Energy Conversion and Management 136 (2017) 27–35

Contents lists available at ScienceDirect

Energy Conversion and Management

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

The production of fuel oil and combustible gas by catalytic pyrolysis of waste tire using waste heat of blast-furnace slag

Siyi Luo [a,*], Yu Feng [b]

[a] School of Environmental and Municipal Engineering, Qingdao University of Technology, 11 Fushun Rd., Qingdao 266033, China
[b] Solid Waste Management Research Institute, Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China

ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form 25 December 2016
Accepted 26 December 2016

Keywords:
Waste tire
Catalytic pyrolysis
Waste heat
Blast furnace slag

ABSTRACT

In this study, a novel "waste energy recycling" strategy is presented, i.e., the sensible heat of blast-furnace (BF) slag is utilized for the production of fuel oil and combustible gas from the pyrolysis of waste tire. The effects of various operating parameters including the slag temperature, the mass ratio of BF slag to tire (B/T) and feedstock size on yields and characteristics of pyrolysis products were systematically studied. The results showed that the presence of BF slag greatly improved the production of derived-oil and increased the contents of H_2 and CO in pyrolysis gases. This can be explained by the catalytic activity of BF slag and the CaO-MgO complex in BF slag can prevent the formation of stable chemical structures in hydrocarbons, speed up the degradation of hydrocarbons, weaken C—C and C—H bonds and make them dissociate more easily, and thereby decrease the activation energy of degradation reactions. Increasing BF slag temperature and B/T ratio, and decreasing feedstock (including both BF slag and tire powder) size favored the heat and mass transfer during pyrolysis process and therefore afforded more liquid and gaseous products. In addition, it was observed that the presence of BF slag decreased viscosity, density, H and O content and increased C content, C/H ratio and calorific value of derived-oil relative to pyrolysis oil derived from solely tire powder, thereby resulting in upgradation of oil quality.

1. Introduction

Tire, due to the addition of degradation-inhibiting fillers in manufacturing process, is difficult for recycling and further processing. In China, the discharge of waste tires reached up to 11 million tons in 2015. Their inappropriate disposal may cause serious environment pollution. On the other hand, such large amounts of waste tires are a potential energy source, and many studies have focused on the thermal treatment (i.e., combustion and pyrolysis) for energy recovery [1–4]. In terms of efficiency for recovering energy and environmental threat of burning emissions, combustion is not a prior choice. Instead, pyrolysis, a thermo-chemical treatment technology, is normally applied for solid wastes recycling and transforming into high calorific fuels or chemicals. The main advantage of pyrolysis process is that it can deal with recalcitrant wastes, and efficiently produce reusable products. The pyrolysis of waste tires can generate solid char (for the production of active carbon or reinforcing filler), liquid oil (which can be directly used as alternative fuel in combustion engines, or be fractionated to similitude gasoline and diesel) and combustible gas.

Nowadays, a significant number of technological equipments with different configurations and layouts have been proposed, designed and tested for waste tires pyrolysis. The main commercially available technologies of pyrolysis with acceptable yields of liquid products include fluidized bed reactors (FBR), circulating fluidized bed reactors (CFBR), conical spouted bed reactor (CSBR), rotary kiln reactors (RKR) and auger reactor (AR). All these reactors have different advantages and disadvantages in terms of technical, economical and ecological indices and are used for different applications. Depending on the main aim of the pyrolysis (e.g., heat generation, electricity generation and fuel (liquid fuels and char) obtention), a specific type of reactor should be chosen preferably.

Usually, each type of reactor offers certain particularities in the heat and mass transfer process and processing capacity. RKR presents important advantages for the large scale operation. Higher oil yields were obtained when operating at 550–650 °C, together with the lowest gas yields [5]. Considering the pyrolysis product distribution, CSBR reactor is chosen when the main pyrolysis goal is to optimize the liquid product yield and simultaneously minimize gas yields. Comparatively, higher liquid yields were obtained in a CSBR than with other technologies [6]. Additionally, it has been

---

* Corresponding author at: School of Environmental and Municipal Engineering, Qingdao University of Technology, 11 Fushun Rd., Qingdao 266033, China.
E-mail address: luosiyi666@126.com (S. Luo).

http://dx.doi.org/10.1016/j.enconman.2016.12.076
0196-8904/

observed that working at higher temperature increased the aromaticity of the oil fraction as well as the quality of char [6]. FBR and CFBR [7,8] have been extensively studied from laboratory scale to pilot plant scale and finally to industrial scale. Compare with others tires pyrolysis technologies [5–10], the heating rate of FBC and CFBC could reach up to about 10^3 °C/s; the derived-oil yield ranged from 32% to 60%, determining by pyrolysis temperatures, particle sizes of tire powder, feed positions, fluidizing gas type and residence time.

The derived-oil, produced by non-destructible and non-biodegradable waste tires, presents some disadvantages over fossil fuel due to its high viscosity, high oxygen content, high sulphur content and poor ignition performance [11]. Hence, several attempts for oil upgrading have been conducted and catalytic pyrolysis has been demonstrated as one of the most promising way [12,13]. The addition of a catalyst during pyrolysis can generally promote the conversion of scrap tires, improve the liquid or gas fraction yield, and upgrade the properties of the products to obtain desired chemicals for specific applications. For instance, Kar et al. [14] found an enhancement in the liquid fraction yield and its fuel properties using an expanded perlite catalyst. Zhang et al. [15] revealed that the NaOH addition reduced favored pyrolysis temperatures and increased liquid fraction yield. Li and coworkers [16] revealed the gas yields obtained with different catalysts were in the order of SAPO-11 > USY > β > ZSM-5 > ZSM-22 > no catalyst. The highest yield of derived-oil (55.65%) was obtained with the ZSM-5 catalyst, while the SAPO-11 catalyst afforded the highest gas yield (10.45%) and the lowest char yield (34.43%). In term of upgrading the properties of products, catalytic pyrolysis of tire was often conducted for the production of single ring aromatic compounds in the liquid fraction such as benzene, toluene, and the m-, p- and o-xylenes using zeolite catalysts (Y-type and ZSM-5) [17].

