

## Removal of carbon residue precursor in waste plastic pyrolysis oil via oxidation

Sukjeong Jeon\*, Jaehong Lee\*, Seong Cheon Kim<sup>\*,\*\*</sup>, Jin-Hyuk Kang<sup>\*\*\*</sup>, Dongho Lee<sup>\*\*\*\*</sup>,  
Hye Ryung Byon<sup>\*\*\*\*\*</sup>, Jeasung Park<sup>\*\*,†</sup>, and Siyoung Q. Choi<sup>\*,\*\*\*\*\*</sup>

\*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST),  
Daejeon 34141, Korea

\*\*Green and Sustainable Materials R&D Department, Korea Institute of Industrial Technology (KITECH),  
Cheonan-si, 31056, Korea

\*\*\*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

\*\*\*\*Process R&D Center, Hanwha Solutions R&D Institute, Daejeon 34128, Korea

\*\*\*\*\*KAIST Institute for the Nanocentury, KAIST, Daejeon 34141, Korea

(Received 26 January 2023 • Revised 13 May 2023 • Accepted 24 May 2023)

**Abstract**—A novel method to remove the carbon residue precursor from waste plastic pyrolysis oil has been developed to improve subsequent pyrolysis oil refining efficiency by reducing fouling. The carbon residue content of the pyrolysis oil that cannot be filtered is reduced by precipitating the carbon residue precursor from the pyrolysis oil under mild conditions. By emulsifying an aqueous solution of oxidant and the pyrolysis oil, the carbon residue precursor was oxidized at the oil-water interface without oxidizing the pyrolysis oil. Enhancing intermolecular interaction by hydrophilic functional groups formed by oxidation induces the precipitation of carbon residue precursors. The precursor removal was determined by the type and reaction time of oxidants.  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  are efficient oxidants, and recycling those oxidant solutions can also remove the carbon residue precursor. The number of recycles with the precursor removal effect was determined by the amount of oxidant remaining in the aqueous solution. Also, a short 15-minute  $\text{FeCl}_3$  reaction can eliminate the precursor. Reducing the reaction time is expected to increase process efficiency, as unnecessary oxidation and energy consumption are decreased. Our research suggests the pretreatment of the pyrolysis oil to reduce the carbon residue content, thereby reducing the fouling during the subsequent pyrolysis oil refining.

Keywords: Carbon Residue Precursor, Waste Plastic Pyrolysis Oil (WPPO), Oxidant Recycling, Coke, Chemical Recycling

### INTRODUCTION

To establish a circular economy for plastics, the chemical recycling of waste plastics is being actively researched [1-10]. Chemical recycling depolymerizes or cracks waste plastic, which may then be used as feedstock to generate chemicals with added value [1,2]. Chemical recycling involves chemolysis, pyrolysis, gasification, and hydrogen technologies, and the type of waste plastic feed determines the recycling process [3,4]. Among them, pyrolysis is an attractive technology because it can process a mixture of polyethylene, polypropylene, and polystyrene, which makes up more than half of all waste plastics, at the same time and generates fewer greenhouse gas emissions than incineration [3,11-13]. However, pyrolysis oil, a liquid product of pyrolysis, requires refining due to impurities and a wide range of boiling points [14,15]. Also, coke, a byproduct of pyrolysis or pyrolysis oil refining, can be deposited on the catalyst and refinery, resulting in catalyst deactivation and fouling [14,16].

Numerous methods for preventing coke deposition have been investigated. The rate of coke formation during refining can be reduced by changing the sites where coke deposition can occur. For example, catalysts are steam-treated to make them less acidic [17,

18], and the metal surface of the reactor is passivated by adding organophosphorus compounds [19-21]. Furthermore, coke or coke precursors generated during oil refining, including pyrolysis, can be removed using processes such as distillation, solvent deasphalting, and hydrogen technologies [22-24]. These upgrading processes are expensive and energy-intensive because they require a considerable amount of energy, a large amount of solvent, and expensive hydrogen, respectively [25-27]. However, depending on the properties of the waste plastic pyrolysis oil, upgrading could be necessary [14,28]. To improve the efficiency of the upgrading process, a pretreatment that eliminates the carbon residue from the pyrolysis oil could be used. Carbon residue is a type of coke that indicates the tendency of coke formation [29]. By lowering the carbon residue content of the pyrolysis oil as a pretreatment, the problems caused by coke generation can be reduced during the pyrolysis oil upgrading.

In this paper, we propose a new method to remove the carbon residue precursor in the waste plastic pyrolysis oil as a pretreatment for pyrolysis oil refining (Fig. 1). As a method, the pyrolysis oil is emulsified with an aqueous solution of an oxidant. By emulsifying, the carbon residue precursor can be selectively oxidized at the oil-water interface under mild conditions without using any surfactant or phase-transfer catalyst. Oxidation of the precursor increases the number of hydrophilic functional groups, such as carbonyl and hydroxyl groups. Not only the interaction of hydrophilic groups but

<sup>†</sup>To whom correspondence should be addressed.

E-mail: jpark@kitech.re.kr, sqchoi@kaist.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

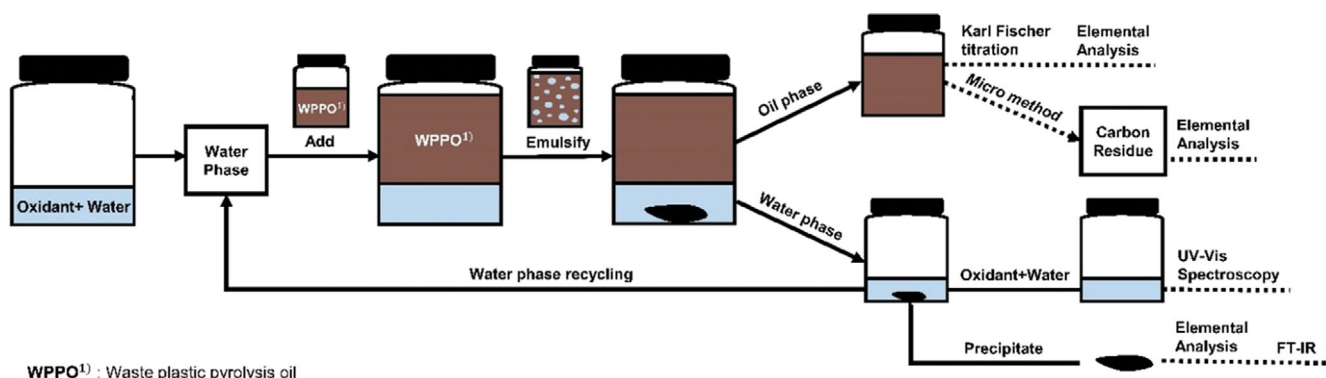


Fig. 1. Schematic illustration of carbon residue precursor removal.

also attractive  $\pi$ - $\pi$  stacking, coulombic interaction, van der Waals interaction, and hydrogen bonding can induce the precipitation of carbon residue precursor in the oxidant solution [30-33]. Furthermore, by recycling the aqueous solution of the oxidant, continuous precipitation and removal of the precursor are feasible. Therefore, we suggest a new technique for eliminating the carbon residue precursor to reduce the carbon residue in the waste plastic pyrolysis oil.

