[Review Paper]

Feedstock Recycling via Waste Plastic Pyrolysis

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Recycling of waste plastics is essential for reducing environmental degradation and ensuring future resource security. The quantity of domestic plastic waste recycled is increasing yearly, reaching 83 % in 2014. However, only 26 % and 4 % of the recycled waste plastic is treated by mechanical and feedstock recycling, respectively, whereas 70 % is treated by energy recovery (incineration). Therefore, the mechanical and feedstock recycling rates must be improved. This review examines the pyrolysis of waste plastics, which is a treatment method classed as feedstock recycling. Pyrolysis can convert waste plastics, which cannot be treated by mechanical recycling, into oils and gases. However, polyvinylchloride (PVC) and poly(ethylene terephthalate) (PET) produce corrosive gases and sublimating substances during pyrolysis, resulting in reduced quality of pyrolysis products, and damage to the treatment plant. Dehydrochlorination and dechlorination of PVC, in addition to catalytic pyrolysis of PET using Ca-based catalysts, have been developed. Recent studies into the pyrolysis of major plastics such as polyethylene (PE), polypropylene (PP), and polystyrene (PS) are summarized here, together with research on the dry and wet treatment of PVC and the catalytic pyrolysis of PET.

Keywords

Pyrolysis, Waste plastic, Feedstock recycling, Liquefaction, Gasification

1. Introduction

Plastics are essential materials for various products such as packaging and containers, electrical and electronic equipment, and automobiles. Japanese production of polymers was reported as 10.6 million t in 2014¹⁾, with the majority prepared from finite fossil resources. Currently, in excess of 150 and 200 different types of polymers and additives, respectively, are produced and distributed within Japan²⁾. Metals and fillers are further mixed with these products to achieve the desired properties, giving innumerable combinations. Thus, no single recycling technique can treat all types of waste plastics. Consequently, waste plastics are commonly treated by mechanical recycling, feedstock recycling, and energy recovery, depending on the waste composition and the purpose of the recycled products.

The Plastic Waste Management Institute reported that 9.3 million t of waste plastics were collected in 2014 in Japan¹⁾. The utilized rate (mechanical recycling + feedstock recycling + energy recovery) for collected waste plastics was 83 %, and is increasing yearly. Utilization can be broken down into 70 % energy recovery, 26 % mechanical recycling, and 4 % feedstock

recycling. According to the Basic Law for Establishing the Recycling-based Society, the order of priority of these techniques is as follows: mechanical recycling > feedstock recycling > energy recovery. Therefore, the ideal and actual situations show a wide gap.

Feedstock recycling is a growing field in Japan, but is challenging due to the mismatch with current domestic recycling systems. However, advances in research and technical development show the potential to achieve an advanced recycling-based society. In Japan, monomerization, blast furnace reduction, coke oven chemical feedstock recycling, liquefaction, and gasification are categorized as feedstock recycling. In this paper, we focus on liquefaction and gasification, which are based on the pyrolysis technique.

Pyrolysis converts polymeric materials into gases, liquids, and solids at high temperatures in the absence of oxygen. This process cleaves various chemical bonds in polymers and additives by the action of only heat, which is advantageous for low-purity waste that cannot be treated by mechanical recycling. Polyethylene (PE), polypropylene (PP), and polystyrene (PS) are the main polymeric materials produced worldwide, so have been widely studied. In addition, these materials are good quality carbon and hydrogen resources (PE and PP: 86 % C and 14 % H; PS: 92 % C and 8 % H). In contrast, the pyrolysis of polyvinyl chloride (PVC) and poly(ethylene terephthalate) (PET)

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Fig. 1 Fluidized Bed Pyrolysis System⁶⁾

resins tends to suffer problems with corrosion, clogging of the treatment facilities, and production of undesirable chlorinated organic compounds. This paper summarizes recent developments in the pyrolysis of major plastics such as PE, PP, and PS, and discusses the pyrolysis of PVC and PET.

