



# Scrap tire pyrolysis using a new type two-stage pyrolyzer: Effects of dolomite and olivine on producing a low-sulfur pyrolysis oil



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## ABSTRACT

Scrap tire pyrolysis was performed using a two-stage pyrolyzer consisting of an auger reactor and a fluidized bed reactor to produce a low-sulfur pyrolysis oil. In the experiments, the effect of the residence time of the feed material in the auger reactor was investigated at ~300 (auger reactor) and 500 °C (fluidized bed reactor). In addition, natural dolomite and olivine and calcined dolomite and olivine were used as the fluidized bed materials to examine their effects on reducing the sulfur content of pyrolysis oil. In the experiments, the yields of the oil from the auger reactor were 1.4–3.7 wt%, and it was enriched with *DL*-limonene whose content in the oil was 40–50 wt%. The yields of the oil from the fluidized bed reactor were 42–46 wt%. The optimum residence time of the feed material in the auger reactor turned out to be 3.5 min. Calcined dolomite and olivine significantly decreased the sulfur content of pyrolysis oil. Metal oxides of the additives appeared to react with H<sub>2</sub>S to form metal sulfides. The sulfur content of pyrolysis oil obtained with calcined olivine was 0.45 wt%.

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## 1. Introduction

According to the rapid population and economy growth, the need for energy source is also growing worldwide. Although fossil fuels, traditional energy resources, still make up the majority of the world's energy consumption, a strong need for different energy sources which can contribute to the future energy has been continually demanded. Waste energy is one of the most effective options to replace fossil fuels, thereby securing energy supplies for the future. Scrap tires, which have energy content of ~30–35 MJ/kg, represent a source of waste energy. Because the durability of scrap tires interferes with their natural-degradation [1], it has been very difficult to find a proper management method for them. Landfill of scrap tires is not encouraged in developed nations because this treatment method consumes a lot of natural space and causes environmental problem. Incineration also faces a challenge to solve problems associated with harmful gas emissions like SO<sub>x</sub>, NO<sub>x</sub>, and dioxins. It is possible that scrap tires can be used in rubber industry as reclaimed rubber, but the toxicity of heavy metals utilized in tire manufacturing process like Zn is concerned [2].

Pyrolysis, a thermo-chemical conversion process, is regarded to

be a more environmentally friendly process than other waste treatment processes, significantly reducing waste volume with considerably lower toxic gas emissions [3]. In inert conditions, pyrolysis can decompose organic matter into gas, liquid and solid phase products. Over the past few decades, many researchers have carried out research on the scrap tires pyrolysis and developed this technology. Aylon et al. performed the pyrolysis of scrap tires and provided power for their pyrolysis process by combustion of gas product [4]. Antoniou et al. studied the potentials of liquid and solid products as energy sources and value-added products and reported that the liquid product could be used as an alternative fuel, and the solid product could be upgraded to activated carbon by an additional activation process [5]. By some researchers, it was verified that activated carbons from scrap tires have effective adsorption ability for cadmium [6], SO<sub>2</sub> [7] and acid dye [8]. The solid product from the pyrolysis of scrap tires was also investigated for regenerated carbon black without additional treatment [9,10]. In particular, Omar et al. made a carbon silica hybrid filler, which could be used in polymer manufacturing as a binder, from scrap tires pyrolysis [11]. As an alternative fuel, the liquid product from the pyrolysis of scrap tires was used in a boiler [12] and a diesel engine [13]. Typical liquid products derived from the scrap tire pyrolysis consist of various hydrocarbons with a small amount of heteroatom-containing compounds. Among these liquid components, *DL*-limonene is noted for its relatively high yield and commercial value [14]. Pakdel

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at al. increased DL-limonene content in the liquid product up to 92 wt% using distillation [15]. The use of the liquid product as an alternative fuel is easy to approach due to the well-established combustion technology and has a great potential than other applications. However, there is a limitation for the liquid product to be used as a fuel because of its high sulfur content. The sulfur content in fuels must be regulated to restrain the production of sulfur oxides. Typical sulfur contents of liquids obtained from the non-catalytic pyrolysis of scrap tires are ~1 wt% [16], which limited the wide use of the liquids. Hence, many researchers have tried to reduce the sulfur content of the liquid product. Hüseyin Aydın and Cumali İlkılıç reported that CaO, Ca(OH)<sub>2</sub> and NaOH reacted with H<sub>2</sub>S generated during pyrolysis, thereby decreasing the sulfur content in liquid product to 0.8 wt% [17,18]. They reported that the H<sub>2</sub>S adsorption on the additives used was a key point to obtain a low sulfur containing liquid product. For the H<sub>2</sub>S adsorption, various metal oxides were investigated by earlier studies [19–21]. Meanwhile, Hu at al. reported that SH radicals were produced during pyrolysis of scrap tires. The SH radicals produced, on one hand, were converted into sulfur containing compounds in the liquid product and they, on the other hand, reacted with metals presented in the feed material such as Zn to form the char product [22].

