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The effects of activated Al_2O_3 on the recycling of light oil from the catalytic pyrolysis of waste printed circuit boards

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ABSTRACT

The effects of employing activated Al_2O_3 during the catalytic pyrolysis of waste printed circuit boards (WPCBs) are investigated, focusing on the recycling of light oil. Variations in the pyrolysis process are studied through analysis of the phase distribution, water content and boiling point fractions of the resulting products. Product composition and carbon number distribution are analyzed using gas chromatography techniques. The use of activated Al_2O_3 increases the light oil fraction and also reduces the quantity of brominated products formed. It was determined that the best yield of light oil and most efficient debromination resulted from catalytic pyrolysis at 600 °C. Applying catalyst-to-feed ratios in the range of 1.0–1.5 also maximizes the yield of light oil. The major oil fraction resulting from catalytic pyrolysis has a boiling point range of 0–250 °C and carbon number range of C6–C9, showing for use as a potential fuel after suitable treatment such as hydrogenation. At a higher catalyst-to-feed ratio of 2.0, activated Al_2O_3 generates a high proportion of light oil fractions containing a significant quantity of chemicals such as phenol (52.67% at 600 °C), although an overall lower yield of oil is obtained. The oil produced in this manner may also be used as a raw material feedstock for the production of various other useful chemicals.

1. Introduction

With the advent of the information age and the associated rapid development of the electronics industry, the printed circuit board (PCB) has been widely used in almost all fields of electric and electronic equipment (EEE), from toys to televisions and computers. The short life-cycle of many of these products, however, generates a significant quantity of waste electric and electronic equipment (WEEE), which has become a very serious environmental concern and which includes a great number of waste PCBs (WPCBs).

The typical PCB is a heterogeneous mixture of organic materials (typically a thermoplastic epoxy resin with flame retardant additives such as bromine (Long et al., 2010)), metals and glass fibers (Guan et al., 2008). The degradation of PCBs is quite difficult, although with proper processing the metals and organic materials that they contain can be recovered for use as raw materials in the manufacture of new products (Guan et al., 2008; Liu et al., 2011).

The pyrolysis of PCBs (either at ambient pressure or under vacuum) has been extensively studied, since it represents a potentially useful alternative recycling technique (Guan et al., 2008; Lopez-Urionabarrenechea et al., 2011). Compared with normal pyrolysis, pyrolysis under vacuum can significantly decrease the energy consumption associated with the pyrolysis of the PCB component materials and thus improve yields

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(Lopez-Urionabarrenechea et al., 2012). Investigations of PCB pyrolysis to date have focused on the composition of the resulting pyrolysis oil (Li et al., 2009a; Zhan and Qiu, 2011), the reaction kinetics (Li et al., 2009b; Zhan and Qiu, 2011), and the bromine distribution within the pyrolysis products (Liu and Hai, 2011). There are few reports of the application of catalysis to the pyrolysis of PCBs.

Recently, there have been many reports of studies concerning the catalytic pyrolysis of other waste organic polymers, including plastics and tires (Balabanovich et al., 2004; Guan et al., 2009; Lopez-Urionabarrenechea et al., 2011). These investigations have shown that the use of a catalyst provides the number of acid sites contributing to the pyrolysis and has several advantages compared with simple thermal processing, such as lower energy consumption, shorter reaction times and good selectivity for generating high value products (Guan et al., 2009).

The recycling of oils resulting from WPCB pyrolysis is currently difficult since these oils contain a significant heavy fraction as well as high levels of bromine. The application of a catalyst during pyrolysis may, to some extent, mitigate these problems by producing a greater proportion of both light and dehalogenated pyrolysis products (Lopez-Urionabarrenechea et al., 2011; Zhao, 2002). Consequently, catalytic pyrolysis may be a more efficient and useful technique for recycling WPCBs. Since coking of the catalyst can severely reduce its effectiveness and thus impact the economics of the pyrolysis, reducing costs by regenerating the catalyst will also be an important aspect of the economics of this process.

