



Quality improvement of pyrolysis oil from waste rubber by adding sawdust



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ARTICLE INFO

Article history:

Received 23 March 2014

Accepted 18 August 2014

Available online 13 September 2014

Keywords:

Waste rubber

Sawdust

Pyrolysis

Pyrolysis oil

Bio-diesel

ABSTRACT

This work was aimed at improving the pyrolysis oil quality of waste rubber by adding larch sawdust. Using a 1 kg/h stainless pyrolysis reactor, the contents of sawdust in rubber were gradually increased from 0%, 50%, 100% and 200% (wt%) during the pyrolysis process. Using a thermo-gravimetric (TG) analyzer coupled with Fourier transform infrared (FTIR) analysis of evolving products (TG–FTIR), the weight loss characteristics of the heat under different mixtures of sawdust/rubber were observed. Using the pyrolysis–gas chromatography (GC)–mass spectrometry (Py–GC/MS), the vapors from the pyrolysis processes were collected and the compositions of the vapors were examined. During the pyrolysis process, the recovery of the pyrolysis gas and its composition were measured in-situ at a reaction temperature of 450 °C and a retaining time of 1.2 s. The results indicated that the efficiency of pyrolysis was increased and the residual carbon was reduced as the percentage of sawdust increased. The adding of sawdust significantly improved the pyrolysis oil quality by reducing the polycyclic aromatic hydrocarbons (PAHs) and nitrogen and sulfur compounds contents, resulting in an improvement in the combustion efficiency of the pyrolysis oil.

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1. Introduction

Used tire disposal has been a growing issue all over the world because the complex composition and structure of tire rubber and its additives make it highly resistant to natural degradation. Over 285 million used tires were scrapped each year and around 300 million tires were estimated to be stockpiled at the end of 2001 (Edil et al., 2004). At the end of 2007, state regulatory agencies reported that 128.36 million scrap tires remain in stockpiles, a reduction of million tires from 2005 (Scrap Tire Markets in the United States 9th Biennial Report, Rubber Manufacturers Association, 2009, http://www.rma.org/scrap_tires/). Most scrapped tires were used for landfills. Due to the increasing amounts of rubber waste and limited landfill capabilities, innovative methods of recycling and reuse of waste tires need to be developed.

Numerous efforts have been made to utilize the used tires effectively and environmentally. A method to use the scrapped tires for leachate drainage layer materials was developed by Edil et al.

(2004). A process of intensification design to convert waste tires to useful raw materials, such as syngas (CO and H₂), was reported by Castaldi et al. (2007). As additives, waste rubber was utilized for improving the mechanical properties of concrete (Eldin and Senouci, 1993, 1994; Khatib and Bayomy, 1999; Hernandez-Olivares et al., 2002) and wood composites (Ayrilmis et al., 2009a,b; Xu and Li, 2012), respectively. In one of our previous studies, rubber particles were pre-treated by a microwave oven and added into wood particles for fabrication of wood/rubber composites (Xu and Li, 2012). The results indicated that the mechanical properties and dimensional stability of the wood/rubber composites were improved due to the adding of rubber particles.

Pyrolysis of car-tire shreds is a promising solution for the recycling of used tires by producing fuel oil, liquid fuel, and natural gas and of commercial carbon as a solid product (Kalitko, 2008). Waste tires were pyrolyzed catalytically in a batch reactor under atmospheric pressure to convert into valuable hydrocarbons by Shah et al. (2007). A number of pyrolysis studies have been carried out to convert wood/biomass into bio-oil (Mohan et al., 2006). Paradela et al. (2009) pyrolyzed three types of wastes: plastics, tires and biomass, to improve the liquid fraction of the pyrolysis products. Navarro et al. (2012) investigated the thermal behavior of solid particles of plastic, tire, coal and biomass as feedstock in

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pyrolysis processes. Cao et al. (2009) examined the co-pyrolysis of wood biomass and waste tires. It was found that there exists a hydrogen transfer and a synthetic effect during co-pyrolysis of the biomass and tires. Bernardo et al. (2012) carried out the experiments for a multistep upgrading of chars obtained in the co-pyrolysis of plastic wastes, pine biomass and used tires. Jin et al. (2012) examined the composition and characteristics of permanent gases that evolved during co-pyrolysis of sawdust and waste tires.

Although rubber pyrolysis oil has high calorific values, it is difficult to be converted into diesel because it consists mainly of hydrocarbon that has a great amount of PAHs, nitrogen and sulfur. PAHs and nitrogen and sulfur compounds in oil can directly affect its efficiency of combustion in engine and has a negative environmental influence (Cao et al., 2009). The previous work regarding co-pyrolysis of biomass and waste rubber focused on the characteristics of pyrolysis gas or pyrolysis oil. However, not much discussion is available on the effect of feedstock on the quality of pyrolysis vapor and oil. To increase the efficiency of rubber pyrolysis and improve the combustion performance of pyrolysis oils, larch sawdust was added into waste rubber pyrolysis. Our hypothesis was that the adding of sawdust into rubber pyrolysis would improve the environmental performance of pyrolysis oil by reducing the contents of PAHs, nitrogen and sulfur. As a result, the adding of sawdust would make the pyrolysis oil easier to be converted to bio-diesel that could be further converted to valuable diesel. The aim of the study is to investigate the influence of adding sawdust to used tire during pyrolysis on the quality of pyrolysis oil produced.

