

An Investigation on Debromination Performance of Sulfur Impregnated Catalyst for E-waste Pyrolysis Process

Nutcharathip Kathongthung, Chanoknunt Khaobang and Chinnathan Areeprasert

Abstract— This paper studied the debromination performance by sulfur impregnated catalysts for printed circuit board pyrolysis process. In-situ catalytic pyrolysis was performed at 500 °C and a heating rate of 50 °C/min. Y-zeolite was used and catalyst and sulfur was loaded at 1%, 5% or 10%. Results showed that a limited amount of pyrolysis oil was obtained, whereas a yield of pyrolysis char was very high, 74-79 wt.%. High sulfur loaded reduced BET surface area of the modified catalyst which affected the debromination performance. The composition of pyrolysis char contains 8-9.5%wt of carbon. The bromide removal in pyrolysis oil was 21.42-64.28%. High amount of bromide was adsorbed in pyrolysis char when 5% sulfur was loaded.

Keywords— bromine, debromination, impregnation PCB, pyrolysis, sulfur, Y-zeolite.

I. INTRODUCTION

Currently, the contamination of various substances in electronic waste (EW) causes environmental problems, especially brominated flame retardants (BFRs), which have been an extensively used integral part of electronic and electrical products [1]. BFRs were considered hazardous because of pollutants such as dioxins and/or benzofurans formation [2]. The purpose of the study is to develop the appropriate technologies for recycling EW with environmental concern including a safety emission released to environment.

The pyrolysis process was one of the most attractive techniques of thermal recycling. Thermal pyrolysis involves the degradation of polymeric materials by heating in the absence of oxygen [3]. The EW products from pyrolysis process were char, oil, and gas, obtained from the pyrolyzer reactor, impinge bottles, and exhaust gas, respectively [4]. However, it was reported that the pyrolysis of EW generates brominated compounds such as hydrogen bromide (HBr) and antimony tribromide (SbBr₃) [5, 6]. The quality of EW pyrolysis products could be feasible by reducing the brominated compounds applying with suitable catalysts. The most common and suitable catalysts for each process are zeolite, alumina, silica-alumina, fluid catalytic cracking catalyst (FCC), and reforming catalyst [3].

Manuscript received March 2, 2020. This research was financially supported by Kasetsart University Research and Development Institute, FF(KU) 25.64.

N. K. Author is with the Department of Safety Engineering, Faculty of Engineering, Kasetsart University.

C. K. Author is with the Department of Mechanical Engineering, Faculty of Engineering, Kasetsart University.

C. A. Author is with the Department of Mechanical Engineering, Faculty of Engineering, Kasetsart University.

The catalyst adsorption capacity was implemented for remediation purposes. The various modifications of sorbents were performed to improve the sorption properties. Many studies have been conducted on sulfur impregnation to improve sorption capacity. Various methods and chemicals are used, such as carbon disulfide (CS₂) [7], sodium sulfide (Na₂S) [8], sulfuric acid (H₂SO₄) [8], and sulphur dioxide (SO₂) [9]. The chemical modification can change sorbents' chemical properties such as specific surface area, pore size, pore-volume, functional groups, surface charge, and bromine adsorption capacity. Moreover, sulfur-containing compounds are readily available, and they are also highly stable.

In this paper, an investigation of the Br removal mechanism using sulfur catalyst during the pyrolysis process was performed. Br removal performance was assessed by with four catalysts in in-situ pyrolysis system. Yield of the main products was collected. The physical and chemical properties of the catalysts were analyzed. The specific surface area and surface structure of the catalysts and Br content in pyrolysis char and oil were studied.

II. MATERIAL AND METHODS

A. Raw material

Representatives of EW in this study were printed circuit boards (PCB) provided by K-recycle Co., Ltd., Nonthaburi, Thailand. The PCB was cut in the form of a square rectangle with 15 × 20 mm. Table 1 shows the proximate and ultimate analyses of a printed circuit board.

TABLE I: PROXIMATE AND ULTIMATE ANALYSES OF PCB

Item	Unit	Value
Proximate analysis		
Moisture	wt.% db.	-
Volatile matter	wt.% db.	29.30
Fixed carbon	wt.% db.	4.70
Ash	wt.% db.	66.0
Ultimate analysis		
Carbon	wt.% db.	21.92
Hydrogen	wt.% db.	1.90
Nitrogen	wt.% db.	0.61
Oxygen	wt.% db.	2.80
Bromine	wt.% db.	6.78

B. Catalyst preparation

The catalyst used in this work was a commercial Y-Zeolite

(YZ). Sulfur loading (1%, 5%, and 10%) into YZ was performed by wet impregnation. First, YZ (10 g) and sulfuric acid (0.52, 2.6, and 5.2 ml) were mixed and then stirred under the condition of 35 °C for 20 min. Finally, the impregnated catalysts were dried at 100 °C for 24 h. The properties of the catalysts are shown in Table II. The impregnation of YZ and sulfur 1%, YZ and sulfur 5%, and YZ and sulfur 10% will be referred to as 1%S-YZ, 5%S-YZ, and 10%S-YZ, respectively.