## MATERIALS AND METHODS

### 1. Materials and Chemicals

Waste plastic pyrolysis oil was supplied by Saehan Recycle Co., Ltd. from Korea. The properties of the pyrolysis oil are shown in Table 1. The flash point of plastic pyrolysis oil does not meet the standard flash point range of 30 to 40 °C required for fuel, due to the varying range of hydrocarbon carbon numbers present in the oil. Particularly, the existence of volatile hydrocarbons with low carbon numbers results in a low flash point. Thus, in order to use pyrolysis oil as gasoline or diesel, it should undergo a separation process based on its carbon number range. Chemicals ( $\text{KMnO}_4$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , KI, NaOH,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ,  $\text{D}_8\text{H}_5\text{KO}_4$ , and  $\text{C}_7\text{H}_6\text{O}_3$ ) used in the experiments were obtained from Sigma-Aldrich.  $\text{H}_2\text{O}_2$  (35% in water) and  $\text{C}_2\text{H}_5\text{OH}$  (95%) were purchased from Junsei Chemical Co., Ltd., and Samchun Pure Chemical Co., Ltd., respectively. Distilled water was used as a solvent.

### 2. Carbon Residue Precursor Precipitation

Four (4) ml of an aqueous solution of each oxidant and 76 ml of pyrolysis oil were placed into a 100 ml vial and magnetically stirred at room temperature for 24 hours. The oxidant solutions were 4 ml  $\text{H}_2\text{O}_2$ , 4 ml distilled water containing 3.16 g of  $\text{FeCl}_3 \cdot$

$6\text{H}_2\text{O}$ , and 4 ml distilled water containing 0.232 g of  $\text{KMnO}_4$ , respectively. The amounts of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{KMnO}_4$  are 80% soluble in water at room temperature. After stirring, phase separation of W/O emulsion occurred and the upper oil phase was separated by pipetting and tested by micro method, Karl Fischer titration, and elemental analysis. In addition, the carbon residue, obtained by the micro method, was analyzed by elemental analysis. In the case of the lower water phase, UV-Vis spectroscopy was used to quantify the amount of oxidant in the liquid phase, and the precipitate was washed with distilled water and dried in an oven at 80 °C for 24 hours. The precipitate was analyzed by elemental analysis and FT-IR spectroscopy.

### 3. Continuous Precipitation by Oxidant Recycling

After 24 hours of stirring the mixture of pyrolysis oil and aqueous solutions of  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$ , respectively, the top oil phase was removed by pipetting. In the 100 ml vial containing the oxidant aqueous solution, 76 ml of new pyrolysis oil was added and magnetically stirred. The recycling procedure, which consisted of separating the pyrolysis oil after stirring and adding new pyrolysis oil, was repeated nine times. Therefore, ten oxidation experiments were conducted with the initial oxidant solution. After the third, fifth, and tenth oxidation, the upper oil phase was analyzed by the micro method and elemental analysis, and the amount of oxidant in the bottom water phase was determined through UV-Vis spectroscopy.

### 4. Quantification of $\text{FeCl}_3$ and $\text{H}_2\text{O}_2$

UV-Vis spectroscopy was conducted to determine the concentration of  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  after reaction, using a UV-Vis spectrometer (UV-2600, Shimadzu). UV analysis solution of  $\text{FeCl}_3$  was prepared with ethanol as a solvent and a 1 : 1 molar ratio of  $\text{FeCl}_3$  to  $\text{C}_7\text{H}_6\text{O}_3$ .  $\text{FeCl}_3$  and  $\text{C}_7\text{H}_6\text{O}_3$  formed  $[\text{FeC}_6\text{H}_4\text{OCOO}]^+$  complex, whose visible area peak at 546 nm was examined. Evaporation of ethanol occurs significantly during the process of making the solution and measurement. To minimize the effect, using a UV cuvette with a stopper is recommended.

UV analysis solution of  $\text{H}_2\text{O}_2$  was prepared by mixing three solutions, A ( $10^5$  fold dilution of the lower water phase), B (0.4 M KI, 0.1 M NaOH, and 0.02 mM  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ), and C (0.1 M  $\text{C}_8\text{H}_5\text{KO}_4$ ), in a 1 : 1 : 1 volume ratio. In the presence of  $\text{H}_2\text{O}_2$  and the catalyst  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ,  $\text{I}^-$  became  $\text{I}_3^-$ , whose absorption peak is 350 nm. The absorbance at 350nm was taken to determine the concentration of  $\text{H}_2\text{O}_2$ .

Table 1. Property of waste plastic pyrolysis oil

Analysis	Result
Carbon residue content	0.119 wt%
Sulfur content	<0.030 wt%
Flash point	24.0
Higher heating value	45.16 MJ/kg
Kinematic viscosity	1.982 mm <sup>2</sup> /s (40 °C)
API gravity	42.2 API

## 5. Karl Fischer Titration

The water content of the pyrolysis oil was measured with a Titrator Compact C10SD (Mettler Toledo). Prior to measuring, the analytical solution (100 ml of Coulomat AG and 20 ml of Composite 5) was agitated for one hour to reach equilibrium. Then, the pyrolysis oil was added to the analytical solution. All procedures were carried out at a voltage of 50 mV.

## 6. Instruments and Measurement

Functional groups were analyzed using an FT-IR spectrometer (Thermo Scientific). CHON elemental analysis of carbon residue was performed using FlashEA 1112 (Thermo Finnigan, Italy) and Flash 2000 series (Thermo Scientific). CHON elemental analysis of the pyrolysis oil and precipitate was performed using Flash Smart (Thermo Fisher Scientific, Germany). Micro method, quantifying the amount of carbon residue, was conducted by MCRT-160 (Alcor Petroleum Instruments, USA).

## RESULTS AND DISCUSSION

### 1. Carbon Residue Precursor Oxidation

After emulsifying the pyrolysis oil and aqueous solution of each oxidant for 24 hours, the color of the water phase changed from Fig. 2(a) to Fig. 2(b), and Fig. 2(c) depicts the precipitate formation. These indicate that the oxidants were reduced after the reaction with the pyrolysis oil. The pyrolysis oil was tested for carbon residue and water content by the micro method and Karl Fischer titration, respectively. Both of these contents are shown in Fig. 3. The carbon residue content was reduced most after reacting with  $\text{FeCl}_3$ , followed by  $\text{H}_2\text{O}_2$ , and slightly increased when reacted with