2. PE, PP, and PS

PE and PP are lightweight, flexible, and water and chemical resistant polymers, and so are often employed in packaging films and containers. In contrast, PS is lightweight, stiff, and thermally insulating, and thus is often used in containers and buffer materials. As previously mentioned, PE, PP, and PS (the 3Ps) are the major components of waste plastics, so the effectiveness of pyrolysis for treating these resins have been extensively investigated. The 3Ps are pyrolyzed into smaller hydrocarbons *via* breakage of the C-C backbone, allyl chain fission, intermolecular hydrogen abstraction, β -scission, hydrogen transfer, radical addition, disproportionation, and radical recombination, as summarized elsewhere^{3)~5)}.

The "Hamburg process" is a fluidized-bed pyrolysis system (**Fig. 1**) in which the plastics are introduced into an auxiliary fluidized bed of quartz sand using a screw feeder or a double lock⁶⁾. The pyrolysis gas is removed from the reactor, fine dust and soot are removed in a cyclone, then the gas is cooled to ambient temperature in a quencher using a cycle of product oil. The gas is then passed through two quenching columns, which are filled with glass bodies, and is condensed into oil. The exhaust gases are used to preheat the fluidizing gas by means of heat exchange. The Hamburg process was investigated for the pyrolysis of mixed plastics consisting of polyethylene (PE), polypropylene (PP), and polystyrene (PS) containing traces of polyvinyl chloride (PVC) at 730 °C⁷⁾. This process yielded

35.0 wt% gases, 48.4 wt% oil, 14.3 wt% distillation residue, and 2.2 wt% char. The produced oil contained important aromatic compounds such as benzene, toluene, xylene (BTX), and styrene in a total yield of 31.4 wt%. In addition, the produced gases had a high calorific value of 50 MJ/kg. PE- and PP-rich mixed plastics were pyrolyzed into olefins, such as 21-29 wt% ethylene, 16-21 wt% propylene, and 5.6-6.6 wt% butadiene in a steam atmosphere⁸⁾. This product composition is similar to that obtained from the steam cracking of naphtha. The catalytic pyrolysis of polyolefins using FCC⁹⁾ and Ziegler-Natta catalysts^{10),11)} reduced the operating temperature and increased the quantity of light hydrocarbons. The effectiveness of the Hamburg process for various polymeric materials is summarized elsewhere^{12)~16)}.

Pyrolysis of polyolefins was investigated using a conical spouted bed reactor (CSBR)^{17)~26)}. The following advantages were obtained: good heat and material transfer, low operating pressure, wide particle size and density without segregation, and absence of defluidization through vigorous contact in the spout and fountain. A 69 wt% gasoline fraction (C₅-C₁₀) was recovered from high density polyethylene (HDPE) without defluidization using an HY zeolite bed material (25 wt% HY zeolite, 30 wt% bentonite, and 45 wt% inert alumina, agglomerated by a wet extrusion method)¹⁸⁾. This fraction fulfils the European Union requirements for commercial gasoline, and its research octane number (RON) index (96.5) is comparable to that of standard automotive fuel.

Pyrolysis is also effective for treating waste plastics. The 3P are easily converted into gas, oil, and wax fractions containing small quantities of char^{27),28)}. Investigation of the effects of HZSM-5 zeolite catalysts on the pyrolysis of waste plastic mixtures (mixtures of HDPE, LDPE, PP, and PS containing traces of PET and PVC, from Slovenia, South-Taiwan, and Hungary) found a significant increase in the aromatic fraction (BTX, ethylbenzene, and styrene)²⁹⁾. In addition, waste plastics, especially PE, PP, and PS, are good resources for hydrogen production by catalytic steam reforming. The H₂ yields from HDPE, PP, PS, and PE-rich mixed plastics were approximately 2.5, 2.6, 1.7, and 2.0 L H₂/g plastic, respectively, at a gasification temperature of 800 °C using a Ni-Mg-Al catalyst prepared by co-precipitation³⁰⁾. The effects of various types of Ni catalysts, such as Ni/Al₂O₃, Ni/MgO, Ni/CeO, Ni/ZSM-5, Ni/CeO₂/Al₂O₃, Ni/CeO₂/ZSM-5, Ni-Al, Ni-Cu-Al, and Ni-Mn-Al were also evaluated in the plastic gasification process^{31)~42)}.