C. Pyrolysis process

The pyrolysis reactor was made from stainless steel (SUS 316) with an internal diameter of 42 mm and a height of 380 mm. A PID controller controlled the electric heater of the pyrolyzer. Raw material and catalyst for each experiment were 50 g and 10 g, respectively. The pyrolysis temperature target was 500 °C with the heating rate was 50 °C/min performed under the nitrogen flow of 50 ml/min. The pyrolysis process was held at a stable temperature of 500 °C for 1 h. During pyrolysis processes, vapor from pyrolysis was condensed in an oil recovery unit using a set of impingers soaked in a cold container. A simplified schematic diagram of the pyrolysis process is shown in Fig. 1.

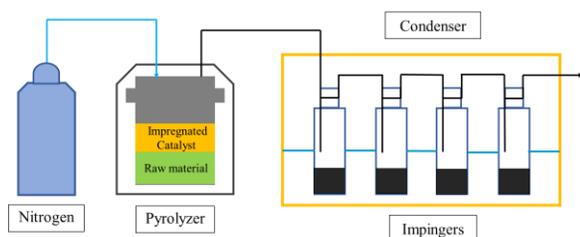


Fig. 1. Simplified schematic diagram of the pyrolysis process.

D. Analysis methods

Proximate analysis was conducted by Simultaneous Thermal Analyzer model 449 F3. Ultimate analysis was conducted by Micro Corder JM 10. Bromine contents in raw material, pyrolysis oil, and char were determined by SHIMADZU LC-10AD Ion chromatography fitted with a Shodex IC NI-424 column at 40 °C and 1.0 ml/min air flow rate. The sample of about 1 g was used with deionized water 10 ml and then they were mixed by vortex mixer around 1 min. The chemical compositions of the catalysts were analyzed by X-ray fluorescence analysis (XRF) under vacuum mode for precise measurement. The surface structure of catalysts in pyrolysis char was analyzed by Scanning electron microscope and energy dispersive x-ray spectrometer (SEM-EDX). The structure of catalysts was analyzed by a powder X-ray diffraction (XRD) using a Rigaku SmartLab X-ray diffractometer at 40 kV and 20 μ A which used Cu K α radiation (1.54 Å) in the 2 θ range from 10–80°. The specific surface area analysis of catalysts was determined by N₂ physical adsorption at 77 K applying the Brunauer - Emmett - Teller (BET), using micromeritics ASAP2020.

III. RESULTS AND DISCUSSION

A. Catalyst Characterization

Four types of catalyst (YZ, 1%S-YZ, 5%S-YZ, 10%S-YZ) were characterized by XRF and BET analyses. Results are concluded in Table II. For impregnation catalysts, it was found that sulfur content increased from the conventional catalyst which was 1.79-10.14 wt.%. On the contrary, silicon content was decreased about 31.9-20.4 wt.%. Sulfur impregnation increased Si/Al ratio and the acidity of catalyst due to desilication in catalyst component [10]. The physical and chemical properties of zeolites varied by SiO₂/Al₂O₃ ratio. A low ratio caused the surface of zeolite to be hydrophilic whereas a high ratio causes the surface to be hydrophobic and stronger chemical reaction [11]. The specific surface area of 1%S-YZ, YZ, 5%S-YZ and 10%S-YZ catalysts was 728.1, 664.1, 346.3 and 7.8 m²/g, respectively. YZ and 1%S-YZ exhibited a larger pore volume as compared to other catalysts. However, 10%S-YZ showed the largest pore size. The results revealed that the specific surface area of impregnation with sulfur loading to YZ catalysts was significantly reduced as compared to YZ without impregnation with sulfur. This due to the reduction of the specific surface area and pore volume of zeolite caused by the sulfur deposit on the surface available pores of the zeolite [10]. XRD pattern of all catalysts used in this study are presented in Fig. 2. According to the standard diffraction datum, YZ has faujasite structure (FAU) [4]. The structure of YZ catalyst was not changed after impregnation. Due to sulfur did not change the structure of YZ but it penetrated into pores of YZ. Therefore, the concentration of XRD peak decreased from the conventional catalyst.

