CHARACTERISTICS OF BY-PRODUCTS AND DIOXIN EMISSION FROM PYROLYSIS PROCESS FOR URETHANE/STYROFOAM WASTE OF ELECTRIC HOME APPLIANCES

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Abstract: EU directive RoHS (Restriction of Hazardous Substances) prohibits marketing of electrical home appliances containing harmful substances such as lead, cadmium, mercury, chromium (VI), Polybrominated biphenyls (PBBs), and Polybrominated diphenyl ethers (PBDE). The enactment of RoHS was a big shock to Asian companies and especially to Japanese companies as they have supplied major portion of their products to the global market. Influenced by RoHS, most countries enacted the regulations and laws related to prohibiting the use of such substances in the home appliances. The recycling rate of home appliances such as washing machine, TV, and air condition is currently above 90%, which is mostly recycled in waste treatment/recycling facilities. In case of refrigerator and washing machine all parts are recycled except urethane/styrofoam (14.36%). During recovery process, the refrigerant (CFCs) from the refrigerator is first recovered. After then copper, iron, aluminum, plastic, and rubber are separated and pass through the crushing and grinding process. The reclaimed metals are almost recycled. Urethane/Styrofoam mixture is collected from urethane separation device. The mixture ratio of urethane and styrofoam is usually 8.6:1, which are difficult to separate. So, in most of the countries, the mixture is disposed of in landfill or is directly incinerated.

In this study, we evaluated the recycling possibility of urethane/styrofoam by a pyrolysis process to generate any usable products such as syngas and use of residue as sorbent-activated carbon. A series of pyrolysis and carbonization experiments for the mixture sample were carried out at various temperatures, and product gas, carbon characteristics and loss of ignition were analyzed to observe the characteristics of products and the feasibility of such technology utilization.

1. Introduction

According to Korean Association of Electronics Environment (KAEE), 1,438.5 thousand units of refrigerators, 1,146.7 thousand units of washing machine, 885.6 thousand units of television, 326.8 thousand units of air conditioner were discarded in 2006. The recycling rate of air conditioner, washing machine and TV is above 90%. All parts of these appliances are recycled except urethane/styrofoam mixture which is mainly generated from refrigerators. Since the separation of urethane/styrofoam from refrigerator is difficult, it is shredded and the portion of steel is recovered with leaving the mixture of urethane/styrofoam as residues. Then most of them are sent to cement kilns to be burnt as auxiliary fuel or are disposed of at landfill. Considering the limited land availability and environmental problems associated to landfilling, others treatment methods such as pyrolysis are to be evaluated for urethane/styrofoam disposal. In this study, we evaluated the recycling possibility of urethane/styrofoam using pyrolysis process. A series of pyrolysis and carbonization experiments were carried out at various temperatures. Yield of by-products, dioxin emission characteristics were also analyzed. The characteristics of by-products: char, gas and oil were studied to evaluate the feasibility of such technology utilization.

2. Experimental

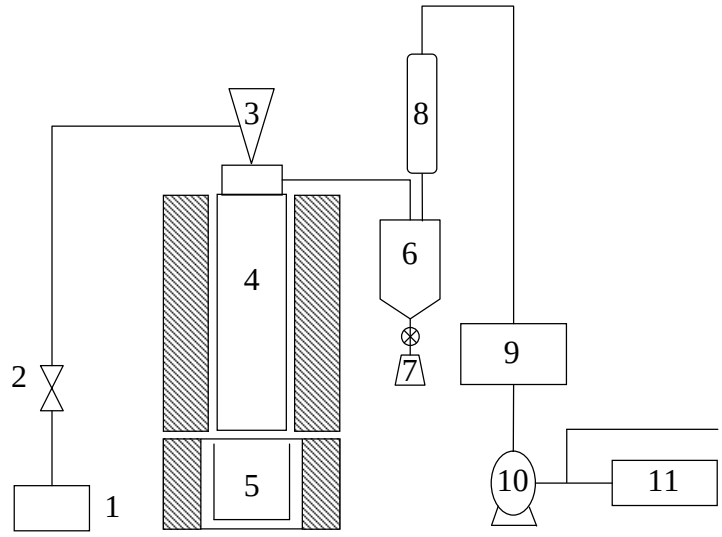
2.1 Sampling of urethane/styrofoam waste