The catalytic pyrolysis process of waste tire is composed of a series of endothermic and exothermic reactions [18]. However, it is an overall endothermic process. The energy is necessary for driving this process, including the energy required to raise the feedstock from room temperature to the reaction one (sensible energy) and the energy to convert the original feedstock into the pyrolysis products (reaction enthalpy). The heat demand can be supplied by different heat sources: (1) burning an auxiliary fuel, (2) burning the gas and/or solid fraction obtained in the process, (3) electric heating, and (4) hot sand or molten salts.

Waste heat is an alternative energy source for the pyrolysis processes, which facilitates energy conservation. The sensible heat of blast furnace (BF) slag is a promising source of waste heat with a temperature of over 1400 °C. One of the most promising ways of recovering heat from BF slag is the dry centrifugal granulation process [19,20], in which the liquid slag is granulated and then cooled rapidly to produce a glassy slag. As the time of granulation is short, and the temperature falls by only about 100–200 °C, the glassy slag with high temperature becomes an ideal waste heat resource and can be used as the heat carrier in endothermic reactions. Zhao et al. [21] studied the combustible gas production from municipal solid waste using hot BF slag as the heat carrier in a fixed-bed reactor. Purwanto et al. [22] reported a hydrogen production process from biogas (CO_2 and CH_4) using hot BF slag as the heat carrier. These results proved that the waste heat from molten slag could supply the energy for hydrogen production. Duan et al. [23] developed a new heat recovery system from hot molten slags. Luo [24] assessed the feasibility of wet sludge gasification by utilization of waste heat in molten slags.

In the previous works, the experimental apparatus was usually fixed-bed reactor and the operation process was typically intermittent. The BF slag and feedstock were blended together in the reactor and kept still during the reaction process, resulting in a poor heat and mass transfer efficiency. In this study, a continuous-operational waste tire pyrolysis system by using high temperature of granulated slag particles as the heat carrier and catalyst was designed. In order to realize the precise control of reaction conditions, the catalytic pyrolysis process and granulation process were conducted in a rotary reactor and a granulation device, respectively. This system was expected to not only realize the recovery of waste heat from liquid BF slags in the form of combustible oil and gas, but also to produce commercially useful glassy slags (used as thermal insulation materials or cement additives, etc.) and solid char product. The objectives of this work are (1) to investigate the reliability of oil and gas production by catalytic pyrolysis of waste tire using hot BF slags as the thermal media and catalyst, (2) to optimize the operation parameters (such as the mass ratio of BF slag to tire, the temperature and size of BF slag particles), and (3) to evaluate the catalytic activity of BF slags in upgrading oil quality.

2. Experiment and methods

2.1. Materials

BF slag was obtained from Qingdao Iron & Steel Company, China. The mineral phase of BF slag was analyzed by powder X-ray diffractometry (XRD), using an X'Pert Pro XRD (Philips, PANalytical B.V., Netherlands). The compositions (wt%) were as follows: 33.7% of SiO_2, 15.0% of Al_2O_3, 42.2% of CaO, 6.6% of MgO as well as some minor iron, sulphur, titanium, manganese, and phosphor oxides. The density of BF slag was 1325 kg m^{-3}.

The raw waste tire, collected in Qingdao City, China, was crushed into tire powders. Ultimate analysis of tire powders was conducted on a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis provided the weight percent of carbon, hydrogen, nitrogen, and sulphur in the samples and the weight percent of oxygen was calculated by difference. ATA Instruments system (TGA 2000, Las Navas) was used to carry out proximate analysis of tire powders (i.e., moisture, volatile matter, fixed carbon, and ash content). The size distributions, proximate and ultimate analysis of tire powders are shown in Tables 1 and 2, respectively.

2.2. Experimental apparatus and procedure

The schematic lab-scale configuration is illustrated in Fig. 1. The system was mainly composed of a packing-bed reactor (for the granulation of molten slags) and a rotary pyrolysis reactor (for the pyrolysis of waste tires using granulated slags as the heat carrier).

In the granulation device, the granulator can produce slag particles with a relatively narrow size range, which can be controlled by varying the rotary-cup speed. The granulated slag particles cooled as they firstly passed through the granulation device and then further cooled in the rotary pyrolysis reactor by the heat exchange with tire powders, both of which provided the rapid cooling.

The rotary reactor was made of stainless steel and surrounded by an insulation layer outside. The effective length of the reactor was 2000 mm with an outside diameter (OD) of 219 mm. In the rotary reactor, a helical vane played the role of increasing residence time of feedstock and enhancing heat transfer between heterogeneous particles. A cyclone dust extractor and a condenser were used in turn as the dedusting unit for pyrolysis gas cleaning and as the cooling unit for gas cooling and oil condensation. There exited temperature gradients along the axial direction of rotary reactor, but it was very difficult to accurately measure. The temperature difference between the inlet (point 2) and the outlet (point 3) of reactor was approximately 200 °C. The temperature