論 文 の 内 容 の 要 旨

論文題目　Carbonization of Non-recyclable Poly(Ethylene) Terephthalate for the Production of Carbon-based Material – A Sustainable Approach for the Realization of Domestic PET Recycling

（リサイクル不能廃ポリエチレンテレフタレートの炭化による炭素材料の生産 - 持続可能な国内循環型PETリサイクルの実現へ）

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Chapter 1: Introduction

The global waste PET treatment has been highly dependent on exporting of waste PET to recycling sites situated in developing countries, which had caused dire environmental problems including terrestrial and marine pollution. The reason for this dependency is due to the lack of domestic recycling facilities in the exporting countries as a result of expensive and inconvenient treatment of non-recyclable PET. This study identified the issues of current waste PET treatments and initiated carbonization as an alternative treatment method. The main objectives of this study is to provide a new method for the effective utilization of non-recyclable PET through the "waste-treats-waste" approach by (i) studying the fundamental experimental investigation and the mechanism of char formation of carbonization of PET, (ii) studying the applicability of the process on non-recyclable PET in the state closest to the "real-world", and (iii) studying the gas adsorption ability of activated char obtained from PET carbonization.

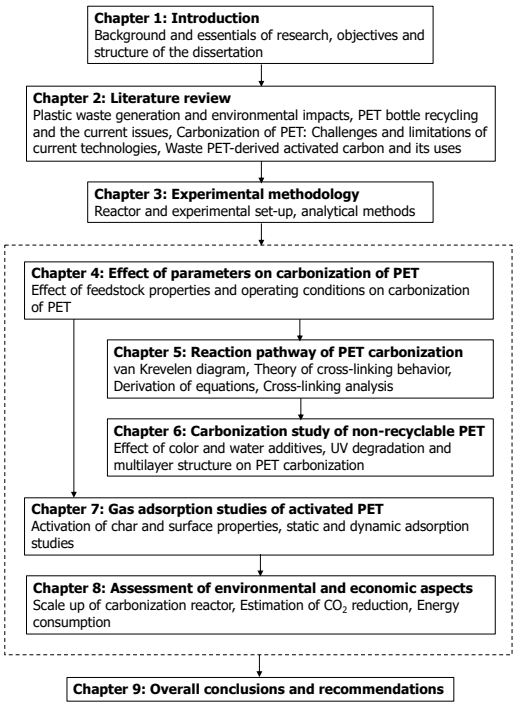

Figure 1: Structure of the dissertation

Chapter 2: The challenges for domestic circulation of PET bottle recycling

A thorough literature investigation was conducted to give better understanding of the general global plastic generation and their potential impacts on the environment. The current PET bottle recycling technologies, the issues of PET recycling and the challenges for domestic circulation of PET recycling in Japan were studied and reviewed in-depth. Studies revealed that factors for dependency of exporting waste PET include the high cost and energy extensive process of recycling non-recyclable PET due to the limitation of conventional recycling methods. This led to the consideration of non-conventional recycling method in which carbonization was chosen due to the valorization of waste PET and its potential of producing valuable carbon-based materials for various applications.

Chapter 3: Experimental methodology

The carbonization process of PET was studied comprehensively by conducting experimental studies in a laboratory scale batch reactor as shown in Figure 2 under varying conditions and conducting thorough analysis on the char, wax and gaseous product. For char, calorific value, ultimate and proximate analysis, FT/IR spectra were obtained. For wax, calorific value and ultimate analysis were obtained, while GC/MS and HPLC analysis were used for qualification and quantification of the compounds. Gaseous products were analyzed using GC/TCD and GC/FID.

