Applied Energy 170 (2016) 140–147

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Non-catalytic pyrolysis of scrap tires using a newly developed two-stage pyrolyzer for the production of a pyrolysis oil with a low sulfur content

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HIGHLIGHTS

- Scrap tire rubber was successfully pyrolyzed in a two-stage pyrolyzer.
- The two-stage pyrolyzer is composed of auger and fluidized bed reactors.
- N_2 and temperatures of ~500 °C were effective for a low-sulfur oil.
- A pyrolysis oil contained only 0.55 wt.% of sulfur and 0.28 wt.% of nitrogen.
- A pyrolysis oil from the auger reactor contained 50 wt.% DL-limonene.

ARTICLE INFO

Article history:
Received 24 December 2015
Received in revised form 12 February 2016
Accepted 20 February 2016

Keywords:
Scrap tire
One-stage pyrolysis
Two-stage pyrolysis
Pyrolysis oil
Sulfur
Limonene

ABSTRACT

The aim of this work was to reduce the sulfur content of pyrolysis oil derived from the scrap tire pyrolysis. In this respect, a series of pyrolysis experiments was conducted in both a fluidized bed reactor (one-stage pyrolysis) and a newly developed two-stage pyrolyzer consisting of an auger reactor and a fluidized bed reactor in series (two-stage pyrolysis). The one-stage pyrolysis was carried out at ~500 and 600 °C with different fluidizing gases (N_2 and product gas). In the experiments, the pyrolysis oil obtained at ~500 °C had a lower sulfur content than that produced at ~600 °C. N_2 was better at producing a low-sulfur pyrolysis oil than product gas. The sulfur contents of the oils obtained from the one-stage pyrolysis ranged from 0.75 to 0.92 wt.%. The two-stage pyrolysis was conducted using product gas as the fluidizing medium at different auger reactor temperatures (~230–450 °C) and at a constant fluidized bed reactor temperature (~510 °C). A pyrolysis oil containing only 0.55 wt.% of sulfur could be produced at the temperatures of the auger reactor of ~330 °C and fluidized bed reactor of ~510 °C. Moreover, the two-stage pyrolysis could produce an oil with a low nitrogen content (0.28 wt.%). A pyrolysis oil obtained from the auger reactor contained DL-limonene up to 50 wt.%.

1. Introduction

The number of tires discarded as scrap has been steadily increasing worldwide, reaching up to 300,000 tons in Korea in 2013 [1]. The management of scrap tires poses serious environmental problems because of their inability to degrade [2,3]. Although existing techniques such as landfill, incineration, and reutilization have been applied for their management, society has continued to demand an economical and sustainable treatment method for scrap tires. Pyrolysis, a process which decomposes organic materials in an inert condition into liquid, gas, and solid products, has received considerable attention as an efficient and environmentally sound method for scrap tires. Products from scrap tire pyrolysis can be used as alternative fuels or chemical feedstocks: for example, the gas product can supply energy needed for the overall endothermic pyrolysis reactions, and the liquid product can replace diesel fuels [4–8] or chemicals such as 1,3-butadien, limonene, benzene, toluene, and xylene, which are currently produced from fossil fuels [9,10]. In addition, many approaches have been taken to produce valuable products such as recycled carbon black and activated carbon from pyrolysis char derived from scrap tires [11–13]. Combustion of tire pyrolysis products initially appears to be a feasible and attractive method because of well-established combustion technologies. However, it is very limited due to the high sulfur contents of pyrolysis products [4,14,15]. Sulfur in the forms of thiophenic and inorganic sulfides in raw scarp tire, which is incorporated by processing aid and through the vulcanization process, generates sulfur oxides when burnt causing air pollution such as smog and acid rain. Meanwhile,

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http://dx.doi.org/10.1016/j.apenergy.2016.02.119
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sulfur in scrap tire is generally transformed into H_2S, CH_3SH, COS and SO_2 during pyrolysis [16,17]. To reduce the sulfur contents of pyrolysis products, various trials have been attempted. Among them, catalytic pyrolysis has been the representative approach, where catalysts such as CaO, NaOH [18], $Ca(OH)_2$ [18,19], $MgCl_2$ [20], Cu [21], Fe [22], and CaC_2 [23] have mainly been tested directly in the pyrolysis process. Meanwhile, other efforts have been devoted to lower sulfur contents in pyrolysis oils. For example, the hydrogenation of pyrolysis oil using NiMo catalysts could reduce the sulfur content of pyrolysis oil to 1000 ppm [24]. However, catalytic pyrolysis did not enable solutions for the deactivation and economic feasibility of the catalytic process. Tire pyrolysis oils were also desulfurized both by oxidation with peroxyformic acid and methanol extraction, and with hydrogen peroxide Fenton catalysts and silica adsorption [25]. In the work, the two methods gave moderate to good yields of desulfurization. Meanwhile, Uçar and Karagöz conducted co-pyrolysis with biomass to remove sulfur in pyrolysis products through the formation of SO_x [26]. In their study, oxygen in the biomass was used as the oxidizing agent for sulfur in scrap tires. The blending of pyrolysis oil from scrap tires with commercial fossil fuels would reduce the sulfur content of the pyrolysis oil. Martínez et al. evaluated fuel properties of tire pyrolysis oils blended with commercial diesel fuel [27] and tested such blends in a diesel engine. In their works, they demonstrated the potential usage of the tire pyrolysis oil for being blended with commercial diesel fuels, at the same time posing an issue on the reduction of sulfur content in the fuel [8].