TABLE II: PROPERTIES OF CATALYSTS

Item	YZ	1%S-YZ	5%S-YZ	10%S-YZ
Si (wt.%)	64.3	31.9	27.6	20.4
Al (wt.%)	16.5	8.77	6.53	4.92
S (wt.%)	-	1.79	6.06	10.14
BET surface (m ² /g)	664.1	728.1	346.3	7.8
Pore volume (cm ³ /g)	0.404	0.399	0.189	0.035
Ave pore size (Å)	24.4	10.98	10.90	88.97

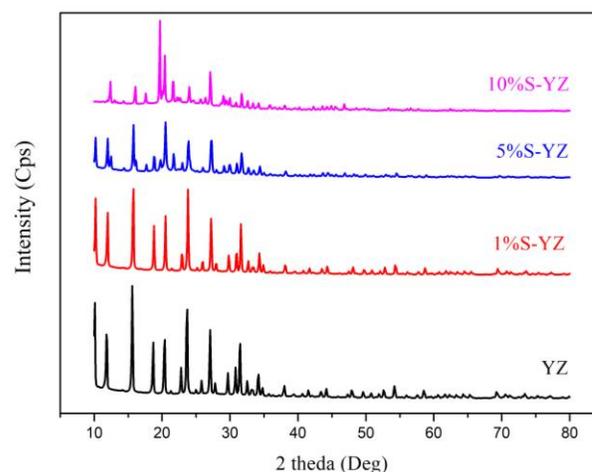


Fig. 2. XRD pattern of catalyst used in this study.

B. Product yield

The product yields are shown in Table III. The yields of pyrolysis chars were 79.43, 74.06, 69.73, and 71.96 wt.% for YZ, 1%S-YZ, 5%S-YZ, and 10%S-YZ catalysts, respectively. The yield of pyrolysis oils were 2.61, 3.99, 7.77, 5.02 wt.% for YZ, 1%S-YZ, 5%S-YZ, and 10%S-YZ catalysts, respectively. This demonstrated that the sulfur-impregnated Y-zeolite affects pyrolysis oil, as sulfur catalysts were able to transform aromatic compounds of substance at temperatures around 250 °C. Moreover, the use of the excess amount of sulfur can cause a negative impact on the reaction rate of activity [12]. Meanwhile, the Y-zeolite catalyst also drastically reduced the oil yield and significantly changed the composition of the pyrolysis products [13]. The reduction or absence of pyrolysis oil caused by the excess catalytic effect and evaporation of volatile matters at a high temperature (500 °C) in the pyrolysis process [14]. The appearance of the PCB product after pyrolysis was char-like in matte black color. It was very friable and could be easily separated from the metal electrical components as shown in Fig. 3. This demonstrated that the pyrolysis char product from PCB pyrolysis can be easily crushed during a mechanical separation or other post-recycling processes.



Fig. 3. The appearance of the pyrolysis char product (a) thermal, (b) YZ, (c) 1%S-YZ, (d) 5%S-YZ, (e) 10%S-YZ.

TABLE III: EFFECT OF THE CATALYST TYPES ON THE PRODUCT YIELD

Yield (wt.%)	Thermal	YZ	1%S-YZ	5%S-YZ	10%S-YZ
Char	68.76	79.43	74.06	69.73	71.96
Oil	10.84	2.61	3.99	7.77	5.02

C. Properties of residue solid

The element compositions and the morphological structure of the pyrolysis residues including the spent catalysts are shown in Table IV and Fig. 4, respectively. The surface of catalysts became denser, especially their sulfur-impregnated types. In contrast, the surface characteristic of the YZ catalyst became less dense. After sulfur impregnation, all the surfaces of YZ catalysts were adhered by floccules sulfur and the reduction of surface area can be visualized, which could be S-containing active substances [15]. The S-YZ catalysts were uniformly distributed on the surface of the pyrolysis char as indicated in Fig. 4. The main composition of solid residue was 8.58 %-9.47 % of carbon content, 20.33 %-20.69 % of silicon, and 5.53 %-6.08 % of aluminum. Silicon and aluminum were from IC components and ceramic capacitor.