Recently, our group developed a new type of two-stage pyrolyzer consisting of an auger reactor and a fluidized bed reactor in series. In a typical pyrolysis of waste material with the two-stage pyrolysis process, the auger reactor, which operates at lower temperatures than the fluidized bed reactor, liberates heteroatom-bonded compounds such as HCl, H<sub>2</sub>S and NH<sub>3</sub> in advance. The feed material which is partially decomposed in the auger reactor is then conveyed to the fluidized bed reactor, where the main pyrolysis reactions occur to produce gas, oil, and char products with low levels of contamination. In the previous study on the pyrolysis of scrap tires [23], the two-stage pyrolyzer confirmed our expected performance to produce a pyrolysis oil with the sulfur content of 0.55 wt% without any aid of catalysts. The present work aimed a further reduction of the sulfur content of pyrolysis oil using natural catalysts which are readily available and not too expensive. For the purpose un-calcined and calcined dolomite and olivine were used as the fluidized bed material, and their effects on the sulfur reduction were compared with one another and also with that of sand. In addition, this study reports the effect of residence time (RT) of the feed material in the auger reactor on the sulfur contents of pyrolysis products.

## 2. Experimental

### 2.1. Feed material characteristics

Scrap tire rubber obtained from a tire recycling company in Korea was in the size range of 1–2 mm. To investigate chemical characteristics of the scrap tire rubber, various analyses were conducted. The results were presented in Table 1.

The proximate analysis, which was conducted following ASTM D3172, showed that the feed material consisted mainly of volatile matter (~76 wt%) and fixed carbon (~19 wt%). The main metal component of the ash was Zn (~4 wt%). The sulfur and nitrogen contents were 2.6 wt% and 0.4 wt%, which were derived mainly from accelerants and vulcanization agent utilized during tire manufacturing.

Prior to determine reaction temperatures for the auger and fluidized bed reactors of the two-stage pyrolysis process, thermogravimetric (TG) analysis of the feed material was performed with a thermogravimetric analyser (TGA Q50, TA Instruments). For the analysis, a sample of scrap tires (10–20 mg) were heated from 30 to 800 °C with heating rates of 5, 10 and 20 °C/min. The TG and

**Table 1**  
Main characteristics of the feed material.

Proximate analysis	Mean ± s.d. (wt%)	Ultimate analysis <sup>b</sup>	Mean ± s.d. (wt%)
Moisture	0.4 ± 0.00	C	93.2 ± 2.33
Volatile matter	68.8 ± 0.39	H	1.7 ± 0.59
Fixed carbon <sup>a</sup>	27.0 ± 0.37	N	0.4 ± 0.02
Ash	4.2 ± 0.03	S	2.6 ± 0.33
		O	2.1 ± 0.09
Metal analysis (ppm)			
Ca	943	K	545
Mg	299	Zn	30105
Al	318	Fe	535

<sup>a</sup> By difference.

<sup>b</sup> Ash free basis, s.d.: standard deviation.

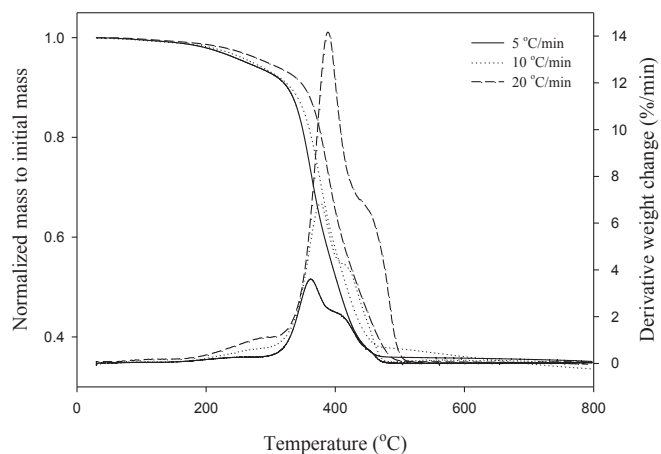
differential thermogravimetric (DTG) curves are presented in Fig. 1.

As can be seen in Fig. 1, the thermal degradation of the sample took place within the temperature range of ~200–500 °C. The first weight loss at ~200–350 °C was likely due to the degradation or volatilization of tire additives such as vulcanization agents. The second and third weight losses appeared to be mainly attributed to the thermal cracking of tire rubbers such as natural, styrene-butadiene and butadiene rubber [24,25]. Seidelt et al. also observed the same degradation pattern as the above [26]. Based on the TG results, the aimed reaction temperatures for the auger and fluidized bed reactors were determined at ~350 and above 500 °C to efficiently extract sulfur-bonded compounds in advance and to fully decompose tire rubbers.

### 2.2. Pyrolysis process

Fig. 2 presents a diagram of the bench scale two-stage pyrolysis process applied in this study.

During pyrolysis, the feed material is conveyed in the first reaction area, the auger reactor, using a screw feeder. After partial decomposition, the feed material is then put into the fluidized bed reactor, wherein the main pyrolysis of feed material occur. The auger and fluidized bed reactors are made of 310S tubes and heated by 4 kW electric heaters, respectively. The auger reactor insulated with gypsum board has a length of 700 mm, an inner diameter of 28 mm, and a thickness of 3 mm, and a K-type thermocouple with a diameter of 6.4 mm is equipped in the middle part of the auger reactor. The fluidized bed reactor also insulated with gypsum board has a height of 380 mm, an inner diameter of 110 mm and a thickness of 3 mm.



**Fig. 1.** TG and DTG curves of the feed material. (This figures show the thermal degradation behaviors of the feed material.).

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