To efficiently reduce sulfur contents in products during scrap tire pyrolysis, our group developed a new type of two-stage pyrolyzer consisting of an auger reactor and a fluidized bed reactor in series. The basic idea for the development was the consideration that sulfur in tires exists mostly in the form of C–S and S–S bonds, and these bonds are broken at lower temperatures compared to the temperatures at which other bonds in tires such as the C–C and C–H bonds are broken [28]. The auger reactor which operates at lower temperatures than the fluidized bed reactor first liberates sulfur-bonded compounds such as H_2S from the feed material. The partially desulfurized feed is then conveyed to the latter part of the two-stage pyrolyzer, the fluidized bed reactor, which plays a main role in the pyrolysis breaking most chemical bonds in tires to produce gas, oil, and char products that have low sulfur contents. In general, the sulfur contents of pyrolysis oils derived from the non-catalytic pyrolysis of scrap tires are ~1 wt.% [2]. Even catalytic pyrolysis of scrap tires produced oils with sulfur contents above 0.5 wt.% [17,23]. If a non-catalytic pyrolysis of scrap tires can solely reduce the sulfur contents of pyrolysis products, commercialization of the tire pyrolysis will be accelerated by overcoming problems related to the application of catalysts. Hence, this study aims to produce a pyrolysis oil with a low sulfur content without the aid of catalysts. It reports experimental results obtained using the two-stage pyrolyzer for the first time. In this work, the one-stage pyrolysis of scrap tires using a fluidized bed reactor was also conducted in order to better understand the characteristics of the two-stage pyrolysis. The main parameters of the present work for the production of a low-sulfur pyrolysis oil were the reaction temperature of each reactor and the type of fluidizing medium.

2. Material and methods

2.1. Feed material characteristics

Scrap tire rubber was supplied from a tire recycling company in Korea. The size of feed material used in this study was 1–2 mm. The characteristics of feed material are summarized in Table 1.

Table 1
Main characteristics of the feed material.

Proximate analysis	Mean ± s.d. (wt.%)	Ultimate analysis[b]	Mean ± s.d. (wt.%)
Moisture	0.3 ± 0.04	C	89.3 ± 2.33
Volatile matter	76.1 ± 1.25	H	5.8 ± 0.59
Fixed carbon[a]	19.4 ± 1.15	N	0.4 ± 0.02
Ash	4.2 ± 0.18	S	2.5 ± 0.33
		O	2.0 ± 0.09
Metal analysis (ppm)			
Ca	714 ± 10.06	K	538 ± 10.06
Mg	285 ± 0.01	Zn	25,153 ± 261.55
Al	304 ± 0.00	Fe	415 ± 0.01

s.d.: standard deviation.
[a] By difference.
[b] Ash free basis.

The proximate analysis, which was conducted according to ASTM D3172, indicates that the feed material mainly consisted of volatiles (~76 wt.%) and fixed carbon (~19 wt.%). The ultimate analysis shows that the heteroatom contents of the feed material were ~5 wt.% with the sulfur content of 2.5 wt.%. The main components of ash were Zn, Ca, K, and Mg.

To investigate the thermal degradation characteristics of the feed material, thermogravimetric analysis (TGA) was conducted, and the results are shown in Fig. 1.

The differential thermogravimetric clearly shows that the feed sample had three decomposition sections. The first region at 200–300 °C results mainly from the weight loss of sulfur or other additives added during the tire manufacture, the second region at 350–480 °C corresponds to the decomposition of natural rubber and styrene–butadiene rubber, and the final region at 450–500 °C is caused by the decomposition of butadiene rubber. This explanation is also provided in a previous work [29].

2.2. Pyrolysis process

In this study, one-stage pyrolysis with a fluidized bed reactor was first performed to investigate the effects of temperature and the type of fluidizing medium on the sulfur content in oil. Detailed explanations of the compositions and operation methods for the one-stage pyrolysis have been presented in earlier papers [30,31]. Fig. 2 presents a diagram of the newly developed two-stage pyrolysis process.

The two-stage process involves a feeding system consisting of a silo and a screw feeder. Feed material leaving the screw feeder

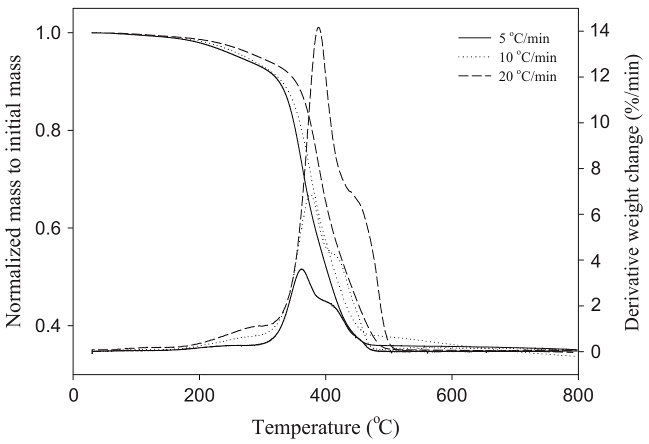

Fig. 1. TG and DTG curves of the feed material.