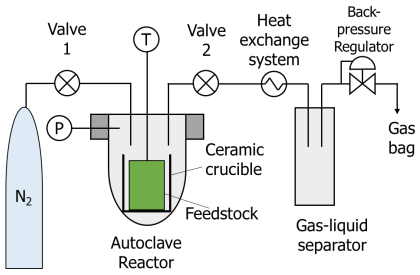

Figure 2: Experimental set-up of carbonization system

Chapter 4: Effect of parameters on carbonization of PET[1]

Due to the inconsistency in past studies and lack of information regarding the characteristics of char, experimental procedures were initialized to study the fundamental effects of operating parameters on the carbonization of PET. The feedstock properties, reaction medium, temperature and residence time were the study focus in the experiments. Commercial clear PET was chosen as the model feedstock and a laboratory scale batch reactor was used to study the effects. Results showed that carbonization of PET at 400-480°C, produces char with high carbon content. Char obtained in this operating condition showed a dark, brittle and hard solid, indicating the complete carbonization of PET. FT/IR analyzation revealed that the complete carbonization of char did not retain any of the structural properties of PET, which has never been reported by any forms of scientific article so far. Analysis of wax was conducted, and results showed that wax mainly consisted of carboxylic acid, benzoic acid. The gaseous product was also analyzed and similar to past studies, carbon dioxide and carbon monoxide were the main components in the gaseous product. The experimental results also demonstrated that feedstock size and treatment method had no evident effects on the product composition and char characteristics due to the singularity of the polymer in feedstock, which is highly beneficial for the treatment of PET as feedstock with physical irregularity.

Chapter 5: Mechanism of char formation based on carbonized product[2]

The phase behavior of PET carbonization and the mechanism of char formation were studied based on the product composition and properties to predict the extend of char formation at specified conditions. The van Krevelen diagram was applied to identify the reaction pathways of phase changes during PET carbonization and results revealed that PET undergoes decarbonylation to produce char with high carbon content; and decarboxylation to form wax with high oxygen and hydrogen content. The findings from the van Krevelen diagram led to the analysis of cross-linking behavior during carbonization. The analysis of cross-linking behavior confirmed that the release of CO due to decarbonylation to form char while the release of CO_2 due to decarboxylation to form aromatic compounds in wax. The findings highly contributed to mending the research gaps and provided clarification to the mechanism of formation of char.

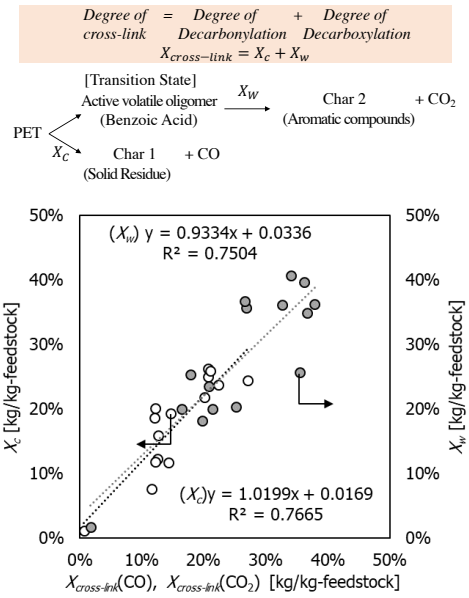

Figure 3: Relationship between $X_{cross-link}(CO)$ and X_C; and the relationship between $X_{cross-link}(CO_2)$ and X_W.

Chapter 6: Effect of contaminants in non-recyclable PET on carbonized product

The applicability of carbonization on feedstocks in the state closest to the "real-world" was studied, in which UV degraded PET, colored PET and multilayer PET were chosen as the study target due to the inapplicability of current recycling technologies to treat these materials. Results showed increasing fixed-carbon yield when PET was exposed to UV degradation. Carbonization of the colored PET showed slight decrease in fixed-carbon yield compared to clear PET due to the presence of colorant additives. Carbonization of multilayer PET, which was PET with oxygen barrier layer (OBL), showed no apparent change in char yield and fixed-carbon yield in char, but produced more aromatic hydrocarbons such as biphenyl and fluorene in wax and more CO_2 in gaseous product. Cobalt oxide was identified in the ash residue of char, indicating the presence of cobalt salt in the oxygen barrier layer. Further investigation confirmed that cobalt oxide catalyzes the decomposition of volatile matter, carboxylic acid to aromatic hydrocarbons and CO_2, indicating the potential use of cobalt oxide to decrease the production of wax and prevent the clogging of pipes. Overall, the findings indicated the potential benefits and applicability of carbonization on non-recyclable PET.