PE and PP can be decomposed into aromatic hydrocarbons using activated carbon impregnated with Pt, Fe, Mo, Zn, Co, Ni, and Cu. PE was converted into aromatic compounds with a maximum yield of 46.2 wt% at 526 °C using 3 wt% Pt/C^{43)~45)}. The maximum

Fig. 2 Pyrolysis Behavior of PVC: (a) TG and DTG Curves with Heating Rate between $0.5\text{ }^{\circ}\text{C min}^{-1}$ and $40\text{ }^{\circ}\text{C min}^{-1}$; (b) Selected Ion Chromatogram of the Major Compounds at $4\text{ }^{\circ}\text{C min}^{-1}$ ⁵²⁾

yield of aromatic compounds was $\sim 30\text{ wt\%}$ from PP at $502\text{ }^{\circ}\text{C}$ using $3\text{ wt\% Pt/C}$. Other catalysts, such as Pt and Rh/ Al_2O_3 ⁴⁶⁾, Ga/ZSM-5⁴⁷⁾, Ru/ Al_2O_3 ^{48),49)}, Pb, Co, and Pb-Co/ BaTiO_3 ⁵⁰⁾, Ni, Co, Fe, Mn, and Zn/AWBN (acid washed bentonite clay)⁵¹⁾, have also been studied for the catalytic pyrolysis of the 3P.

Based on the numerous studies focusing on the pyrolysis of PE, PP, and PS, we concluded that 3P waste can be converted into high value-added products by this process, with new advances reported every year. However, the presence of PVC and PET in 3P waste causes deterioration in the pyrolysis product quality, together with corrosion and clogging of the treatment facilities. Overcoming these problems will be important in the future.

3. PVC

PVC is strong, pliable, and flame resistant, which are ideal characteristics for use in films, pipes, and cable materials. The most unique characteristic of PVC is its high chlorine content, which accounts for $57\text{ wt\%}$ of pure PVC resin, and allows for high volumes of PVC to be manufactured with relatively low amounts of hydrocarbon feedstock.

The authors previously investigated the pyrolysis behavior of PVC resin by combined thermogravimetry-mass spectroscopy (TG-MS)⁵²⁾, as shown in Fig. 2. The weight loss during PVC pyrolysis occurs in two stages, firstly at $200\text{--}350\text{ }^{\circ}\text{C}$, then above $350\text{ }^{\circ}\text{C}$. The first stage corresponds mainly to dehydrochlorination, resulting in the production of HCl and a solid residue with a polyene structure. In addition, the $m/z = 36$ in Fig. 2(b) corresponds to HCl, suggesting two-stage dehydrochlorination, and implies that two different types of bonds (e.g., head to head and head to tail) are dehydrochlorinated. PVC pyrolysis produced $52.9\text{ wt\%}$ HCl during at $700\text{ }^{\circ}\text{C}$ ^{27),28)}, and $56.3\text{ wt\%}$ HCl at $740\text{ }^{\circ}\text{C}$ ⁶⁾. Benzene and other aromatic hydrocarbons were also

formed due to cyclization reactions in the first and second stages. Detailed mechanisms for the dehydrochlorination and subsequent hydrocarbon formation during PVC pyrolysis were summarized previously^{53),54)}.

These significant amounts of HCl formed during pyrolysis result in the corrosion of treatment facilities, as previously mentioned. Additionally, the “Act on the Promotion of Sorted Garbage Collection and Recycling of Containers and Packaging” specifies that pyrolysis oil must have a chlorine content of $<100\text{ ppm}$ ^{55),56)}. Thus, chlorine removal from plastic waste or pyrolysis products is necessary for the treatment of PVC-containing plastics.