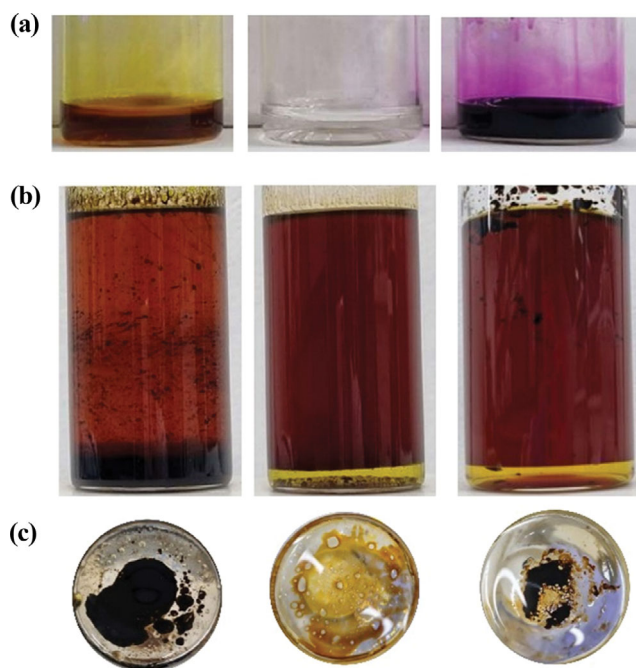


Fig. 2. (a) Aqueous solution of oxidants, (b) Phase separation of the aqueous solution and pyrolysis oil after a 24-hour reaction, (c) Precipitate formation after a 24-hour reaction:  $\text{FeCl}_3$  (left column),  $\text{H}_2\text{O}_2$  (middle column),  $\text{KMnO}_4$  (right column).

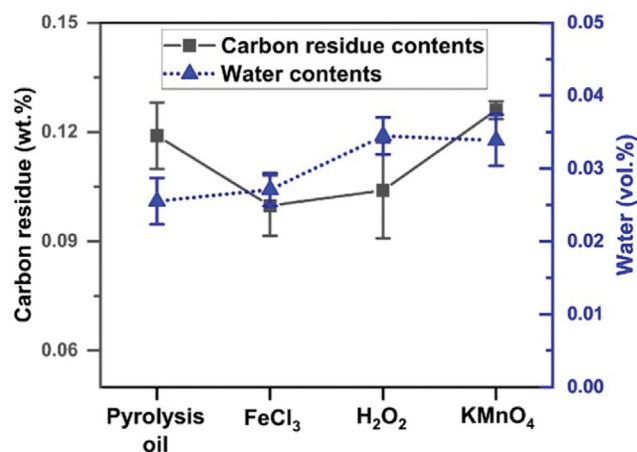


Fig. 3. Analysis of pyrolysis oil (a) Carbon residue content (square), (b) Water content (triangle).

$\text{KMnO}_4$ . The water content of the pyrolysis oil increased slightly after each reaction; however, the increment is negligible compared to the amount of water in the oxidant solution.

To understand how the carbon residue content changed as a result of the reaction, elemental analysis of the pyrolysis oil was conducted, as shown in Fig. 4. As our goal is to selectively oxidize the carbon residue precursor, not the pyrolysis oil, an examination was carried out to confirm the change in the degree of oxidation of the pyrolysis oil. Oxygen content and O/C ratio increased slightly only in the pyrolysis oil following the  $\text{H}_2\text{O}_2$  reaction. However, this does not imply that the pyrolysis oil was oxidized. Due to its heterogeneity, the variation in oxygen content of the pyrolysis oil was considerable, and all of the pyrolysis oil after oxidation was within 1 standard deviation of the mean.

Also, an elemental analysis of the carbon residue was conducted to observe the compositional change of the carbon residue. After reacting with  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$ , respectively, the oxygen content of the carbon residue decreased noticeably, as shown in Fig. 5. Considering the elemental analysis data of the pyrolysis oil and carbon

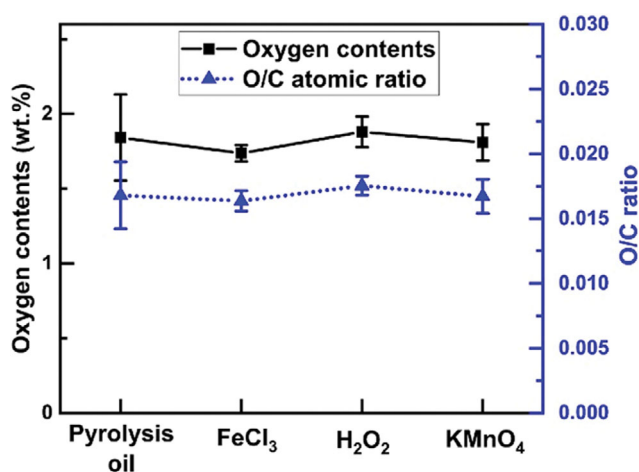


Fig. 4. Elemental analysis of pyrolysis oil (a) Oxygen content (square), (b) O/C atomic ratio (triangle).

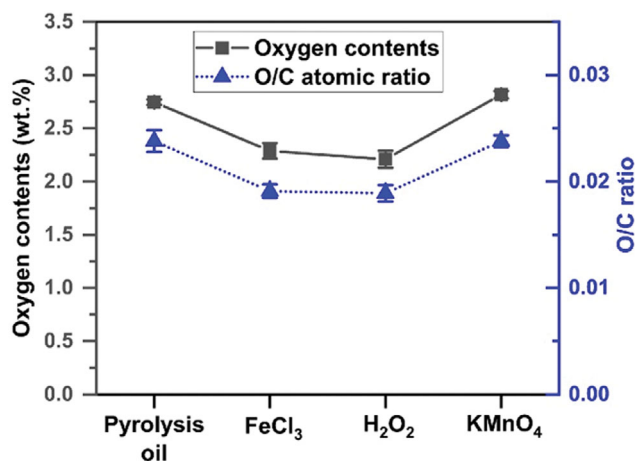


Fig. 5. Elemental analysis of carbon residue (a) Oxygen content (square), (b) O/C atomic ratio (triangle).

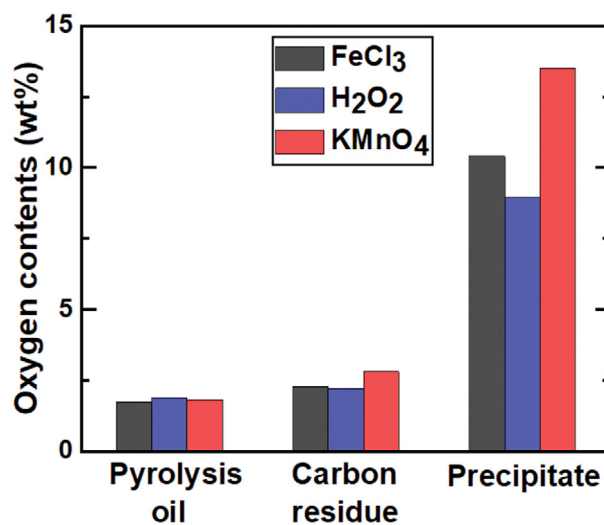


Fig. 6. Comparison of the oxygen content of the pyrolysis oil, carbon residue, and precipitate after a 24-hour reaction.

residue, we anticipated that oxygen-containing precursors or oxidized precursors may be removed and found in the precipitate.

