	60.4	28.5	33.7

increase in temperature from 350 to 400 °C and then increases with the increase in temperature. Up to 65 wt% of the total sulfur was removed at a temperature of 350 °C and a heating rate of 10 °C/min. The minimum percent of sulfur removal (36–46 wt%) was found at 400 °C. The total sulfur removal for 1 °C/min was maintained at 45–50 wt% from 350 to 1000 °C. Lin [3] reported that when pyrolysis temperatures are high, the pore structure of coal collapses, changing the solid fuel matrix structure which inhibits further release of sulfur. The same hypothesis may apply to the release of sulfur from TDF when pyrolysis temperatures were higher than 447, 483 and 497 °C, corresponding to the final devolatilization temperature reported for 1, 5 and 10 °C/min, respectively [6]. It was observed that the volatilization yield increases as the pyrolysis temperature increases, but the heat recovery and solid char recovery from the analysis of solid char decreases as the pyrolysis temperature increases. The experimental results indicate that there was no significant change in product yield at the different heating rates. However, there

was a slight decrease in the overall heating value when pyrolysis temperatures were greater than 400 °C. The percent desulfurization reached the maximum value at 65%, 56% and 53% for 10, 5 and 1 °C/min, respectively. There was a decrease in the percent desulfurization as the percent devolatilization was greater than 30–35%. In addition, Table 1 reveals that the percent desulfurization was not dependent on the heating rate when the percent devolatilization was higher than 40%.

The results in Fig. 1 show that percent removal of sulfur in the TDF is initially affected by the pyrolysis temperature. However, the overall desulfurization as well as the rate of desulfurization of the pyrolysis reaction, shows only minor influences from the heating rate. There was a small influence of heating rate, but a significant change in the percent removal of sulfur was only observed when the temperature is higher than 350 °C.

The graphical representations of the sulfur contents in the solid char, oil, and TDF are shown in Fig. 2, and those of the sulfur removal as a function of devolatilization are

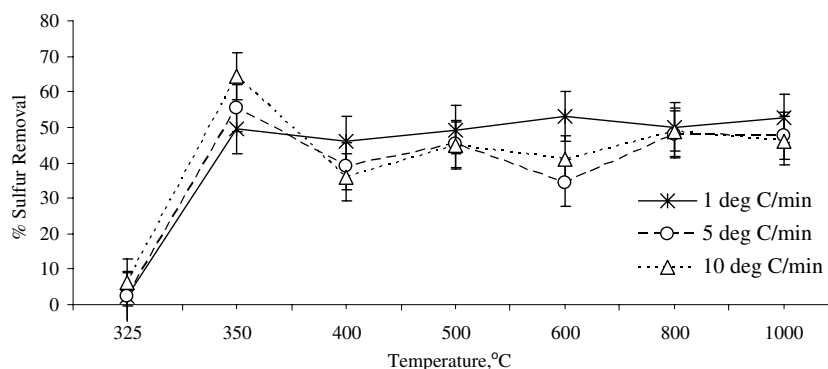


Fig. 1. Percent sulfur removal in TDF during pyrolysis at different heating rates.

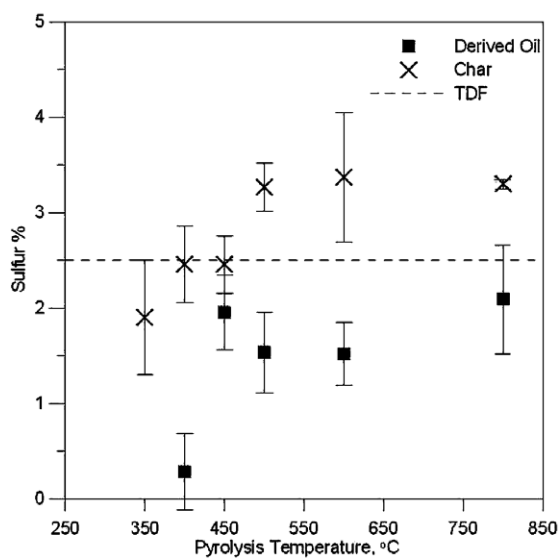


Fig. 2. Percent sulfur in derived oil and solid char compared to the original parent sulfur content in TDF versus pyrolysis temperature.

