Untreated and HNO₃-treated pyrolysis char as catalysts for pyrolysis of waste tire: In-depth analysis of tire-derived products and char characterization

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ABSTRACT

The pyrolysis char produced in the pyrolysis of scrap tire rubber has few market outlets, reducing the economic viability. Thus, the char properties was firstly studied in this work, and then untreated and 5 M HNO₃-treated chars were investigated for their potentials as the catalysts for pyrolysis of waste tire. The product distribution and the quality of tire pyrolysis oil were examined. The gas products were analyzed by using GC/FID whereas the oil products were analyzed by using SIMDIST-GC and GC × GC/TOF-MS. Sulfur and nitrogen contents were determined by using CHNS-analyzer. The catalysts were also characterized by using BET, XRD, XRF, FTIR, FE-SEM, and TG/DTA. The results indicated that the surface area and pore size of treated char were enhanced by the acid treatment. Furthermore, it can be noted that the increase in the total acidity of treated char was caused by the enhancement of carboxyl (-COOH) group on the surface. Additionally, the treatment using 5 M HNO₃ can demineralize and significantly reduce sulfur content in the char. When employed as a catalyst, the HNO₃-treated char increased the gas production due to its enhanced acidity, surface area and pore size, consequently promoting the greater cracking activity. However, both untreated and treated chars dramatically decreased gas oil, light vacuum gas oil, and heavy vacuum gas oil, leading to the drastic enhancement of gasoline and kerosene. Moreover, even though the char catalysts cannot reduce nitrogen content in oil, they can greatly remove sulfur in oil (approximately 26.6–27.3%). Nevertheless, the untreated char that contained a larger content of elements or minerals than the treated one gave significantly higher petrochemical production, which indicates that deminerization by the acid treatment may not always be needed for better activity, especially for petrochemical production.

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1. Introduction

With the strong global need in automobile usage, a huge amount of waste tires has been increasingly discarded. Due to the fact that the disposal of waste tires is a serious environmental problem, reprocessing via pyrolysis is an interesting alternative. However, the solid product or pyrolytic char from tire pyrolysis, whose amount ranges from 22 to 50 wt% depending on the type of reactors and the pyrolysis conditions [1], has few market outlets, reducing the economic viability. In terms of applications, the pyrolytic char has the opportunity to be used as an alternative resource for producing adsorbents for water and air purification, fuel mate-

rials, or catalyst supports. The structure of pyrolytic char was similar to graphite, but covalent bonding between its graphene sheets showed imperfections in its production [2]. The crystalline pyrolytic carbon has a distorted lattice structure with random unassociated carbon atoms [3]. The major elements of pyrolytic char are carbon (81.5–82.8 wt%), hydrogen (0.32–1.0 wt%), sulfur (1.7–3.3 wt%), and nitrogen (0.2–0.5 wt%) [4,5]. However, it was noted that pyrolytic char still contained some contaminants such as sulfur, heavy metals, volatile matters, and trace oil, which need to be carefully removed [6,7].

In general, the production of commercial activated carbon from pyrolytic char is achieved by thermal treatment, combined with carbonization and activation with activating agents such as stream, CO₂ or air [8]. The results showed that the method can provide high surface area carbon, which was suitable for adsorption applications. Bernardo et al. suggested that acid leaching can be applied to remove a trace of oil from activated carbon [7]. Moreover, in order

to decrease the ash content of chars, a demineralization procedure using hydrogen peroxide was successfully applied, which highly removed the majority of the metallic elements. Moreover, among the treatments using some acids and H_2O_2, the HNO_3 treatment of pyrolysis char resulted in the highest sulfur removal. The attractive point is that HNO_3 was able to maintain pore structure, unlike the other acids. Soltani et al. found that pyrolytic char from used cigarette filters, modified by using nitric leaching, had 57.8% greater surface acidity than the non-modified char, which was confirmed by Boehm titration method [9]. Chars produced after thermal or chemical treatments are mostly used as adsorbents for removal contaminants; for instances, a variety of metals such as Cr [10], Cd [11] and Hg [12] and a variety of chemicals such as benzene derivatives [13], p-cresol [14], and phenol and dye [15]. Moreover, chars produced from animal bones were utilized for environmental applications [16] such as fluoride adsorption [17].

Nevertheless, chars derived from various sources have been also tested as catalysts for many reactions. For instances, char-supported iron catalyst was found to decompose NOx precursors (e.g. HCN and NH_3) efficiently during the steam reforming process [18]. Biomass chars [19,20] and coal chars [19,21] were found to be effective catalysts for tar reforming in gasification processes, and the activity of a catalyst for reforming tar did not directly depend on the surface area and pore volume; however, it was related to carbon structure in the char support [21]. Char obtained from biomass gasification was also tested for methane decomposition, and the results showed that the inorganics in the char play a significant role in the catalytic activity whereas carbon was found to play an important role both as a catalyst and a support for the inorganics [22]. Bio-chars made from switchgrass and red oak bark were co-pyrolyzed with woody biomass, and a significant influence of the bio-chars was observed on the bio-oil yields, moisture content and pH value of bio-oils in association with a significant decrease in the carbon yield in the bio-oil when switchgrass bio-char was used [23].