## 2. Precipitation of Carbon Residue Precursor in the Water Phase

The precipitate in Fig. 2(c) was observed from a bottom view of Fig. 2(b) after removing the oil and water phases. The precipitate may consist of hydrocarbons from the oil phase and reduced oxidants. FeCl<sub>3</sub> is reduced into FeCl<sub>2</sub>, which is soluble in water and does not precipitate. On the other hand, H<sub>2</sub>O is formed by the reduction of H<sub>2</sub>O<sub>2</sub>, while KMnO<sub>4</sub>, under neutral conditions, is reduced to MnO<sub>2</sub>, which is insoluble in water and forms precipitates. In addition to the differences in the kind of reduced oxidant, the amount of oxidant added initially and the reaction caused by the oxidant affect the quantity and composition of the precipitate. The amount of the precipitate is shown in Table 2 and varies depending on the oxidant. The standard deviation in Table 2 is for the amount of precipitate generated after the reaction.

To analyze the composition of the precipitate, elemental analysis and FT-IR spectroscopy were performed. The oxygen content of the precipitate was higher than those of the pyrolysis oil and carbon residue, as indicated in Fig. 6. We can infer that the high oxygen content is due to the precipitation of oxygen-containing hydrocarbons. Also, after KMnO<sub>4</sub> reaction, MnO<sub>2</sub> is included in the oxygen content of the precipitate.

Functional group analysis of the precipitate was performed to observe the hydrophilic functional groups of the hydrocarbon that had precipitated. We expected that oxygen-containing hydrophilic functional groups would be abundant in the precipitate due to its high oxygen content. Also, the reaction caused by the oxidant can be deduced from the data on the functional groups. Fig. 7 shows

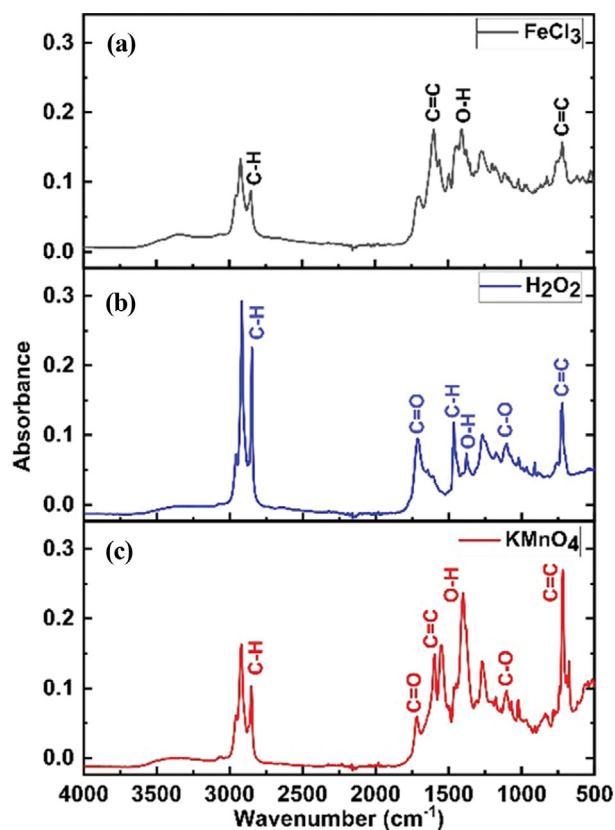


Fig. 7. FT-IR spectra of the precipitate after oxidation by each oxidant (a) FeCl<sub>3</sub>, (b) H<sub>2</sub>O<sub>2</sub>, (c) KMnO<sub>4</sub>.

Table 2. Amount of precipitate in the water phase after the reaction

Oxidant	Pyrolysis oil (g)	Oxidant (g)	Precipitate (g)	Standard deviation (n=3)
FeCl <sub>3</sub>	60.4	3.16	0.610	0.0512
H <sub>2</sub> O <sub>2</sub>	60.3	1.57	0.121	0.0254
KMnO <sub>4</sub>	60.6	0.232	0.481	0.0862



the FT-IR spectrum of three precipitates. Peaks in all three precipitates were observed at  $718\text{ cm}^{-1}$  and  $2,848\text{--}2,923\text{ cm}^{-1}$ . The earlier peak represents C=C bending in the alkene, whereas the latter range indicates C-H stretching in the aliphatic chain [30]. Other than the common peaks, unique peaks differ in their absorbance and wavenumbers. In the case of  $\text{FeCl}_3$  precipitate, O-H bending for alcohol or carboxylic acid at  $1,408\text{ cm}^{-1}$  and C=C for cyclic alkene at  $1,599\text{ cm}^{-1}$  are shown. Thus, there are cyclic alkene and alkene in the precipitate and O-H bonding as a hydrophilic functional group. Under acid-catalyzed conditions, the O-H bond can be formed by hydration of an alkene and ring-opening reaction of an epoxide [34,35].

In contrast, the precipitate of the  $\text{H}_2\text{O}_2$  reaction showed four unique peaks. It were C-O stretching for aliphatic ether or secondary alcohol at  $1,102\text{ cm}^{-1}$ , O-H bending of alcohol or phenol at  $1,376\text{ cm}^{-1}$ , C-H bending of methylene group in alkane at  $1,462\text{ cm}^{-1}$ , and C=O stretching of carbonyl groups including carboxyl groups at  $1,712\text{ cm}^{-1}$ . An especially noticeable one is the carbonyl group, which can be explained that benzyl alcohol, primary alcohol, aldehyde, and cycloalkene can be changed into a product with carboxylic acid. Additionally, the oxidation of secondary alcohol and aryl carbinol, respectively, might result in the production of ketone and aldehyde. On the other hand, epoxide, which was oxidized from alkene, presents C-O. There have been numerous researches on the oxidation of hydrocarbons by  $\text{H}_2\text{O}_2$ , although most of these examples employed catalysts for high yields [36–38]. However, because our system did not use any catalyst, the oxidized products may be relatively small.

In contrast, the precipitate of the  $\text{KMnO}_4$  reaction shows four distinct peaks. The peaks include C=C stretching of cyclic alkene at  $1,594\text{ cm}^{-1}$ , C=O stretching of carbonyl groups including carboxyl groups at  $1,716\text{ cm}^{-1}$ , O-H bending of alcohol or carboxylic acid at  $1,399\text{ cm}^{-1}$ , and C-O stretching of aliphatic ether or secondary alcohol at  $1,102\text{ cm}^{-1}$ . In particular, O-H bending stands out. This is because diol or carboxylic acid can be produced during oxidation by  $\text{KMnO}_4$ . The oxidation of an alkene converts a double bond into a single bond while forming two hydroxyl groups [39]. On the other hand, when the side chain of an aromatic molecule is oxidized, carboxylic acid is generated [40].

In all three precipitates, an abundance of oxygen and hydrophilic functional groups was observed. In addition to the intermolecular attraction by hydrophilic functional groups, van der Waals force, attractive  $\pi$ - $\pi$  stacking, and hydrogen bonding can induce the precipitation of hydrocarbon molecules [30–33]. After the reaction of  $\text{FeCl}_3$  and  $\text{KMnO}_4$ , in addition to the hydrocarbon, oxidant or reduced oxidant may also be present in the precipitate on their own or forming a metal coordination complex with the hydrocarbon.