Urethane/styrofoam waste is the last material that remains after collecting valuable materials (recyclable parts, valuable metals: Cu, Ni, Au and so on) from electric/electronic home appliance wastes (especially refrigerator, washing machine) at recycling facility. Samples were collected after crushing and pulverizing process to feed samples homogeneously and to reduce error during experiments.

2.2 Pyrolysis reactor and operational procedure

Fig. 1 presents a schematic diagram of lab-scale pyrolysis system. The feeder in the system was designed to operate in semi-batch mode. Reduction atmosphere in reactor was maintained by purging N_2. Char was collected in crucibles (5). For collecting oil, two cooling systems were used. Firstly, cool water was continuously circulated in the condenser (8) for cooling. And secondly, cooled by ice in the impinger train. As pyrolysis gas passes through 4 impinger sets with ice in the bottom, oil was condensed and collected. Gas samples were collected in Tedlar bag for further analysis. Experiments were carried out at input rate of urethane/styrofoam of 7g per 30 seconds, and pyrolysis temperature experimented was varying from 500 to 800 ^{o}C.

By-products (gas, oil, and char) generated at each pyrolysis experimental temperature were evaluated carefully by observing the mass distribution to estimate the yield of them. The characteristics of generated gas, oil, and char were studied. Dioxin in exhaust gas was sampled and analysed by Korean standard methods.



1- nitrogen supply; 2- nitrogen controller; 3- feeder; 4- reactor #1; 5- reactor #2; 6- cyclone; 7- residue collector; 8- condenser #1; 9- condenser #2; 10- pump; 11- Tedlar bag

Fig. 1 Schematic diagram of lab scale pyrolysis system

HHV (High Heating Value) of oil was analyzed using bomb calorimeter (AC-350, LECO). SEM (Scanning Electron Microscope) analysis of char was done in SEM analyzer (JSm-5410, JEOL). Adsorption capacity of char and activated carbon were measured using KS M1802 (Korean standard method: activated carbon experiment method). Adsorption amount (Q) and decolorization capability (M) was calculated using residual concentration of methylene blue, and residual concentration was calculated from calibration curve.

Tab. 1 Equation of adsorption and decolorization

① Adsorption amount	② Decolorization capability
Q = ((1,200-C)*25/1,000)/S Q = Methylene blue adsorption amount (mg/g) C = Methylene blue residual concentration (mg/L) S = mass of sample (g) 1,200 = Methylene blue concentration (mg/L)	M = Q/1.2 M = Methylene blue decolorization capability (mL/g) Q = Methylene blue adsorption amount (mg/g) 1.2 = Methylene blue liquids concentration (g/L)

3. Results and discussion

3.1 Yield of gas, oil and char, and HHV of oil

Yield result of by-products generated at each experimental temperature is presented in Fig. 2. As pyrolysis temperature increased, residue mass of char decreased. But oil mass and gas showed opposite tendency with increasing products by temperatures. At 500^{o}C, weight loss was minimum (about 70 wt.%), and was maximum at 800 ^{o}C, (about 90 wt.%). Oil and

gas mass was related with each other, that is, oil mass was high at higher cooling efficiency of condenser. Temperature of circulating water at condenser and ice impinger set were almost same during these experiments. As temperature was higher, HHV of oil was higher as shown in Fig.3, which ranged from 6,000 to 8,000 kcal/kg.

