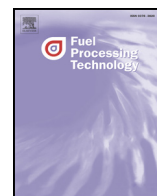




Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Catalytic pyrolysis of flame retarded high impact polystyrene over various solid acid catalysts

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ARTICLE INFO

Article history:

Received 11 November 2015
 Received in revised form 3 January 2016
 Accepted 14 January 2016
 Available online xxx

Keywords:

Br-HIPS
 Catalytic pyrolysis
 Zeolites
 Mesoporous catalysts
 Debromination

ABSTRACT

The catalytic pyrolysis of flame retarded high impact polystyrene (Br-HIPS) was performed in the presence of five different solid acid catalysts in order to remove the bromine from the derived pyrolysis oil. The catalysts were three zeolite materials (HY, H β and HZSM-5) and two mesoporous solids (all-silica MCM-41 and active Al₂O₃). The results showed that in the presence of HY and H β zeolites, a reduction of approximate 50 wt.% in oil yield and a corresponding increase in wax and gas yields were obtained compared to thermal degradation. The addition of HZSM-5 showed less impact on product distribution and produced more oil compared with the other zeolites. The mesoporous catalyst of all-silica MCM-41 obtained the highest oil yield of 67.9 wt.% and reduced the wax yield to 8.73 wt.%. In terms of the composition of the pyrolysis oil, HZSM-5 and all-silica MCM-41 were favorable to produce more valuable single ring aromatics, such as toluene, ethylbenzene and cumene. Moreover, the catalysts exhibited pronounced debromination performance, especially the H β catalyst, achieving the debromination efficiency of 70.47%. The results confirmed the catalytic pyrolysis of Br-HIPS and debromination performance was well related to the textural properties of catalysts.

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1. Introduction

Plastics, one of the fastest consumption in daily life, are continuously increasing worldwide, leading in parallel to growing plastic waste generation and accounting for about 30% of all waste electrical and electronic equipment (WEEE) [1]. Plastics are mainly derived from petrochemicals and composed primarily of hydrocarbons but also contain additives such as antioxidants, flame retardants and other stabilizers, which make the plastics difficult to be biodegraded [2]. Considering high-value chemicals and high energy density of plastics, studies on feedstock recycling of plastic wastes have been performed to convert the polymeric materials into valuable chemicals and fuels in recent decades [3–5]. However, the plastic fraction of WEEE commonly contains brominated flame retardants (BFRs), which can behave as precursors in the formation of dioxins and/or benzofurans [6]. For the sake of hazardous plastic wastes, advanced treatment methods are essential to eliminate the toxic flame retardant additives for the feedstock recycling of WEEE plastics. Therefore, researchers have been trying to improve the feedstock recycling process and bring back the waste plastics into the manufacturing line by generating high quality bromine-free chemicals and alternative fuel-like products [7,8].

High impact polystyrene (HIPS), which approximately accounts for 30% of all WEEE plastics and contains high concentration of

polybrominated diphenyl ethers (PBDEs) and Sb₂O₃ additives [9], has been the main subject of feedstock recycling treatment in recent years [9–13]. The pyrolysis and catalytic pyrolysis are the most widely used feedstock recycling technologies for the conversion of Br-HIPS into valuable chemicals and fuel oils. Compared with the thermal pyrolysis, the catalytic pyrolysis not only reduces the degradation temperature but also exhibits shape selectivity to produce high-quality liquid and higher value products or even bromine-free chemicals [5,14–16]. Bhaskar et al. [15,16] reported that calcium- and iron-based composites were effective in debromination of polymers mixed with Br-HIPS. Brebu et al. [17,18] investigated the catalytic pyrolysis of acrylonitrile-butadiene-styrene (ABS) over different iron oxides and proved that the primary degradation products were influenced by the composition and crystalline structure of the catalyst. It was also reported that Ca-based additives (CaO, Ca(OH)₂, oyster shell) exhibited positive effect on the removal of bromine content in Br-HIPS oil [19]. Blazso and Czegeny [20] investigated the pyrolysis of brominated epoxy resin using pyrolysis-GC/MS and found the concentrations of brominated compounds decreased in the presence of zeolites and further upgrading of the pyrolysis oil was required for commercial applications. Furthermore, Hall and Williams [21] studied the effect of ZSM-5 and Y-zeolite on debromination in the pyrolysis of Br-HIPS and Br-ABS. It was demonstrated that both ZSM-5 and Y-zeolite could remove brominated compounds from the volatile pyrolysis products of Br-HIPS. But the catalyst also drastically reduced the oil yield and significantly changed the composition of the pyrolysis products. In fact, the authors also