Since tire-derived char (TDC) is cheap, and it is enormously produced from waste tire pyrolysis (40–60% yield), it is essential to find its potential usages and applications in order to solve the problems arisen from a gigantic inventory of TDC in a tire pyrolysis plant. One interesting application is to use TDC as a catalyst for catalyzing a reaction, and one perfect solution is to use TDC as the catalyst in a waste tire pyrolysis plant. Moreover, based on our estimation of molecular sizes of hydrocarbons in tire-derived oil (TDO), mesoporous materials with the pore sizes in the range of 20–30 Å (e.g. char) were recommended as catalysts for handling all hydrocarbon groups in TDO, especially aromatics [24]. In addition, the surface functional groups on char [25] and acid functional groups after acid treatment [9] were expected to enhance the cracking. The objective of this work was therefore to investigate the potential of using untreated and 5 M HNO_3-treated chars as catalysts for waste tire pyrolysis together with in-depth analysis of tire-derived products and char characterization. From this purpose, untreated and 5 M HNO_3-treated chars were expected to convert heavy oil fraction into lighter products, and then produce greater quality of oil.

2. Experimentals

2.1. Catalyst preparation

In order to treat tire-derived char (TDC), nitric acid was used as a surface cleaning chemical. The TDO was firstly immersed in a 5 M HNO_3 solution (commercial HNO_3: RCI Labscan, 65% purity; density 1.39 g/mL) with the TDC to acid ratio of 1 g: 7.5 mL at room temperature under stirring condition (300 rpm) for 1 h. The 5 M HNO_3-treated char was subsequently washed until pH 7, and then

dried at 105 °C overnight. Finally, the catalyst was pelletized and then sieved to the particle sizes in the range of 40–60 mesh.

2.2. Catalyst characterization

Thermogravimetric/Differential Thermal Analysis, TG/DTA, (Perkin Elmer/Pyris Diamond), was performed to determine the thermal characteristics as well as the amount of moisture (50–105 °C), volatility or coke deposited on spent catalysts (105–850 °C), and fixed carbon (>850 °C). This analysis was conformed to ASTM D3172-07 and ASTM D3173-03. The contents of carbon, hydrogen, nitrogen, and sulfur in the waste tire feed and char catalysts were acquired from using LECO®Elemetal Analyzer (TruSpec®S). X-ray fluorescence (XRF) spectrometry (AXIOS PW4400) was used to determine the concentrations of elements in the waste tire feed and catalysts. The samples were mixed with boric acid with the sample to boric acid mass ratio of 1:3. X-ray diffraction (XRD) instrument (Rikagu) was used to determine the crystalline phase of catalysts. The scanned angle started from 5° to 60° with a scanning speed of 5°/min. Thermo Finnigan/Sorptomatic 1990 equipment was used to determine the physical properties of catalysts. The approximate 0.5 g of a catalyst was degassed under vacuum at 250 °C for 18 h prior to analysis. Field Emission-Scanning Electron Micrographs (FE-SEM, JEOL/JSM 5200) was employed to examine the microstructure morphology of the catalysts. The samples were dried at 105 °C for 24 h, and then were coated by Pt for 150–200 s. A Nicolet 6700 Fourier Transform Infrared Spectrometer (FTIR) was used to collect the spectra and the wave numbers of functional groups on pyrolytic chars. The samples were mixed with KBr with the sample to KBr mass ratio of 1:1200. In addition, total acidity was determined by using back titration (3 replicates) [26].

2.3. Pyrolysis process

The wasted tire tread (Bridgestone TURANZA GR-80) was prepared as a raw material, which was free of fiber and steel. It was consequently scraped, and then sieved (20–40 mesh). The experimental setup (see Fig. 1) was the same as indicated in our published papers [27–29], and the pyrolysis conditions have been achieved from our successive studies [30,31]. The reactor was divided into two zones; that are, the lower zone (pyrolysis zone) was loaded with 30 g of tire, and the upper zone (catalytic zone) was loaded with 7.5 g of a catalyst. The two zones were heated from room temperature to 500 °C and 350 °C, respectively, with a heating rate of 10 °C/min at atmospheric pressure. After that the final temperatures were held for 120 min in order to ensure that the tire sample was completely decomposed. The evolved gas was purged using a 25 mL/min of nitrogen through two condensers, aiming to separate the liquid product, called tire-derived oil (TDO), from incondensable gas.

2.4. Product analysis

TDO and TDC were weighed to determine the amount of gas yield based on mass balance. As first, TDO was dissolved in n-pentane with the oil to n-pentane mass ratio of 1:40 for asphaltene separation. The obtained oil is called maltene. Then, a 30 μL maltene solution, diluted in 2 mL carbon disulfide (CS_2), was analyzed for its composition by using Gas Chromatograph with Time-of-Flight Mass Spectrometer (GC × GC/TOF-MS). The GC × GC-TOF/MS apparatus was equipped with an Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA), a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA), and a thermal modulator. The chromatography part of the instrument was operated by using two GC columns. The 1st GC column was a non-polar Rtx®-5Sil MS, and the 2nd GC column was a polar Rxi®-17 MS. Furthermore, the diluted