3.2 Dioxin emission in exhaust gas

Dioxins concentration in gas leaving from the process at different pyrolysis temperature is presented in Fig. 4. At 500 °C, 600 °C, 700 °C, 800 °C, dioxins concentrations were 946.999 ng-TEQ/Sm^3, 38.449ng-TEQ/Sm^3, 24.493ng-TEQ/Sm^3, 4.756ng-TEQ/ Sm^3, respectively. At the temperature of 500 °C, the formation of dioxins was high since it could be closed to synthesized temperature zone as known as de novo synthesis reaction. Concentration percentage ratio of 2,3,7,8-isomer at different pyrolysis temperature is presented in Fig. 5. Among isomers, 2,3,4,7,8-PeCDF in PCDFs was 20-40%; 1,2,3,7,8-PeCDD in PCDDs was 10-30%. Higher portion of PCDFs was synthesized than PCDDs in all the experimental pyrolysis temperatures since pyrolysis reaction was done in reduced condition.

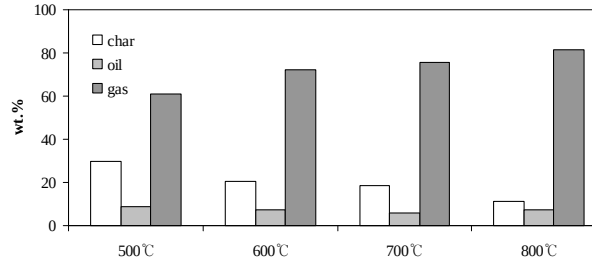


Fig. 2 Yield of gas, oil and char

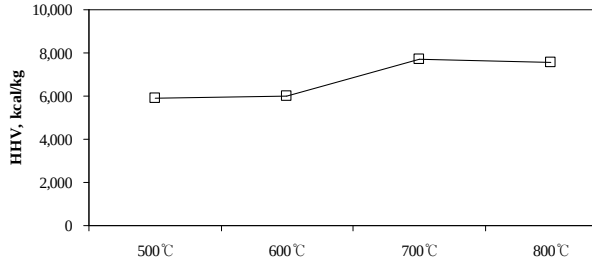


Fig. 3 High heating value of oil

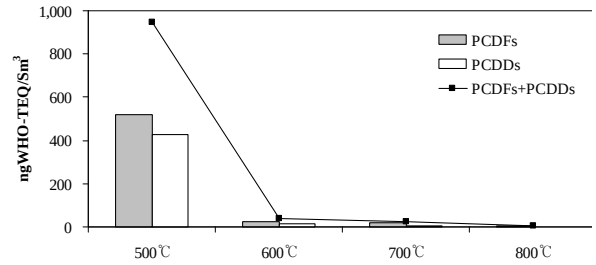


Fig. 4 PCDDs/Fs concentration with pyrolysis temp.

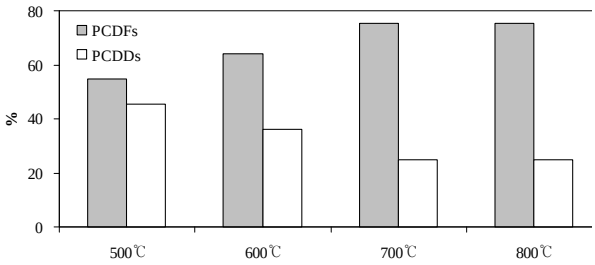
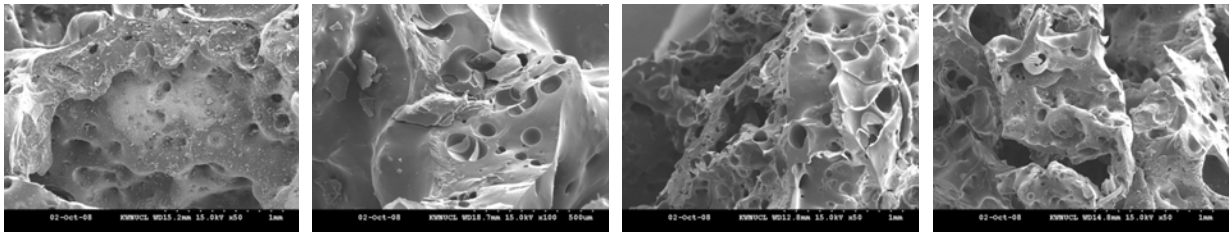


Fig. 5 Percentage concentration distribution of PCDDs/Fs

3.4 Absorption ability of char

Fig. 6 shows the SEM result of urethane carbide produced as char. As temperature was higher, fineness of pore was increased, size of pore was smaller. However, the difference between them was negligible. Also, absorption capacity of carbide pyrolyzed at different temperatures was similar.