However, the carbon residue content and oxygen content of the remaining carbon residue were only reduced after reactions with  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$ . We can conclude that the precipitate of the  $\text{KMnO}_4$  reaction contains hydrocarbons that are not the carbon residue precursor.  $\text{KMnO}_4$  is a powerful oxidant that can oxidize a variety of hydrocarbons, including olefins and aromatic molecules [41,42]. As a result, we can infer that the hydrocarbons that are not the carbon residue precursor are predominantly oxidized and precipitated.

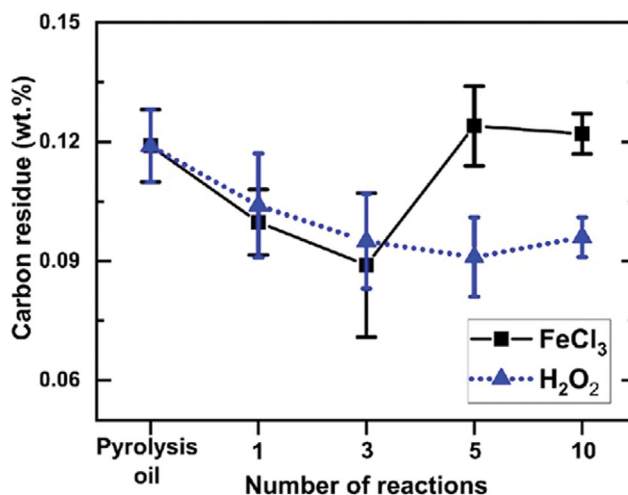


Fig. 8. Analysis of the carbon residue content of pyrolysis oil in relation to the number of 24-hour reactions of an oxidant solution (a)  $\text{FeCl}_3$  (square), (b)  $\text{H}_2\text{O}_2$  (triangle).

### 3. Carbon Residue Precursor Removal through Oxidant Recycling

After reacting the pyrolysis oil for 24 hours with  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  aqueous solutions, the carbon residue content was reduced. We selected these two oxidants to perform an experiment on continuous oxidation by recycling the oxidant aqueous solution. The aim of the experiment is to confirm that the carbon residue content decreases after a reaction with the recycled oxidant solution. If the content decreases, the number of reactions that can remove the carbon residue can be examined in order to reduce the amount of oxidant solution wasted. To test the effect of the recycled oxidant, we compared the carbon residue contents of the 1st, 3rd, 5th, and 10th pyrolysis oils.

Fig. 8 shows the carbon residue content of the pyrolysis oil based on the number of 24-hour reactions of the oxidant solution. After reacting with recycled  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  solutions, respectively, the carbon residue content of pyrolysis oil was reduced; however, the number of reactions showing reducing effects differed. The carbon residue content of the 10th pyrolysis oil that reacted with  $\text{H}_2\text{O}_2$  solution was reduced to a similar extent as that of the first pyrolysis oil. In contrast, the content of the fifth and tenth pyrolysis oils after reacting with  $\text{FeCl}_3$  showed little change, with the content remaining within one standard deviation of the mean of the initial pyrolysis oil. The deviation in carbon residue content is due to the heterogeneity of the pyrolysis oil. We assumed that the difference in the tendency of carbon residue content could be affected by the amount of oxidant remaining after the reactions. Hence, UV-Vis spectroscopy was used to determine the amount of oxidant left in the water phase.

UV spectra of the water phase after the reaction are presented in Fig. 9. The spectrum of the  $[\text{FeC}_6\text{H}_4\text{OCOO}]^+$  complex, which was formed by  $\text{Fe}^{3+}$  and  $\text{C}_7\text{H}_6\text{O}_3$  in a 1 : 1 molar ratio, is shown in Fig. 9(a). The  $[\text{FeC}_6\text{H}_4\text{OCOO}]^+$  absorption peak appears at 546 nm [43,44]. In the second spectrum (Fig. 9(b)), the absorption peak appears at 350 nm due to  $\text{H}_2\text{O}_2$ . It was formed from the oxidation of  $\Gamma^-$  in the presence of  $\text{H}_2\text{O}_2$  [45,46]. Both spectra show that the ab-

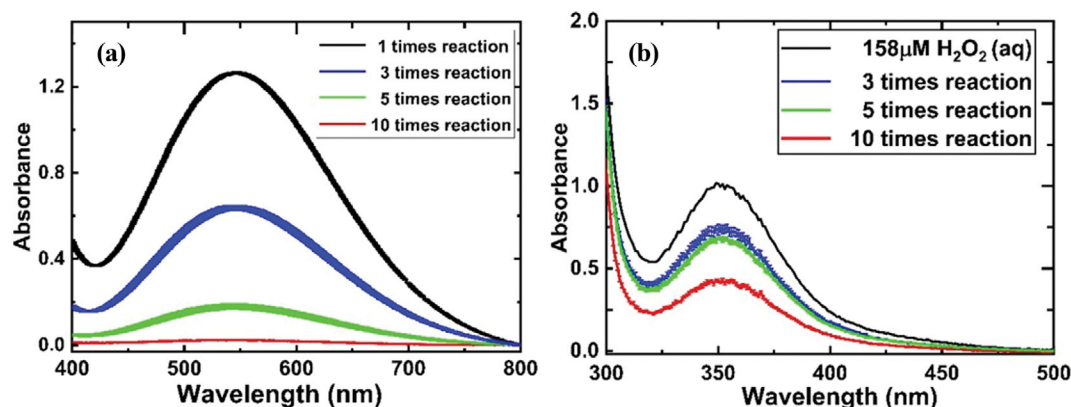


Fig. 9. UV-vis absorption spectra of the water phase based on the number of 24-hour reactions of an oxidant solution (a)  $[\text{FeC}_6\text{H}_4\text{OCOO}]^+$  complex in the ethanol, (b)  $\text{I}_3^-$  in the aqueous solution.

Table 3. Amount of oxidant remaining after a certain number of reactions

		Number of reactions		
		3	5	10
Remaining	$\text{FeCl}_3$	24.6	6.90	0.902
oxidant (%)	$\text{H}_2\text{O}_2$	72.4	67.4	42.0

sorbance of each peak declines as the number of oxidant reactions increases. This data can imply that the oxidant is present in the precipitate or was reduced during the reaction with the pyrolysis oil. To determine the change in the amount of oxidant, the amounts of remaining  $\text{FeCl}_3$  and  $\text{H}_2\text{O}_2$  were calculated based on absorbance data, as shown in Table 3. By correlating carbon residue and UV data, carbon residue was eliminated in all three consecutive processes, leaving 24.6%  $\text{FeCl}_3$  after three reactions. Assuming equal amounts of  $\text{FeCl}_3$  are consumed in each of the three reactions, 25.1% per reaction is consumed. Therefore, the residual 24.6% after three reactions may not be enough to oxidize the fifth and tenth pyrolysis oils. In the case of  $\text{H}_2\text{O}_2$ , however, 42.0% remained even after the tenth reaction, showing that the carbon residue removal effect can persist until the tenth pyrolysis oil.