TABLE IV: RESIDUE COMPOSITION FROM CONVENTIONAL PYROLYSIS AND PYROLYSIS WITH CATALYSTS (WT.%)

Item	Thermal	YZ	1%S-YZ	5%S-YZ	10%S-YZ
C	8.62	8.58	8.79	9.47	8.74
O	52.5	52.61	51.18	50.45	52.4
Na	0.29	-	-	-	-
Mg	0.23	0.53	0.28	0.7	0.41
Al	5.69	5.97	5.75	5.53	6.08
Si	20.69	20.5	20.58	20.39	20.33
Ca	11.67	11.47	12.28	13.47	10.48
Ti	0.32	0.33	-	-	0.34
S	-	-	-	-	0.24

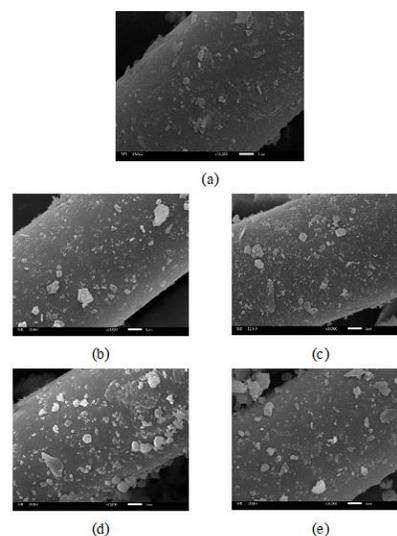


Fig. 4. SEM pictures of (a) thermal (b) YZ, (c) 1%S-YZ, (d) 5%S-YZ and (e) 10%S-YZ catalyst surface used in this study.

D. Debromination by sulfur loading catalysts

The bromide content in the pyrolysis char and oil are shown in Table V. For thermal pyrolysis, it was found that the yield of bromide content was 8.09 wt.% of pyrolysis char and 12.67 wt.% of pyrolysis oil. This demonstrated that the bromide content in pyrolysis char of YZ and 1%S-YZ decreased from that of the thermal pyrolysis, which was about 64.81% and 74.07%, respectively. The bromide content in pyrolysis oil of YZ and 1%S-YZ was also decreased from that of thermal

pyrolysis, accounting 47.61% and 64.28%, respectively. Because Y-zeolite was an acidity catalyst, it supported cracking of the brominated compounds in PCB samples into HBr whereas the loaded sulfur was insufficient for further conversion of Br₂ from HBr [10]. In the case of 10%S-YZ, it was found that the bromide content in pyrolysis char and pyrolysis oil was decreased from thermal pyrolysis, which was about 75.92% and 21.42%, respectively. This is because the 10%S-YZ has small specific surface area, pore volume, and average pore size due to excessive loading of sulfur that caused negative effects catalyst properties [12, 15]. Eventually, it affected the efficiency of Br absorption. For 5%S-YZ, the bromide content in pyrolysis char and pyrolysis oil was 22.22% and 38.09% decreased from thermal pyrolysis, respectively. This is because sulfur reacted to HBr and yielded Br₂ and it confirmed by the increase of Br content in pyrolysis char of 5%S-YZ compared with YZ and 1%S-YZ. The main reaction between bromine and sulfur in the pyrolysis process was the dissociation of HBr to Br₂ as shown in the equation 1 [16].

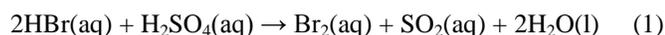


TABLE V: BROMINE CONTENTS FROM PCB PYROLYSIS

Bromide content (wt.% of Br in raw PCB)	Thermal	YZ	1%S-YZ	5%S-YZ	10%S-YZ
Char	8.09	2.82	2.09	6.43	1.93
Oil	12.67	6.76	4.66	7.83	9.87

IV. CONCLUSION

This work was performed an investigation on the adsorption mechanism of sulfur impregnated YZ for debromination from PCB pyrolysis process. Catalysts used in the experiment were YZ, 1%S-YZ, 5%S-YZ, and 10%S-YZ. The results showed that the PCB had the limit amount of pyrolysis oil (3-10 wt.%), but a high yield of pyrolysis char (74-79 wt.%). The pyrolysis char's compositions were 8.58-9.57% (C), 5.53-6.08% (Al), 20.33-20.69% (Si), and 10.48-13.47% (Ca). The Br removal in pyrolysis oil with S-loaded on YZ catalyst was 21.42-64.28%. The amount of sulfur loaded affected the performance of the catalyst. In conclusion, 5%S-YZ showed good debromination performance for PCB pyrolysis process.

ACKNOWLEDGMENT

This research was financially supported by Kasetsart University Research and Development Institute, FF(KU) 25.64.