The preferred option for Cl removal from PVC is “dry treatment” by heating prior to liquefaction or gasification, which is categorized as “dehydrochlorination.” The dehydrochlorination of PVC is a seemingly simple reaction, expected to form only HCl and polyene structures. However, as the extent of dehydrochlorination increases and polyene structures become dominant, a series of terminating reactions occur, such as cyclization and crosslinking, locking the remaining chloride within stable structures^{53),54)}. Removal of these isolated chloride atoms is extremely difficult, so complete chlorine removal through only dry treatment is difficult. To overcome this issue, the authors investigated the steam-assisted dehydrochlorination of PVC under atmospheric pressure⁵⁷⁾. Figure 3(a) shows the dehydrochlorination behavior of both pure PVC resin and flexible PVC polymer in the presence and absence of a flow of $50\text{ vol\%}$ steam in N_2 , demonstrating that steam addition enhances dehydrochlorination. Infrared spectroscopy showed that the steam-treated samples exhibited a peak corresponding to an OH group at $\sim 3400\text{ cm}^{-1}$, suggesting that steam (H_2O) acted as a nucleophile to substitute Cl with an OH moiety. Thus, the presence of steam enhanced dehydrochlorination.

Dehydrochlorination using a single screw extruder

Fig. 3 (a) Time Dependence of PVC Dehydrochlorination for Both Resin and Flexible PVC Samples Treated at 230 °C Both with and without Steam; (b) FT-IR Spectra of Fresh and Dehydrochlorinated PVC Resin after Treatment for 60 min at a Steam Concentration of 50 vol% at Various Temperatures⁵⁷⁾

Fig. 4 Single-screw Extruder Employed in the Dehydrochlorination Experiments⁵⁸⁾

was studied for municipal waste plastics (43 % PP, 29 % PE, 8 % PS, 7 % PVC, 1 % PVDC, 9 % PET, and 3 % others) (**Fig. 4**)⁵⁸⁾. The plastic materials were then compressed (melted), metered (fixed feeding), and discharged. The lowest residual Cl content in the treated sample (*i.e.*, 0.27 wt%) was achieved at 375 °C with a feeding rate of 43.6 kg h⁻¹, and a residence time of 94 s (feed screw: 75 rpm; discharge screw: 75 rpm).

An alternative technique for Cl removal from PVC is “wet treatment” prior to liquefaction or gasification, which is otherwise known as “dechlorination.” The authors previously reported that dechlorination of PVC materials using an alkaline solution (**Fig. 5(a)**) progresses by two pathways, E2 elimination and S_N2 substitution (**Fig. 5(a)**)^{59)–65)}. For example, pure PVC

resin was dechlorinated at 190 °C in a 1.0 M NaOH/ethylene glycol (EG) solution at atmospheric pressure, resulting in 97.8 % dechlorination⁶²⁾. The effectiveness of this system was confirmed using flexible PVC tubing, resulting in complete dechlorination⁶¹⁾. Ball mill-assisted dechlorination was also developed (**Fig. 5(b)**), with enhanced dechlorination rate for both flexible and rigid PVC materials of 97 % and 84 %, respectively, compared to 80 % and 40 % in the absence of ball milling (**Figs. 5(c)** and **5(d)**). The Y₂O₃-ZrO₂ balls used have high mechanical strength, so are highly durable for the milling process. The chlorine present in the EG solution following dechlorination can be recovered by electrodialysis using either ion-exchange membranes⁶⁶⁾ or an alumina/zeolite membrane⁶⁷⁾,

Fig. 5 Dechlorination of PVC Using NaOH/EG Solution^{(60),(62)}: (a) Simple Dechlorination System; (b) Ball-mill Assisted Dechlorination System; (c) Dechlorination Behavior of Flexible PVC in the Presence and Absence of Ball-milling; (d) Dechlorination Behavior of Rigid PVC in the Presence and Absence of Ball-milling

allowing simultaneous recovery of Cl and regeneration of EG. Other combinations, such as NaOH/dimethyl sulfoxide (DMSO)⁽⁶⁸⁾ and ammonia solution⁽⁶⁹⁾, have also been reported, resulting in quantitative dechlorination. In addition, the S_N2 substitution was also applied for “PVC upgrading” using various nucleophiles^{(70)~(78)}, which can add new properties to PVC while maintaining the basic PVC properties. For example, only 3.8 % of the Cl present in PVC was substituted with isothiocyanate (–N=C=S) at 100 °C in tetrahydrofuran (THF)/dimethyl sulfoxide (DMSO) solution, which showed reduced adhesion of bacteria (*Staphylococcus capitis*) by 79 % (Fig. 6)⁽⁷⁸⁾. This finding may be very important in the use of PVC in sanitary goods, wall-paper, and so on.