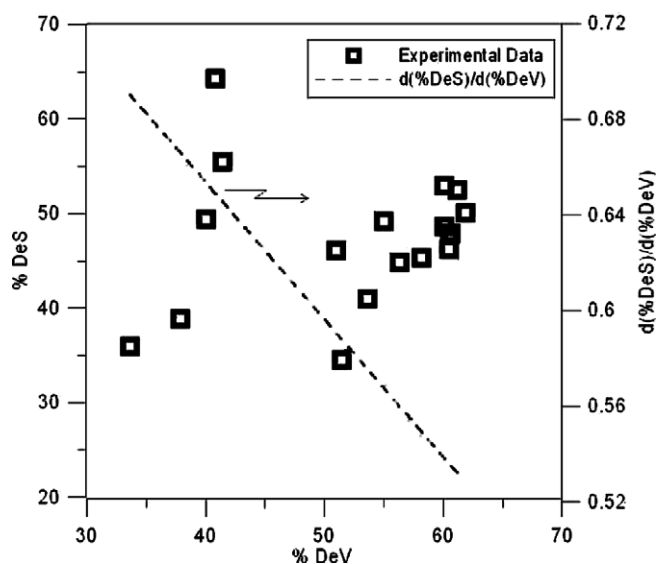


Fig. 3. Percent desulfurization versus percent devolatilization and the rate of sulfur removal as a function of volatiles.

shown in Fig. 3. Our previously reported work [6] indicated that the overall derived oil yield was essentially unaffected by the heating rate. However, the maximum oil yields were found at the heating rate of 5 °C/min, and so the pyrolysis experiments for the derived oil were performed at that specific heating rate. The GC-AED analysis of the derived oils has identified the following sulfur-containing compounds: 2- and 3-methylthiophene, 2,3- and 2,5-dimethylthiophene and 2-ethylthiophene based on the available chemical standards [12]. However, we were unable to find any dibenzothiophenes or more complex sulfur-containing compounds in the oil unlike reported in another study [13]. The sulfur compounds identified in the oil seems to be less

complex than that of diesel fuels at similar sulfur content level [12]. Fig. 2 shows that the initial sulfur percentage of the oil was less than 0.2 wt% at 400 °C and was increased rapidly to about 2 wt% with the increase in temperature. Fig. 2 reveals that within 350–850 °C, also called the devolatilization range of the TDF, the majority of sulfur remains in the solid char rather than being released into the oil or the condensed vapor phase. This is also consistent with the study by Leung et al [14]. The percent of sulfur in the derived oil and solid char increases with the increase in temperature, maximizes at 450–500 °C and then seems to remain constant. When the reaction temperature increases, the amount of decomposable organic compound including sulfur and gaseous products, increases. As such, when the reaction temperature is higher than 500 °C, the decomposition of fixed carbon increased slightly, and the derived oil production was increased. Sulfur in the TDF derived oils has also been reported by other researchers. For example, Cunliffe and Williams [15] reported sulfur concentrations of 1.3–1.4% (by weight of TDF) in the oil derived from the pyrolysis of TDF at 20 °C/min in the range 450–600 °C. Murena [16] reported only 1 wt% of sulfur present in the liquid products derived from the pyrolysis of TDF in an autoclave at 380 and 400 °C. The same study also showed that as the pyrolysis temperature increases, there was an increase in the concentration of sulfur in the solid char. A two stage thermal cracking process of TDF as a function of temperature may be used to explain this phenomenon [17]. First, the TDF is depolymerized at a temperature of less than 500 °C. In this phase, the rapid dissolution of the TDF occurs and the weakest bonds are broken. Second, the rubber is devolatilized at a temperature of more than 600 °C. At this stage, the release of volatile compounds including sulfur compounds, takes place in the derived oil. Mainly sulfur is retained in the solid char but maximized in the derived oil at lower temperature, whereas the post-cracking reaction explains the decrease of sulfur compounds in the derived oil at higher temperatures. Although not measured in this study, H₂S can be expected as a major gaseous sulfur product in tire pyrolysis, as shown in a similar study [16] as well as during coal liquefaction.

Fig. 3 shows that, generally, the proportion of sulfur removed by pyrolysis increased as the temperature and the degree of devolatilization increased. By assuming a first order reaction of sulfur decomposition rate similar to the percent devolatilization [2,3,16], the rate of sulfur removal as a function of volatiles was developed. During the temperature range of 325–400 °C, dissolution of TDF in the liquid phase took place by the rupturing of the weakest bonds [16]. This agrees with the results in Fig. 2 that many S-bonds were broken with the release of H₂S into the gas phase [16], so that the sulfur content was found more in the solid char than in the derived oil. Thermal decomposition has been shown to be one of the reactions which decomposes sulfur-containing compounds into gaseous sulfur products (H₂S and/or SO₂) [18] at relatively moderate

temperatures. The data in Fig. 3 indicate that the rate of sulfur evolution as a function of volatiles decreases with an increase of pyrolysis temperature. The maximum rate occurred as a level of devolatilization less than 10% indicating that the sulfur fraction which is released is released early in the devolatilization process.

Fig. 4 reveals that the percent solid char recovery decreases linearly with the increase in the percent devolatilization. It was found that 45% of sulfur was removed whereas 45% of solid char were recovered at 47% devolatilization. In addition, Fig. 4 shows potential for high desulfurization and low solid char recovery at high devolatilization. A possibility of change in the TDF structure after 50% devolatilization may limit sulfur removal ability in the pyrolysis process. The percent removal of sulfur is proportional to the percent of devolatilization, which is opposite to the percent recovery of a solid char. This may be due to the fact that desulfurization products were entrained less at lower temperature, whereas at higher temperatures devolatilization increased desulfurization.