REFERENCES

- [1] Wu, H., et al., *Fuel Oil Production from Two-Stage Pyrolysis-Catalytic Reforming of Brominated High Impact Polystyrene Using Zeolite and Iron Oxide Loaded Zeolite Catalysts*. Open Journal of Ecology, 2015. **05**(04): p. 136-146. <https://doi.org/10.4236/oje.2015.54012>
- [2] Ma, C. and T. Kamo, *Two-stage catalytic pyrolysis and debromination of printed circuit boards: Effect of zero-valent Fe and Ni metals*. Journal of Analytical and Applied Pyrolysis, 2018. **134**: p. 614-620. <https://doi.org/10.1016/j.jaap.2018.08.012>

- [3] Kumar, S., et al., *Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine*. Energy Conversion and Management, 2013. **74**: p. 323-331. <https://doi.org/10.1016/j.enconman.2013.05.028>
- [4] Areeprasert, C. and C. Khaobang, *Pyrolysis and catalytic reforming of ABS/PC and PCB using biochar and e-waste char as alternative green catalysts for oil and metal recovery*. Fuel Processing Technology, 2018. **182**: p. 26-36. <https://doi.org/10.1016/j.fuproc.2018.10.006>
- [5] Chen, T., et al., *Catalytic performance and debromination of Fe-Ni bimetallic MCM-41 catalyst for the two-stage pyrolysis of waste computer casing plastic*. Chemosphere, 2020. **248**: p. 125964.
- [6] Yang, X., et al., *Pyrolysis and dehalogenation of plastics from waste electrical and electronic equipment (WEEE): a review*. Waste Manag, 2013. **33**(2): p. 462-73. <https://doi.org/10.1016/j.wasman.2012.07.025>
- [7] Silva, H.S., et al., *Adsorption of mercury (II) from liquid solutions using modified activated carbons*. 2010. **13**(2): p. 129-134.
- [8] Liu, W., et al., *A sulfur-resistant CuS-modified active coke for mercury removal from municipal solid waste incineration flue gas*. Environ Sci Pollut Res Int, 2019. **26**(24): p. 24831-24839. <https://doi.org/10.1007/s11356-019-05645-6>
- [9] Cai, J.H., C.Q.J.I. Jia, and E.C. Research, *Mercury removal from aqueous solution using coke-derived sulfur-impregnated activated carbons*. 2010. **49**(6): p. 2716-2721.
- [10] Ugrina, M., et al., *Preparation and Characterization of the Sulfur-Impregnated Natural Zeolite Clinoptilolite for Hg(II) Removal from Aqueous Solutions*. Processes, 2021. **9**(2).
- [11] Wang, C., et al., *Quantitative arrangement of Si/Al ratio of natural zeolite using acid treatment*. 2019. **498**: p. 143874.
- [12] Furimsky, E. and F.E.J.C.T. Massoth, *Deactivation of hydroprocessing catalysts*. 1999. **52**(4): p. 381-495.
- [13] Hall, W.J., P.T.J.J.o.a. Williams, and a. pyrolysis, *Removal of organobromine compounds from the pyrolysis oils of flame retarded plastics using zeolite catalysts*. 2008. **81**(2): p. 139-147.
- [14] Santella, C., et al., *Thermal and catalytic pyrolysis of a mixture of plastics from small waste electrical and electronic equipment (WEEE)*. Waste Manag, 2016. **54**: p. 143-52. <https://doi.org/10.1016/j.wasman.2016.05.005>
- [15] Baldauf, W., et al., *Upgrading of flash pyrolysis oil and utilization in refineries*. 1994. **7**(1-6): p. 237-244.
- [16] Qiao, J., et al., *Overlooked role of sulfur-centered radicals during bromate reduction by sulfite*. 2019. **53**(17): p. 10320-10328



My name is Nutcharithp Kathongthung. I was born on 30 October 1994 at Phrae. I graduated with a bachelor's degree in Applied Science, Major Environmental Technology. King Mongkut's University of Technology North Bangkok, Thailand and year degree was earned in 2018. I am studying master's degree of Engineering in Safety Engineering at Kasetsart University Bangkaen campus, Thailand.



His name is Chanoknunt Khaobang. He was born on 22 June 1991 at Bangkok. He graduated with a bachelor's degree in Mechanical Engineering at Kasetsart University Sriracha campus Chonburi, Thailand and master's degree in Mechanical Engineering at Kasetsart University Bangkaen campus, Bangkok, Thailand. He is studying Doctor of Engineering in Mechanical Engineering at Kasetsart University Bangkaen campus, Thailand.



His name is Dr. Chinnathan Areeprasert. He graduated with a bachelor's degree in Mechanical Engineering at Kasetsart University Bangkaen campus, graduated with a master's and doctor degree in Environmental Science and Technology Engineering at Tokyo Institute of Technology, Japan. He is Associate Professor in the faculty of engineering, Kasetsart University Bangkaen campus, Thailand.