Cl capture by solid absorbents during pyrolysis has also been examined. The main studies discussing the pyrolysis of PVC-containing plastics are summarized in **Table 1**. Mixtures of PE/PP/PS/PVC (weight ratio = 3/3/3/1) were pyrolyzed in the presence of a Ca–C absorbent, prepared by the calcination of mixtures of 90 wt% calcium carbonate (CaCO₃) and 10 wt% phenol resin, using a two-step fixed bed reactor⁽⁷⁹⁾. The liquid and gas yields were not affected by the presence of Ca–C absorbent, giving yields of 67 wt% and 24 wt%, respectively, compared to yields of 63 wt% and 24 wt% in the absence of Ca–C, due to blockage of Cl contamination of the oil by the Ca–C absorbent. Approximately

Fig. 6 Antibacterial Effect of PVC Substituted with Isothiocyanate Groups⁽⁷⁸⁾

5 equivalents of Ca–C were employed, so no Cl was detected following 4 repeated runs. Ca- and Fe-based absorbents, synthesized by the calcination of mixtures

Table 1 Summary of Previous Research on Catalytic Pyrolysis of PVC Plastics

Authors	Plastics ^{a)}	Catalyst or absorbent ^{b)}	Equipment ^{c)} and conditions	Results
Bhaskar <i>et al.</i> ⁷⁹⁾	PE/PP/PS/PVC (3/3/3/1) Amount: 10 g	Ca-C Amount: 4 g	Equipment Two-step fixed bed reactor Conditions Pyrolysis bed: 120 °C (hold 60 min) → (3 °C min ⁻¹) → 430 °C; Catalyst bed: 350 °C	➤ Thermal: Liquid 63 wt%, Gas 24 wt%, Residue 13 wt%, 360 ppm Cl in liquid ➤ With Ca-C: Liquid 67 wt%, Gas 23 wt%, Residue 10 wt%, 0 ppm Cl in liquid
Sakata <i>et al.</i> ⁸⁰⁾	PVC/HIPS-Br (4/1) Amount: 10 g	Fe-C Amount: 4 g	Equipment Single-step fixed bed reactor Conditions Pyrolysis and catalyst bed: 120 °C (hold 60 min) → (3 °C min ⁻¹) → 430 °C	➤ Thermal: Liquid 48 wt%, Gas 21 wt%, Residue 31 wt%, 4300 ppm Cl and 55000 ppm Br in liquid ➤ With Fe-C: Liquid 38 wt%, Gas 12 wt%, Residue 48 wt%, 0 ppm of Cl and Br in liquid
	PP/PE/PS/PVC/HIPS-Br (3/3/2/1/1) Amount: 10 g	Ca-C Amount: 4 g		➤ Thermal: Liquid 71 wt%, Gas 17 wt%, Residue 12 wt%, 1120 ppm Cl and 7300 ppm Br in liquid ➤ With Ca-C: Liquid 66 wt%, Gas 25 wt%, Residue 9 wt%, 0 ppm of Cl and Br in liquid
	MPW Amount: 10 g	Ca-C Amount: 4 g		➤ Thermal: Liquid 60 wt%, Gas 25 wt%, Residue 15 wt%, 1170 ppm Cl and 40 ppm Br in liquid ➤ With Ca-C: Liquid 60 wt%, Gas 25 wt%, Residue 15 wt%, 590 ppm Cl in liquid
Brebu <i>et al.</i> ⁸²⁾	PE/PP/PS/PVC/ABS-Br (3/3/2/1/1) Amount: 10 g	CaCO ₃ FeOOH Ca-C Fe-C Dolomite Amount: 10 g	Equipment Single-step fixed bed reactor Conditions Pyrolysis and catalyst bed: r.t. → (5 °C min ⁻¹) → 450 °C	➤ Liquid 59-67 wt%, Gas 17-20 wt%, Residue 13-17 wt% ➤ Cl in oil: Thermal (4972 ppm) > FeOOH (3370 ppm) > Fe-C (1014 ppm) > CaCO ₃ (355 ppm) > Ca-C (113 ppm) ➤ Br in oil: Thermal (1924 ppm) > CaCO ₃ (1161 ppm) > Ca-C (418 ppm) > Fe-C (170 ppm) > FeOOH (104 ppm)
Cho <i>et al.</i> ⁸³⁾	MPW (Cl: 11300 ppm) Amount: 800 g	CaO Amount: 43 g Ca(OH) ₂ Amount: 28 g Oyster shell Amount: 76 g	Equipment Fluidized-bed reactor Conditions Bed temperature: about 710 °C	➤ Liquid 60-62 wt%, Gas 30-31 wt%, Residue 6-7 wt% ➤ Cl in oil: Thermal (502 ppm) > CaO (58 ppm) > oyster shell (57 ppm) > Ca(OH) ₂ (55 ppm)