2. Materials and methods

The rubber particles with an average size of 80–90 screen meshes were purchased from Ketai Rubber Scrap Mill, Tianjin, China. Sourced from Small Xing-An Mountain, China, the larch wood was dried and smashed into particles. Using a screen, particles with an average size of 80–100 screen mesh were sorted out. Table 1 presents the composition of the sawdust and rubber used in this study, in which, the rubber data were provided by the rubber scrap mill and the sawdust information was determined using the ElementarVario EL Analyzer in laboratory. According to the European Committee for standardization (CEN/TS 14961, 2005), the “ultimate” analysis gives the composition of the biomass in wt% of carbon, hydrogen and oxygen (the major components) as well as sulfur and nitrogen (if any). The ultimate analysis in Table 1 reports the elemental carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) on a dry basis because otherwise moisture is indicated as additional hydrogen and oxygen. According to Chinese Standards GB/T 17664-1999, the proximate analysis classified the sawdust and rubber in terms of its moisture (M_{ad}), volatile matter (V_{ad}), fixed carbon (FC_{ad}) and ash (A_{ad}).

In Table 1, the ultimate analysis indicated that the larch sawdust contained less C and more O than the rubber. Proximate analysis illustrated that the sawdust had a higher moisture content and lower fixed carbon content than the rubber.

Using a special connect manner, the NETZSCH STA449F3 thermo-gravimetric analyzer was coupled with Bruker TENSOR 27 Fourier transform infrared analyzer (TG-FTIR). With a flow rate of 50 mL/min and a heating rate of 10 °C/min, nitrogen was used as a protection gas in the chamber. The pyrolysis temperature ranged from 30 to 900 °C. During the experiment, the FTIR mode number of 4000–600/cm, 4-time scans/s and a resolution of 1/cm were used.

The CDS 5150 pyrolyzer coupled with GCMS-QP2010Plus gas chromatography-mass spectrometry (Py-GC/MS) was used to observe the weight loss characteristics under different mixtures of sawdust/rubber. GC/MS had EI source, DM-5 (60 m × 0.25 mm × 0.25 μm) and NIST08 MS data base. A heating rate of 20 °C/s, a temperature of 600 °C and a time-duration of 10 s were used for Py. An inlet temperature of 250 °C, a He gas flow rate of 1.0 mL/min and a flow split-ratio of 100:1 were used for GC. A heating schedule was pre-set as: the temperature remained at 50 °C for 5 min, increased to 250 °C at a rate of 10 °C/min and then remained for 15 min. A junction temperature of 250 °C, an ion temperature of 200 °C, an EI source electron energy of 70 eV and a scan range of 40–450 μm were used in this study.

A laboratory-made 1-kg/h stainless pyrolysis reactor (Fig. 1) with adjustable reaction temperature, heating rate, retaining time and catalyst type was used for the pyrolysis. During the pyrolysis process, the contents of sawdust in rubber were gradually increased from 0%, 50%, 100% and 200% (wt%). Under a non-oxygen condition, the rubber particles with or without sawdust were placed in a reactor that was pre-heated at 450 °C for 1.2 s. The initiation of primary pyrolysis reactions at this temperature released volatiles and formed char. The char was collected by a tourbillion separator. The flow of hot volatiles went toward first-stage cooler with a temperature of 20 °C, resulting in first-stage pyrolysis oil. Having gone through first-stage cooler, the volatiles moved toward the second-stage cooler with a temperature of 5 °C, resulting in second-stage pyrolysis oil.

During the pyrolysis, 0.2 μL pyrolysis oil was collected using a micro collection pin. The pyrolysis oil was injected into GC/MS with an inlet temperature of 280 °C, a He gas flow rate of 1.0 mL/min and a split-flow ratio of 30:1. A heating schedule was pre-set as: the temperature remained at 50 °C for 5 min, increased to 280 °C at a rate of 5°/min and then remained for 15 min. A junction temperature of 280 °C, an ion temperature of 250 °C, an EI source electron energy of 70 eV and a scan range of 20–400 μm were used for MS.

3. Results and discussion

3.1. TG and DTG analysis

Fig. 2a shows that there were four stages in the pyrolysis process: pre-pyrolysis stage (30–270 °C), principal pyrolysis stage (270–480 °C), small molecular gas generation stage (480–750 °C) and ash degradation stage (750–900 °C). When 0 wt%, 50 wt%, 100 wt% and 200 wt% sawdust was added, the final residual carbon (900 °C) was 43.4 wt%, 36.6 wt%, 31.1 wt% and 24.9 wt%,

Table 1
Proximate analysis and ultimate analysis of waste rubber and larch sawdust.

Materials	Ultimate analysis (wt%)					Proximate analysis (wt%)			
	C	H	O ^b	N	S	M_{ad} ^a	V_{ad}	FC_{ad} ^b	A_{ad}
Rubber	84.10	6.69	7.21	0.39	1.61	4.70	54.53	26.28	14.49
Sawdust	53.40	4.64	41.85	0.11	0.00	10.94	71.59	16.68	0.79

^a Subscript “ad” stands for air-dried condition.

^b Oxygen and fixed carbon contents were determined by difference.

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