500℃ 600℃ 700℃ 800℃

Fig. 6 SEM result of urethane carbide

Calibration curve (Fig. 7) is made using absorbance with methylene-blue concentration. Using this, adsorption amount and decolorization capability was calculated. The adsorption capacity and its decolorization were calculated relatively to activated carbon, considering the value for activated carbon as 100%. The relative adsorption was 99.16 to 99.85% and decolorization was 99.81 to 99.85%. The various char samples obtained from different pyrolysis temperatures did not show big differences with its adsorption capacity. The adsorption and decolorization capacity of char was almost similar with activated carbon. This shows that the char from pyrolysis of urathane/styrofoam wastes can be used as sorbent.

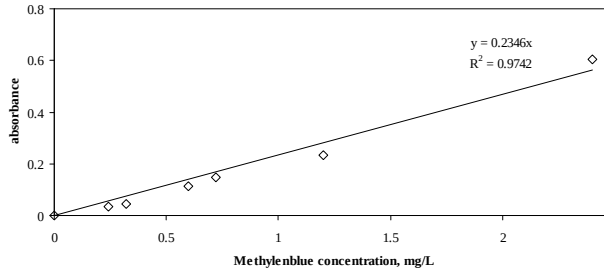


Fig. 7 Calibration curve

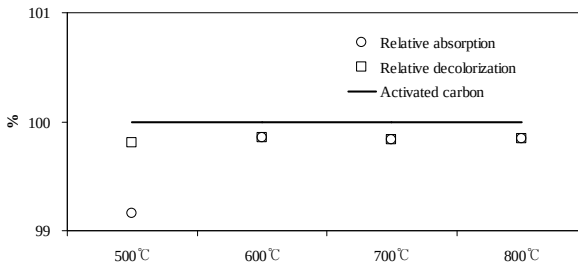


Fig. 8 Evaluation of absorption and decolorization of char relative to AC

4. Conclusions

Recycling possibility using the prolysis of urethane/styrofoam wastes generated from dismantling plants of home electric appliances was evaluated at a bench scale apparatus. With changing pyrolysis temperatures, yield of different phase products, dioxin content in gas, and properties of char were observed for utilization of products. As pyrolysis temperature increased, residue mass of char decreased while yields of oil and gas products increased. As temperature was higher, HHV of oil was higher, which ranged from 6,000 to 8,000 kcal/kg. At 500 ^{o}C, 600 ^{o}C, 700 ^{o}C, 800 ^{o}C, dioxin concentrations in gas were 946.999 ng-TEQ/Sm^3, 38.449ng-TEQ/Sm^3, 24.493ng-TEQ/Sm^3, 4.756ng-TEQ/ Sm^3, respectively. So less dioxin is generally formed in pyrolysis process, however the dioxin synthesis reaction could be occurred at the temperature around 500 ^{o}C or less with a little amount of oxygen existing. For

produced char, as temperature was higher pore fineness increased and size of pore was smaller. However the difference between them was negligible. Absorption capacity of char, pyrolyzed at different temperatures, was similar**.** The relative adsorption of char to activated carbon commercially available was 99.2 to 99.8% and decolorization showed about 99.8%. Thus, the adsorption and decolorization capacity of char was almost similar with activated carbon. Further feasibility studies including economic evaluation will be made prior to utilize pyrolysis technology to recover energy or usable by-products with the construction of a pilot scale plant.

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