a) Values in () are weight ratio of mixtures

b) Ca-C: synthesized by calcination of 90 wt% CaCO₃ and 10 wt% phenol resin; Fe-C: Synthesized by calcination of 90 wt% α -FeOOH and 10 wt% phenol resin.

c) Single-step fixed bed reactor: pyrolysis bed and catalyst bed are presence in a same furnace; Two-step fixed bed reactor: pyrolysis bed and catalyst bed are located in separate furnaces.

of 90 wt% iron oxyhydroxide (FeOOH) and 10 wt% phenol resin, were also evaluated for both PVC-containing plastics and brominated flame retardant-containing plastics, such as high-impact polystyrene (HIPS-Br)⁸⁰⁾. In all cases, liquid, gas, and residue yields were not significantly affected by the use of Ca-C and Fe-C absorbents. Therefore, Ca-C and Fe-C absorbents have no catalytic effect on the pyrolysis of organic compounds, but completely removed both Cl and Br from PE/PP/PS/PVC/HIPS-Br mixtures. In addition, X-ray diffraction (XRD) detected CaCl₂·nH₂O

($n = 2$ and 4) and FeCl₂ in the used absorbents, which implies that HCl gas is produced during PVC pyrolysis and is subsequently absorbed. In contrast, Ca-C absorbent did not completely remove Cl from liquid products derived from municipal plastic wastes (MPW), with approximately 590 ppm remaining. The MPW contained PET and small quantities of acrylonitrile-butadiene-styrene (ABS) in addition to the 3P and PVC, so chlorinated organic compounds were formed, which were difficult to remove using these absorbents⁸¹⁾. Therefore, complete removal of Cl and Br from ABS-

Br and PVC-containing 3P is challenging. However, FeOOH and Fe-C absorbents were effective in removing organic bromine from degradation oils, whereas Ca-C and CaCO_3 were most effective for chlorine removal⁸². Calcium-based absorbents, such as CaO, calcium hydroxide (Ca(OH)_2), and oyster shell, removed Cl from pyrolysis oil, resulting in only 55–58 ppm Cl compared to 502 ppm in the absence of Ca-based absorbents⁸³.

4. PET

PET is the most commonly used polyester resin for the production of various items such as bottles, fibers, sheets, and films, due to its high transparency, light weight, chemical resistance, and gas barrier properties. PET bottles are made of high-purity PET resin with few additives, which allows direct mechanical recycling. In addition, various solvolysis techniques such as hydrolysis^{84)~88)}, methanolysis^{89)~91)}, glycolysis^{92)~94)}, and aminolysis^{95)~97)} allow PET decomposition into monomers. The main advantage of solvolysis is the recovery of monomers at a relatively low temperature. However, the presence of metals, additives, and other resins in PET obstruct frequent recycling of the solvent without regeneration.

Pyrolysis allows the avoidance of solvent use, but PET produces high boiling point organic acids such as terephthalic acid (TPA) and benzoic acid (BA), along with a large amount of carbonaceous residues during pyrolysis^{98)~101)}, which cause corrosion and clogging of the treatment facilities⁵⁸⁾. FeOOH catalysts decompose these sublimating products into acetophenone, benzene, and phenol rich oils^{102),103)}. In addition, oil production from PP/PET mixtures was increased by $\text{TiO}_2/\text{SiO}_2$ catalysts due to hydride abstraction from PP pyrolysates on the Lewis acid sites onto PET pyrolysates on the catalyst, which broke the PET down into lighter hydrocarbons *via* β -scission¹⁰⁴⁾.