#### 4. Carbon Residue Precursor Removal by Changing the Reaction Time

Previously, we confirmed that a 24-hour reaction with a recycled oxidant solution is able to remove the carbon residue in the pyrolysis oil. Here, to test the removal effect on a short time scale, the carbon residue content was examined while the reaction time was reduced. Unnecessary oxidation will be avoided if the carbon residue content is reduced by shortening the reaction time. Thus, the consumption of oxidant is lessened and more pyrolysis oil can be upgraded simultaneously, which is expected to improve the efficiency of the process.

The reaction time with the oxidant solution was set to 15 minutes, one hour, and three hours. The carbon residue content after each reaction was tested, as shown in Fig. 10. After a 15-min, 1-h, and 3-h reaction with the  $\text{H}_2\text{O}_2$  solution, the amount of carbon residue in the pyrolysis oil was almost the same as it was before the reaction. This demonstrates that a short  $\text{H}_2\text{O}_2$  reaction does

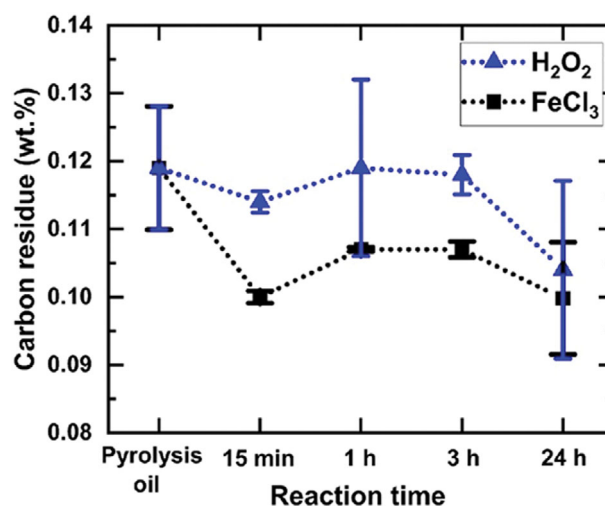


Fig. 10. Analysis of carbon residue content of pyrolysis oil with different reaction times (a)  $\text{FeCl}_3$  (square), (b)  $\text{H}_2\text{O}_2$  (triangle).

not significantly affect getting rid of the carbon residue. On the other hand, the carbon residue was removed after a 15-min reaction with  $\text{FeCl}_3$ . We reasoned that the difference in removing the carbon residue could be related to oxidation rate. The activity of  $\text{H}_2\text{O}_2$  oxidation is relatively low, hence previous research utilized catalysts to facilitate [47-49] or by increasing the temperature [37].

As with the continuous 24-hour reaction, a continuous 15-minute oxidation with  $\text{FeCl}_3$  was conducted. However, the pyrolysis oil that was used for 15-min of continuous reaction had much more carbon residue than the other pyrolysis oil. So, only the current value of pyrolysis oil was taken into account. Depending on the number of reactions with an aqueous solution of  $\text{FeCl}_3$ , the amount of carbon residue and  $\text{FeCl}_3$  was analyzed. As shown in Fig. 11, nearly identical amount of carbon residue was removed until the fifth pyrolysis oil. However, the amount of carbon residue reduction in the tenth pyrolysis oil was less. Differences in the degree of reduction can be correlated with changes in the quantity of  $\text{FeCl}_3$ . Therefore, the remaining amount of  $\text{FeCl}_3$  was quantified using UV-vis spectroscopy, as shown in Table 4 and Fig. S3. Compared to the 24-hour continuous reaction, the 15-minute continuous reac-

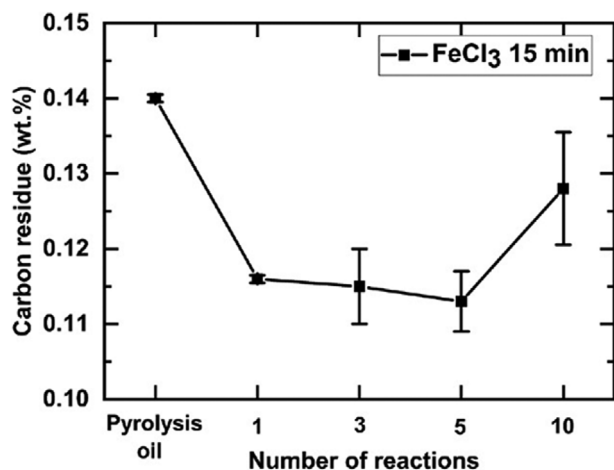


Fig. 11. Analysis of carbon residue content of pyrolysis oil with different reaction numbers of 15-minute reactions of FeCl<sub>3</sub> solution.

Table 4. Analysis of FeCl<sub>3</sub> remaining after different numbers of 15-minute reactions with pyrolysis oil

	Number of reactions		
	3	5	10
Remaining FeCl <sub>3</sub> (%)	88.6	82.4	50.4

tion resulted in a lower decrease in FeCl<sub>3</sub> content, which remained at 50.4% after ten reactions. So, the 15-minute reaction can be more economical and takes less time to remove the carbon residue.

## CONCLUSIONS

We have proposed a new method to remove the carbon residue precursor, which cannot be filtered, from the waste plastic pyrolysis oil. By emulsifying the pyrolysis oil and the aqueous solution of oxidant, the hydrophilicity of the carbon residue precursor was increased at the oil/water interface through oxidation. In addition to the existing weak attractions between the carbon residue precursors, attraction by the generated hydrophilic functional group induced precipitation of the precursor. Finally, the precipitate can form in the water phase and can be easily separated. The carbon residue precursor was oxidized by varying the type of oxidant and the reaction time under the same mild conditions. The carbon residue content of pyrolysis oil decreased after a 24-hour reaction with FeCl<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> solutions, respectively. In both cases, the carbon residue precursor was selectively oxidized in that the oxygen content of the carbon residue decreased while the pyrolysis oil did not. The number of continuous 24-hour oxidations that could remove the carbon residue was three for FeCl<sub>3</sub> and ten for H<sub>2</sub>O<sub>2</sub> solution. The difference in the number of recycles was determined by the amount of remaining oxidant. In short reaction times, the 15-minute reaction with FeCl<sub>3</sub> solution was effective at removing the carbon residue. However, the three hour reaction with H<sub>2</sub>O<sub>2</sub> solution was not. Without using a catalyst or a surfactant, carbon residue can be removed by precipitating the carbon residue precursor,

whose hydrophilicity has been increased by oxidation. The decrease in carbon residue can imply a decrease in coke formation during subsequent pyrolysis oil refining. By reducing fouling, the efficiency of the refinement can be improved, and our study might contribute to the commercialization of chemical recycling of waste plastics.

## ACKNOWLEDGEMENT

This research was supported by the Korea Evaluation Institute of Industrial Technology [Grant number 20015430].

## NOTES

The authors declare that there is no competing financial interest.

## SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

## REFERENCES

1. J.-P. Lange, *Green Chem.*, **4**, 546 (2002).
2. J.-P. Lange, *ACS Sustain. Chem. Eng.*, **9**, 15722 (2021).
3. K. Ragaert, L. Delva and K. Van Geem, *Waste Manage.*, **69**, 24 (2017).
4. A. Rahimi and J. García, *Nat. Rev. Chem.*, **1**, 0046 (2017).
5. C. Sun, Y. Jiang, Z. Zhang, S. Zhao and L. Guo, *Macromol. Res.*, **29**, 543 (2021).
6. Z. Wei, Y. Wang, X. Fu, L. Jiang, Y. Wang, A. Yuan, H. Xu and J. Lei, *Macromol. Res.*, **29**, 562 (2021).
7. L. Wang, S. Yan, L. Zhang, Y. Mai, W. Li and H. Pang, *Macromol. Res.*, **29**, 462 (2021).
8. S. Jung and I. Ro, *Korean J. Chem. Eng.*, **40**, 693 (2023).
9. J. Lai, Y. Meng, Y. Yan, E. Lester, T. Wu and C. H. Pang, *Korean J. Chem. Eng.*, **38**, 2235 (2021).
10. H. Almohamadi, M. Alamoudi, U. Ahmed, R. Shamsuddin and K. Smith, *Korean J. Chem. Eng.*, **38**, 2208 (2021).
11. J. Esteban, F. J. Colomer, M. Carlos and A. Gallardo, *Project Manage. Eng.*, **1**, 131 (2015).
12. Y. Xue, S. Zhou, R. C. Brown, A. Kelkar and X. Bai, *Fuel*, **156**, 40 (2015).
13. Z. J. Low, J. C. Wong, K. H. Ngoi, C. H. Chia, H.-J. Kim, H.-C. Kim and M. Ree, *Macromol. Res.*, **29**, 230 (2021).
14. S. Belbessai, A. Azara and N. Abatzoglou, *Processes*, **10**, 733 (2022).
15. M. Kusenberger, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. De Meester and K. M. Van Geem, *Waste Manage.*, **138**, 83 (2022).
16. M. Kusenberger, M. Roosen, A. Zayoud, M. R. Djokic, H. Dao Thi, S. De Meester, K. Ragaert, U. Kresovic and K. M. Van Geem, *Waste Manage.*, **141**, 104 (2022).
17. A. De Lucas, P. Canizares, A. Durán and A. Carrero, *Appl. Catal. A: Gen.*, **154**, 221 (1997).
18. A. Eschenbacher, R. J. Varghese, M. S. Abbas-Abadi and K. M. Van Geem, *Chem. Eng. J.*, **428**, 132087 (2022).

19. S. Catak, K. Hemelsoet, L. Hermosilla, M. Waroquier and V. Van Speybroeck, *Chem. Eur. J.*, **17**, 12027 (2011).
20. P. Das, S. Prasad and D. Kunzru, *Ind. Eng. Chem. Res.*, **31**, 2251 (1992).
21. K. K. Ghosh and D. Kunzru, *Ind. Eng. Chem. Res.*, **27**, 559 (1988).
22. Z. Dobó, G. Kecsmár, G. Nagy, T. Koós, G. Muránszky and M. Ayari, *Energy Fuels*, **35**, 2347 (2021).
23. R. Miandad, M. A. Barakat, A. S. Aburiazaiza, M. Rehan, I. M. I. Ismail and A. S. Nizami, *Int. Biodeterior. Biodegrad.*, **119**, 239 (2017).
24. C. Vasile, M. A. Brebu, T. Karayildirim, J. Yanik and H. Darie, *Fuel*, **86**, 477 (2007).
25. M. Elsherif, Z. A. Manan and M. Z. Kamsah, *J. Nat. Gas. Sci. Eng.*, **24**, 346 (2015).
26. M. A. Gadalla, Z. Olujic, P. J. Jansens, M. Jobson and R. Smith, *Environ. Sci. Technol.*, **39**, 6860 (2005).
27. J. M. Lee, S. Shin, S. Ahn, J. H. Chun, K. B. Lee, S. Mun, S. G. Jeon, J. G. Na and N. S. Nho, *Fuel Process. Technol.*, **119**, 204 (2014).
28. S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos and A. Dutta, *J. Environ. Manage.*, **197**, 177 (2017).
29. ASTM Method D 4530-07 Standard Test Method for Determination of Carbon Residue (Micro Method).
30. S. Choi, D. H. Byun, K. Lee, J.-D. Kim and N. S. Nho, *J. Pet. Sci. Eng.*, **146**, 21 (2016).
31. M. R. Gray, R. R. Tykwinski, J. M. Stryker and X. Tan, *Energy Fuels*, **25**, 3125 (2011).
32. J. Murgich, *Pet. Sci. Technol.*, **20**, 983 (2002).
33. M. E. Abdel Aziz, G. R. Saad and M. T. Abou El-khair, *Macromol. Res.*, **30**, 900 (2022).
34. V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, **10**, 252 (1977).
35. R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959).
36. R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, **16**, 1977 (2003).
37. X. Lu, H. Xu, J. Yan, W.-J. Zhou, A. Liebens and P. Wu, *J. Catal.*, **358**, 89 (2018).
38. Z. Y. Pastukhova, V. V. Levitin, E. A. Katsman and L. G. Bruk, *Kinet. Catal.*, **62**, 604 (2021).
39. R. S. Varma and K. P. Naicker, *Tetrahedron Lett.*, **39**, 7463 (1998).
40. A. Abiko, J. C. Roberts, T. Takemasa and S. Masamune, *Tetrahedron Lett.*, **27**, 4537 (1986).
41. S. Wolfe, C. F. Ingold and R. U. Lemieux, *J. Am. Chem. Soc.*, **103**, 938 (1981).
42. G. S. Brown, L. L. Barton and B. M. Thomson, *Waste Manage.*, **23**, 737 (2003).
43. R. R. Warriar, M. Paul and M. V. Vineetha, *Genet. Plant Physiol.*, **3**, 90 (2013).
44. O. Khalipova, S. Kuznetsova and V. Kozik, *AIP Conf. Proc.*, **1772** (2016).
45. A. D. Awtrey and R. E. Connick, *J. Am. Chem. Soc.*, **73**, 1842 (1951).
46. C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).
47. T. M. Florence, *J. Inorg. Biochem.*, **22**, 221 (1984).
48. R. C. C. Costa, M. de Fátima Fontes Lelis, L. C. A. Oliveira, J. D. Fabris, J. D. Ardisson, R. R. V. A. Rios, C. N. Silva and R. M. Lago, *Catal. Commun.*, **4**, 525 (2003).
49. J. M. Fraile, C. Gil, J. A. Mayoral, B. Muel, L. Roldán, E. Vispe, S. Calderón and F. Puente, *Appl. Catal. B: Environ.*, **180**, 680 (2016).