In terms of emissions of SO₂ from the combustion of the char alone, Fig. 5 shows the impact of pyrolysis on the emission rate of SO₂ (lbs-SO₂/MMBtu) versus the pyrolysis temperature. As seen in Fig. 5, the SO₂ emission rate initially decreases at low pyrolysis temperature as sulfur is preferentially removed as compared to heating value, but then increases for all pyrolysis ramp rates up to a consistent amount of ~5.5 lbs-SO₂/MMBtu at pyrolysis temperatures above 500 °C. The average trend line shown in Fig. 5 was obtained by plotting a cubic spline fit on the averaged data for the three heating rates for each temperature. At temperatures below 400 °C, the data indicate that it may be possible to reduce the emissions rate of SO₂ for the char as compared to the parent TDF, but further tests would be needed in order to optimize the reduction amount.

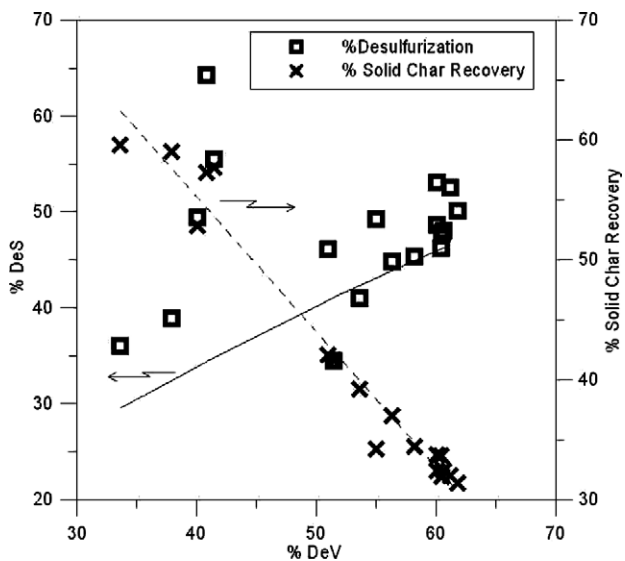


Fig. 4. Percent sulfur removal (%DeS) and percent solid char recovery (%ash) versus percent devolatilization (%DeV).

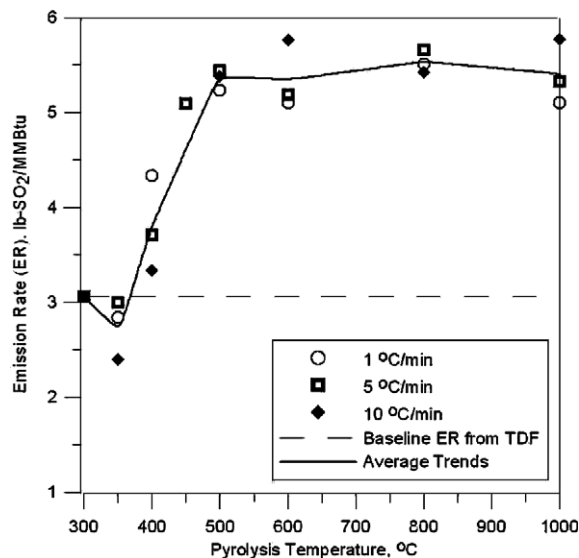


Fig. 5. Emission rate of SO₂ from the pyrolysis char of TDF.

4. Conclusions

The distribution and percent removal of sulfur in char and derived oil obtained from pyrolysis of used tires were investigated. The impacts of the two important factors, the heating rate and final temperature were investigated in this study. The major observations include:

- The influences of heating rate and pyrolysis temperature were investigated from 350 to 1000 °C, a range where substantial devolatilization occurred. The overall desulfurization of the pyrolysis reaction was essentially unaffected by the heating rates, however, the rates investigated in this study (1–10 °C/min) is in a narrow range. Desulfurization increased as the temperature increased from 350 to 400 °C, and remained almost constant from 400 to 1000 °C.
- Sulfur in TDF partitions to the gas, liquid and solid char during pyrolysis. In general, approximately half of the original sulfur remained in the solid char rather than being released as condensed vapor phase within the range of 350–850 °C.
- The emission rate of SO₂ (lbs-SO₂/MBtu) in the pyrolysis char is seen to decrease initially with pyrolysis temperatures below 400 °C, but then increases reaching a plateau at temperatures above 500 °C.

This study has shown that a pyrolysis reactor could be designed and operated to produce specific products from used tires under certain operating conditions. The desired desulfurization rate can be achieved by setting up specific conditions so that the pyrolytic TDF char can become a lower sulfur fuel than the raw TDF, especially at lower temperatures. It is recommended that this type of pre-treatment process should be considered in decision making processes where used tires might be used as a fuel,

such as incineration, and power generation and in rotary kilns.

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