The authors have also reported the conversion of PET into benzene-rich oil during pyrolysis in the presence of Ca(OH)_2 , CaO, and steam^{105)~113)}. Benzene is one of the most important petrochemical feedstocks, and the high abundance of limestone resources in Japan favors such a process. Benzene yield and purity in the pyrolysis oil obtained under different conditions are summarized in **Fig. 7**. Benzene yield and purity are only 23 % and 30 wt%, respectively, in the absence of additives (Entry 1). The mixture of PET/CaO improved the yield and purity because decarboxylation of TPA is promoted (Entry 2). Furthermore, the mixture of PET/ Ca(OH)_2 significantly enhanced both yield and purity to 88 % and 79 wt%, respectively (Entry 3)¹⁰⁵⁾. This process was carried out at 700 °C using a Ca(OH)_2 /PET molar ratio of 10. The benzene production process from PET/ Ca(OH)_2 mixture is summarized in **Fig. 8**.

Fig. 7 Benzene Yield and Purity in the Pyrolysis Oil Obtained at Different Conditions^{105),109)~111)}

Fig. 8 Scheme of Benzene Production during Pyrolysis of PET/ Ca(OH)_2 Mixture

Initially, calcium hydroxide is decomposed into CaO and steam, followed by hydrolysis of PET by steam derived from Ca(OH)_2 , producing TPA. The produced TPA and CaO formed calcium terephthalate (CaTP), which subsequently decomposed into benzene and CO_2 *via* decarboxylation of the TPA carboxyl group and decarbonation of CaCO_3 . The resulting CaO can then be recycled for the decarboxylation of TPA.

Other metal hydroxides, such as aluminum hydroxide (Al(OH)_3), magnesium hydroxide (Mg(OH)_2), Ca(OH)_2 , and barium hydroxide (Ba(OH)_2), were evaluated for benzene production¹⁰⁷⁾. Benzene production was mainly affected by catalyst basicity, resulting in high benzene yield of 81 % and purity of 90 wt% in the presence of Ca(OH)_2 and Ba(OH)_2 . The effectiveness of benzene production using Ca(OH)_2 was confirmed for both pure PET resin, and for metals and additives containing PET wastes, resulting in comparable yields and compositions of product oils and gases from low-purity PET wastes¹¹⁴⁾. PET incorporated into 3P plastics can also be converted into benzene using a hard burnt lime fluidized bed without TPA production¹⁰⁸⁾. In contrast, TPA was present in the wax fraction derived from experiments using quartz sand.

Fig. 9 Scheme of Two-step Process for Benzene Production from PET

The authors also reported a two-step process for benzene production from PET waste using a CaO fixed bed^{(109)~(113)}. This process can recover metals separately from benzene-rich oil by dividing the processes into steam decomposition of PET-metal composites and decarboxylation of TPA using CaO (**Fig. 9**). Initially, the PET-metal composites are hydrolyzed by steam into gaseous TPA, whereas the metals remain in solid form. The gaseous TPA is then passed through a CaO fixed bed, resulting in selective conversion to benzene. The one-step process in the presence of Ca(OH)₂ (**Fig. 7**, Entry 3) shows the highest benzene yield because of the excellent contact between PET and Ca(OH)₂ during decomposition. However, the high temperature of 700 °C simultaneously induces pyrolysis of PET, resulting in lower benzene purity compared with the oils obtained from the two-step process (**Fig. 7**, Entries 4-7). The benzene yield of 48 % and purity of 78 wt% obtained at hydrolysis temperature of 450 °C and CaO bed temperature of 700 °C (**Fig. 7**, Entry 4) are improved at lower temperatures, resulting in 64 % yield and 83 wt% purity (**Fig. 7**, Entry 5). Maximum benzene yield of 74 % and purity of 97 wt% were obtained from PET resin by managing the temperatures of both hydrolysis chamber and CaO bed (**Fig. 7**, Entry 6)⁽¹¹⁰⁾. Furthermore, maximum benzene yield of 84 % and >99 wt% purity were achieved for the oil produced from TPA (**Fig. 7**, Entry 7)⁽¹¹¹⁾. The authors also applied this process for the recovery of incorporated metals from X-ray films and magnetic tape and cards⁽¹¹³⁾. The X-ray films contained silver, whereas the magnetic tape contained maghemite (γ -Fe₂O₃), and the magnetic cards contained both γ -Fe₂O₃ and anatase (TiO₂). These metals were recovered quantitatively by steam decomposition at 450 °C without changes to their crystal structures or compositions. In the second step, the TPA from the first step was decarboxylated by CaO at 700 °C, producing benzene-rich oil. The maghemite (γ -Fe₂O₃) incorporated in the magnetic tape and cards decarboxylated TPA, whereas the aluminum present in the cards slightly enhanced hydrogen production. However, in the presence of CaO, these metals had no adverse effects on the benzene-rich oil. In addition, additives such as plasticizers and emulsifiers contained