## Supporting Information

### Removal of carbon residue precursor in waste plastic pyrolysis oil via oxidation

Sukjeong Jeon\*, Jaehong Lee\*, Seong Cheon Kim<sup>\*,\*\*</sup>, Jin-Hyuk Kang<sup>\*\*\*</sup>, Dongho Lee<sup>\*\*\*\*</sup>,  
Hye Ryung Byon<sup>\*\*\*\*\*,\*\*\*,†</sup>, Jeasung Park<sup>\*\*\*,†</sup>, and Siyoung Q. Choi<sup>\*,\*\*\*\*\*,†</sup>

\*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST),  
Daejeon 34141, Korea

\*\*Green and Sustainable Materials R&D Department, Korea Institute of Industrial Technology (KITECH),  
Cheonan-si, 31056, Korea

\*\*\*Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea

\*\*\*\*Process R&D Center, Hanwha Solutions R&D Institute, Daejeon 34128, Korea

\*\*\*\*\*KAIST Institute for the Nanocentury, KAIST, Daejeon 34141, Korea

(Received 26 January 2023 • Revised 13 May 2023 • Accepted 24 May 2023)

#### MATERIALS AND METHODS

##### A. Micro Method

Micro method is used to determine the amount of carbon residue in the pyrolysis oil [1]. Carbon residue is produced during the pyrolysis of pyrolysis oil under an N<sub>2</sub> atmosphere at temperatures

up to 500 °C. The carbon residue content is calculated by measuring the pyrolysis oil and the carbon residue produced. If the calculated content is less than 0.1% (m/m), the pyrolysis oil is further distilled to leave the residual oil (10% (V/V)). The carbon residue content is determined by measuring the mass of the carbon residue that is produced after the pyrolysis of 10% (V/V) residual oil.

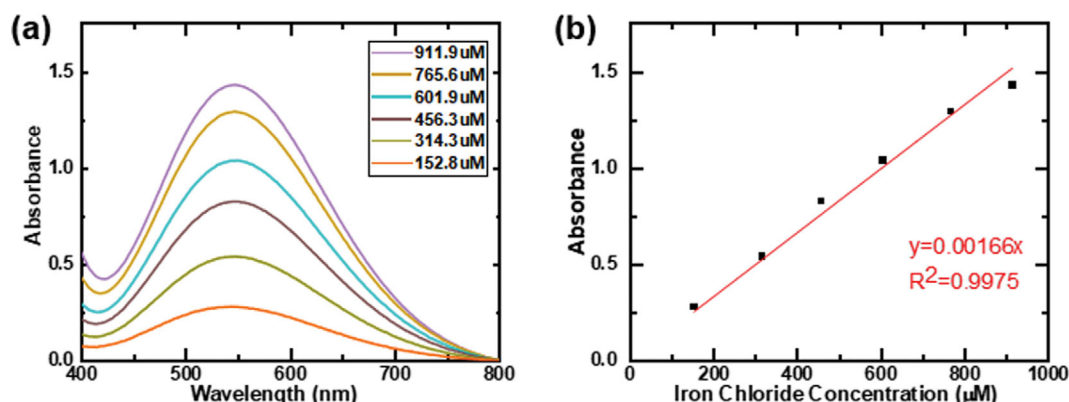


Fig. S1. (a) UV-vis spectra according to FeCl<sub>3</sub> concentration (b) Linear relationship between FeCl<sub>3</sub> concentration and absorbance at 546 nm.

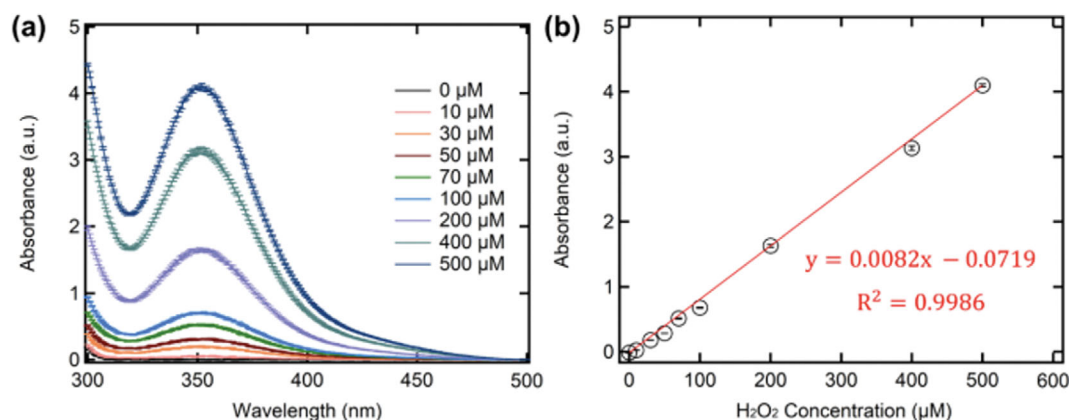


Fig. S2. (a) UV-vis spectra according to H<sub>2</sub>O<sub>2</sub> concentration (b) Linear relationship between H<sub>2</sub>O<sub>2</sub> concentration and absorbance at 353 nm [2].

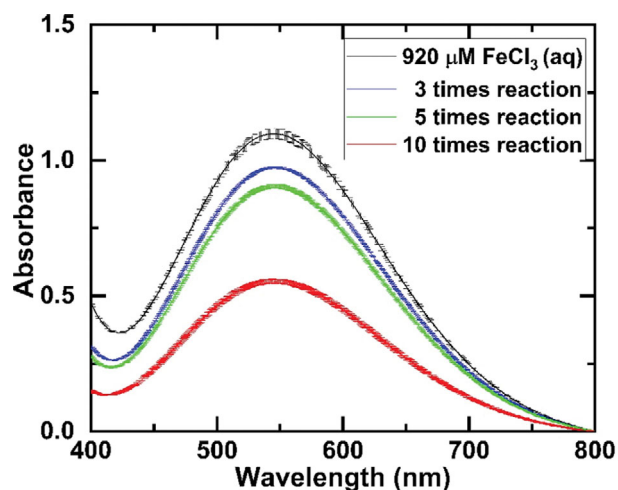


Fig. S3. UV-vis absorption spectrum of  $[\text{FeC}_6\text{H}_4\text{OCOO}]^+$  complex in the ethanol in relation to the number of oxidant solution reactions for 15-min.

## B. Oxidant Selection

$\text{FeCl}_3$ ,  $\text{H}_2\text{O}_2$ , and  $\text{KMnO}_4$  were selected as oxidants for the carbon residue precursor. These oxidants have a high standard reduction potential value; hence, they can act as strong oxidants. In addition, they are in a solid or liquid state that can dissolve in water. This enables reactions at a wide interface between the aqueous oxidant and oil phases, as well as easy separation of the aqueous oxidant solution after the reaction.

## C. Quantification of Oxidant

UV-vis spectroscopy was used to determine the amount of oxidant. The water phase was diluted to a concentration that satisfied the Beer-Lambert law. The dilution concentration should be lower than  $912 \mu\text{M}$  for  $\text{FeCl}_3$  and  $500 \mu\text{M}$  for  $\text{H}_2\text{O}_2$  [2]. After the dilution, the absorbance was measured, and the absorbance data was used to calculate the oxidant concentration.

## REFERENCES

1. ASTM D 4530.
2. K. Lee, H.-R. Lee, Y. H. Kim, J. Park, S. Cho, S. Li, M. Seo and S. Q. Choi, *ACS Cent. Sci.*, **8**, 1265 (2022).