The purpose of the present study was to investigate the effectiveness of spherical activated Al_2O_3 particles on the catalytic pyrolysis of WPCBs under vacuum. This material is widely used in catalysis for two main reasons: (1) it is a mesoporous material, meaning that gaseous compounds are able to enter into its porous structure and remain there for relatively long periods of time, leading to higher cracking rates (Guan et al., 2009) and (2) it possesses a large quantity of acid sites (primarily Lewis acids) (Sun et al., 2003) that tend to produce aromatic hydrocarbon with short carbon chains as the result of secondary cracking reactions.

In this paper, the catalytic pyrolysis of WPCBs using different quantities of activated Al_2O_3 at different temperatures is discussed. The data include: (1) the proportional yields of gas, liquid and solid products, (2) the yields of light oil, (3) the characteristics and composition of the resulting pyrolysis oil and (4) the proportions of oil and water in the pyrolysis liquid. This paper therefore describes the effects of using a combination of pyrolysis, catalysis and vacuum to convert WPCBs into potential useful fuel or chemical feedstock resources.

2. Materials and methods

2.1. Materials

The WPCBs were derived from Guangzhou Valuda Group Company Limited (Guangdong, People's Republic of China). In preparation for processing, the WPCBs were first pulverized, after which copper was removed, leaving only the epoxy resin, glass fiber and brominated flame retardants. During preliminary trials, three parallel catalytic pyrolysis processes using either USY, ZSM-5 or spherical activated Al_2O_3 were investigated in previous study (Wang et al., 2014). The Al_2O_3 was determined to have the most pronounced effect and so was used for all further work. The activated Al_2O_3 is an industrial product (Product ID: 71010293916) with activation derived from Pingxiang Sanhe Ceramics Company Limited (Jiangxi, People's Republic of China). The characteristics of the pulverized PCB material and the spherical activated Al_2O_3 particles are presented in Tables 1 and 2, respectively.

Table 1 – Composition and properties of pulverized PCBs.

Property	Value
Glass fiber	54.2%
Organic compounds	45.8%

Table 2 – Properties of the activated Al_2O_3 particles.

Property	Value
Crystalline phase	Y
Al_2O_3	≥93%
Na_2O	0.15–0.3%
BET (m^2/g)	≥200
Bulk density (g/mL)	0.70–0.80
Pore volume (mL/g)	0.4
Particle size (mm)	3–5

2.2. Equipment and methods

The experimental set-up and process flow are shown in Fig. 1. Pyrolysis of the PCB material was carried out in a tube furnace controlled by a programmable heating system, attached to a condensation separation system under vacuum. In a typical process run, 100 g of PCB sample covered with the desired quantity of catalyst was placed in the reactor and the entire system was sealed and evacuated to 10 kPa. The system was heated at a rate of 10 °C/min to the final temperature and held there for 60 min to ensure that pyrolysis of the sample was completed, after which the sample, still under vacuum, was allowed to cool to room temperature. The pyrolysis gases passed through a series of gas–liquid separators. These gases either condensed in the Graham condenser and were collected in condensate bottle 1 or cooled in the Allihn condenser and were collected in bottle 2, or were trapped in the NaOH absorption solution (note that condensate bottle 2 also served to prevent this absorption liquid flowing back into bottle 1 during the post-reaction furnace cooling process).

Both solid and liquid product yields were determined by weighing the products, while gas yields were calculated from the difference between the initial weight of pulverized PCB and the sum of the solid and liquid yields. The solid products, along with the Al_2O_3, were placed in a muffle oven and heated at 650 °C for 60 min to remove coking carbon, and then the Al_2O_3 can be recycled.

2.3. Analytical techniques

All pyrolysis oils obtained were characterized using a variety of analytical techniques. Boiling point range distributions were determined according to the ASTM D2887-2008 standard method using gas chromatography with flame ionization detection (GC-FID). The relationship between boiling point and retention time was established by running the D2887 calibration mix (DRH-002N-10X, AccuStandard) over the range from C7 to C44. The compositions and relative proportions of the various oil fractions were ascertained from gas chromatography coupled with mass spectrometry (GC–MS,