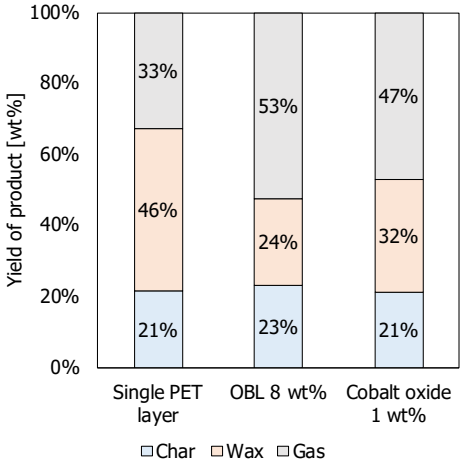

Figure 4: Comparison of product distribution of carbonization

Chapter 7: Gas adsorption study of activated char

In order to evaluate the performance of non-recyclable PET through the "waste-treats-waste" approach, char obtained from PET carbonization was activated using the conventional physical activation method to determine its CO_2 adsorption ability. Char showed distinct surface changes upon activation, where formation of fine pores on the surface was observed. Findings showed that the maximum CO_2 uptake in equilibrium and CO_2 separation ability from stream of the activated char was comparable to commercial adsorbents and that temperature change had little to no effects on the adsorption of CO_2.

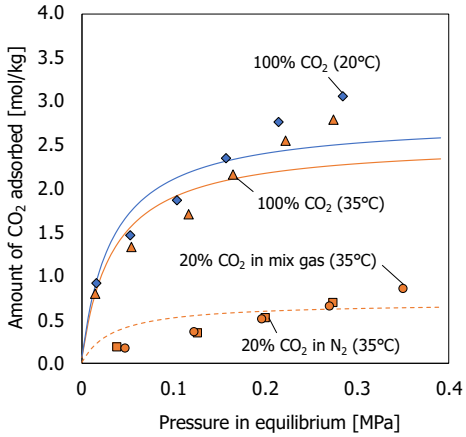

Figure 5: Experimental and predicted adsorption isotherms based on the Langmuir isotherm model

Chapter 8: Assessment of CO_2 emission and cost estimation

Assessment based on the energy consumption and CO_2 emission were conducted in order to determine the feasibility of PET carbonization in the realization of domestic circulation of waste PET. Figure 6 shows the CO_2 emission and profit of operation for case of mechanical recycling, carbonization and PSA system (blue line) compared to case of mechanical recycling and carbonization (green line). Total of 49 domestic recycling factories and carbonization facilities were able to produce enough profit for the installments and operations of maximum 32 PSA facilities, which is able to help mitigate the total CO_2 produced from the overall combined operation, leading to approximately zero carbon emission. Overall, replacement of incineration with carbonization resulted in drastic cut in annual CO_2 emission without causing a drastic decrease in economic value, which further affirms the advantage of carbonization in the treatment of waste PET.

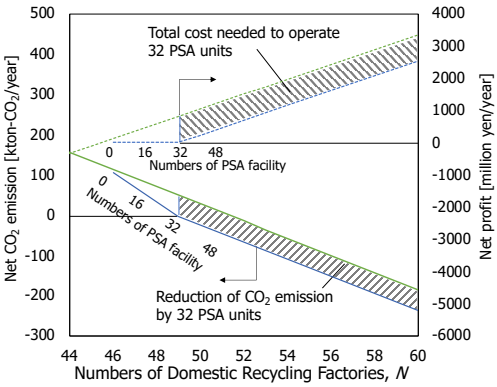

Figure 6: Annual CO_2 emission and annual profit of combined operations

Chapter 9: Conclusion

This study was able to effectively treat non-recyclable PET by overcoming the issues of current treatments through carbonization to produce valuable carbon material, in addition to understanding the mechanism of char formation and evaluate the applicability of carbonized product through the "waste-treats-waste" approach. The outcomes of this study will be highly beneficial for the development of new materials from waste to encourage the improvement of the material value of other plastic wastes as a solution for the global plastic problems.

[1] Chia et al., *JSMCWM*, **30** (2019) 541-542; [2] Chia et al., *Waste Management*, **108** (2020) 62-69.