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claimed that the composition of the pyrolysis oil did not greatly alter and the organobromine compounds reduced in the presence of fluidized catalytic cracker catalyst [22].

The previous researchers mainly conducted pure polyolefins or simple mixtures of them and focused on performance of catalysts and degradation mechanisms over various solid acids, including zeolites, clays and silica-alumina [23–31]. However, the catalytic activities on the degradation of Br-HIPS over solid acid catalysts have scarcely been studied due to its specific thermal degradation characteristics and the formation of brominated products [20–22].

Different catalytic activities of solid acid catalysts are related to their acidic and textural properties, which have been reported to play a key role in catalytic cracking performance of polymers [25–31]. Therefore, understanding the behavior of the catalytic pyrolysis of Br-HIPS is essential to evaluate the potential application of catalytic treatment in commercial feedstock recycling processes.

In this study, the catalytic pyrolysis of Br-HIPS over various solid acid catalysts was carried out in a fixed bed reactor at a final pyrolysis temperature of 410 °C. Three zeolite materials (HY, H β and HZSM-5) and two mesoporous solids (all-silica MCM-41 and active Al₂O₃) were applied. The exhaustive characterization of the catalysts and the pyrolysis products was presented with the aim of better understanding performance of solid acid catalysts on the catalytic pyrolysis of Br-HIPS. Meanwhile, the effect of the catalysts on the migration and transformation behaviors of bromine existing in the pyrolysis products was demonstrated for enhancing the potential benefits of feedstock recycling for high quality bromine-free fuel oils.

2. Experimental

2.1. Materials

Commercially available HIPS was supplied by Qimei Co., Ltd. Zhenjiang, China. The HIPS containing flame retardant decabromodiphenyl oxide (DDO) and synergist Sb₂O₃ (Br-HIPS) was prepared by melt blending in an internal mixer working at 190 °C for 15 min [13]. Both samples were pulverized into particles of 0.6 mm with a pulverizer that was refrigerated with liquid nitrogen. The proximate and ultimate analyses of Br-HIPS are presented in Table 1. The zeolite catalysts (HY, H β and HZSM-5) and all-silica MCM-41 powders (particle diameter smaller than 5 μ m) used in this study were supplied by the catalyst factory of Nankai University in Tianjin, China. Active Al₂O₃ was obtained from Sigma-Aldrich (<0.15 mm).

2.2. Experiment procedures

The experiments were performed in a fixed bed reactor (Fig. 1). The reactor was a quartz tube with 46 cm height and 41 mm in inner diameter, which was heated by an electrical furnace equipped with a temperature controller. Before the catalytic pyrolysis experiments, the Br-HIPS sample and the catalyst were mixed thoroughly (the catalyst and the Br-HIPS sample at a mass ratio 1:9), then a 10 g aliquot of the mixture sample was fed into a crucible (OD 30 mm, height 50 mm), and placed inside the reactor. For comparison, the thermal degradation of Br-HIPS

without catalyst was carried out under the same experimental condition. In all the experiments, the reactor was purged with N₂ stream (100 ml min⁻¹) for 30 min, and then heated to 410 °C at a rate of 10 °C min⁻¹ under the N₂ flow rate of 30 ml min⁻¹. The target temperature was held for 90 min.