in the samples had no negative influence on benzene production^{(113), (114)}.

5. Conclusion

This review summarized a number of studies of the pyrolysis of PE, PP, PS, PVC, and PET. The main research trend in plastic pyrolysis concentrates on PE, PP, and PS, which account for ~70 % of total plastic production. The research trend has gradually shifted to catalytic pyrolysis systems, such as catalyst development, to improve both the yield and quality of pyrolysis oils and gases. The studies discussed in this review were mainly on the laboratory scale, but demonstrate the great potential for obtaining high quality oils and gases, which can substitute for natural oil and gas.

In contrast, the pyrolysis of PVC and PET has received less attention compared to 3P due to the difficulty in recovering useful products. In addition, these materials are converted into harmful compounds during pyrolysis, which cause a number of issues, including deterioration in the quality of the pyrolysis products. Therefore, waste plastics containing high amounts of PVC and PET are commonly avoided in current feedstock recycling systems, despite the main components of 3P in the waste. Thus, the increase in recycling rates in terms of feedstock recycling has slowed. These issues with PVC and PET during pyrolysis must be solved to promote recycling rates of municipal plastic wastes while maximizing product quality. The studies in this review, including the author's own work, describe the key developments in the treatment of PVC- and PET-containing plastic wastes, which will be important for the development of future recycling systems. Progress in both plastic recycling and the development of recycling techniques should be accelerated to ensure the conservation of resources along with a sustainable economy due to the finite nature of fossil fuels.

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要 旨

廃プラスチックの熱分解による化学原料化・燃料化

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環境負荷低減および将来的な国内資源確保の観点から、廃プラスチックのリサイクルの推進は必要不可欠である。国内における廃プラスチックの有効利用率は年々増加しており、2014年には83%に達している。しかし、有効利用率に占めるマテリアルリサイクルおよびケミカルリサイクルの割合はわずか26%および4%と低く、残りの70%は熱回収に留まっている。つまり、マテリアルリサイクルやケミカルリサイクルによる有効利用率を向上できるポテンシャルは極めて大きい。本稿では、ケミカルリサイクルの一つである廃プラスチックの熱分解法に着目する。熱分解法は、マテリアルリサイクルに適用困難な混合廃プラスチック等の油化およびガス化を可能とする。しかし、現実には、ポリ塩化ビニル (PVC) やポリエチレンテレフタレート (PET) が、熱分解により腐食性ガスや高沸点の昇

華性物質を生成し、熱分解生成物品位の低下および処理設備の腐食・閉塞（そく）の原因となるため、これら樹脂の含有量の多い廃プラスチックは依然として処理が困難となっている。著者らは、これまで、これら問題点の打開を目指し、PVCの乾式法および湿式法による脱塩化水素および脱塩素プロセス、石灰を用いたPETの熱分解油化について検討を進めてきた。本稿では、まず主要な樹脂であるポリエチレン (PE)、ポリプロピレン (PP)、およびポリスチレン (PS) に関する熱分解研究の現状について総括し、著者らの報告してきたPVCの脱塩化水素および脱塩素プロセス、さらに石灰を用いたPETの熱分解油化プロセスを中心にPVCやPETの熱分解研究について紹介する。

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