The volatile products exited from the reactor were cooled by an ice/salt bath condenser to trap the liquid products. The condenser was followed by a fiber filter to prevent any organic materials from entering into the subsequent alkali solution (Na₂CO₃/NaHCO₃) flask which was used to trap HBr or Br₂. The remaining gases were not collected for analysis.

The thermal and catalytic pyrolysis of the Br-HIPS plastic resulted in the formation of mainly oil, wax, gas and char residue. The mass of pyrolysis oil collected in the tar trap was measured before and after each experiment. Then the mass of wax coated on the wall of the reactor was determined by measuring the mass of the quartz reactor before and after each experiment. A small amount of trapped products coated on the U-tube was dissolved in the chloroform and filtered to distill at reduced pressure to separate the oil and wax, which was weighed accurately [32]. The char residue mass was determined by measuring the mass of the crucible before and after each experiment. The yield of char was calculated as follows:

$$\text{yield of char (wt.\%)} = \frac{m(\text{residue}) - m(\text{catalyst})}{m(\text{Br-HIPS})} \times 100\%. \quad (1)$$

The mass of gaseous products was obtained by the method of difference.

2.3. Analytical methods

The ultimate and proximate analyses of the sample were respectively determined using an elemental analyzer (Vario Micro cube, Elementar Inc., Germany) and TGA-2000 (Las Navas Instruments, Spain). The bromine content of the sample was determined by the EPA method 5050 provided in our previous study [13]. The antimony content of the sample was determined by first digesting an aliquot of the sample in a mixture of sulfuric and nitric acid and then analyzing the solution using inductive coupled plasma-mass spectrometry (ICP-MS).

SiO₂/Al₂O₃ ratio of the catalysts was measured by X-ray fluorescence (XRF) on a model XRF-EAGLE III instrument (EDAX Inc., USA) with an X-ray tube with a rhodium anode (40 kV and 70 mA). The physical structure of the catalysts was conducted using a powder X-ray diffraction (XRD) X'Pert PROX diffractometer with monochromatic Cu K α radiation (PANalytical B.V., 40 kV and 40 mA). The patterns were recorded in the 2 θ range of 5–80° at a scanning rate of 12° min⁻¹ and the all-silica MCM-41 catalyst was detected in the 2 θ range of 1–15° since its special crystalline structure. SEM images were obtained on a field-emission scanning electron microscopy (FE-SEM, Zeiss SIGMA). The textural properties of the catalysts were determined using a nitrogen (N₂) adsorption apparatus (ASAP-2020, Micromeritics) at 77 K. Surface areas were calculated using the BET equation and external surface areas and micropores volume were obtained by applying the t-plot method. Total pore volume was measured at P/P₀ = 0.99 and pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method.

Temperature programmed desorption of NH₃ (NH₃-TPD) was performed on the ChemiSorb 2720 (Micromeritics) to measure the acid properties of the catalysts. Prior to NH₃-TPD experiments, the samples (100 mg) were pretreated under He flow at 500 °C for 1 h. Then, they were saturated with NH₃ at a flow rate of 30 ml min⁻¹ for about 30 min. In order to avoid the physisorption of NH₃, the saturated samples were flushed in the He atmosphere at 50 °C for 2 h. Then, the desorption experiments were carried out by heating the samples in He (30 ml min⁻¹) from 50 °C to 800 °C with a heating rate of 10 °C min⁻¹.

Table 1
Main characteristics of the Br-HIPS sample.

Proximate analysis	wt.%	Ultimate analysis ^a	wt.%
Moisture	0.1	C	79.5
Volatile matter	99.5	H	6.8
Fixed carbon	0	N	0.1
Ash	0.4	O ^b	1.1
		Br	7.8
		Sb	4.7

^a Dry and ash free basis.

^b By difference.

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