1. Global Trends in Waste Plastic Recycling

Plastics are widely used in our daily life owing to being light, inexpensive, having good processability, and having ease of functionalization by combining additives. Global plastic production has increased from 1.5 million tons (Mt) in 1950 to 359 Mt in 2018. Over the last ten years (2008-2018), plastic production has increased by ~1.5 times\(^1\,\,^2\). Almost half of the global plastic is produced in Asian countries such as China (30 %), Japan (4 %), and other Asian countries (17 %), and in North American Free Trade Agreement (NAFTA) countries (18 %), Europe (17 %), followed by other countries (14 %)\(^3\). The packaging sector accounted for 36 % of global plastic demand in 2015\(^9\), which was the biggest segment, and which was a common tendency in EU (39.9 %)\(^3\) and Japan (41 %)\(^3\).

The constant growth of waste plastic generation is observed in global primary plastics waste generation data (Fig. 1)\(^3\). According to the report from the Ellen MacArthur Foundation, 78 Mt of plastic packaging materials was produced in 2013, of which 40 % was treated by landfilling, 32 % was leaked into the environment, 14 % was incinerated for energy recovery, and only 14 % was recycled\(^6\). Domestically, 8.9 Mt of waste plastics were generated in 2018, of which 84 % (mechanical: 23 %; feedstock: 4 %; energy recovery: 57 %) was recycled or utilized as an energy source and 16 % was treated by incineration without energy recovery and landfill (Fig. 2)\(^4\).

Behind the recent rapid growth in the demand for plastic recycling, there are global trends such as Sustainable Development Goals (SDGs)\(^3\) and circular economy\(^8\). In addition, recent focus on ocean plastics pollution\(^9\,\,\,\,14\) and the decision by China to ban waste plastics import\(^15\) have caused significant impacts on several industrial sectors around the world.

The SDGs, including 17 goals and 169 targets, aim to tackle poverty, health, and environmental conservation issues and achieve a better and more sustainable world by 2030\(^1\). The concept of SDGs has been involved in the Fifth Basic Environment Plans (2018)\(^16\)
Plastic treatment is one of the highest priority targets in the circular economy concept, leading the European Strategy for Plastics in a Circular Economy (2018)\textsuperscript{18}). The strategy targets the following: all plastic containers and wraps to become reusable and recyclable by 2030, and more than half of all plastics produced in Europe to be recycled, quadrupling the demand for recycled materials and strengthening the recycling industry. The European Commission established the Circular Plastics Alliance, which covers the entire plastics value chain and includes 209 industry, academic, and government organizations, is an initiative that aims to expand the EU market for reprocessed plastics to 10 Mt by 2025\textsuperscript{19}).

In Japan, the Fourth Fundamental Plan for Establishing a Sound Material-Cycle Society (2018)\textsuperscript{17)} in Japan, and aims toward a sustainable society through integration of environment, economy, and society.

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In Japan, the Fourth Fundamental Plan for Establishing a Sound Material-Cycle Society (2018)\textsuperscript{17)} includes establishing the Resource Circulation Strategy for Plastics, which was formulated in May 2019\textsuperscript{20}). The strategy has sloganized “3R + Renewable,” which aims to promote reduction, reuse, recycling, and use of bio-based plastics. The strategy has established several milestones: 25% reduction of single-use plastics in total by 2030, 60% reuse/recycling of plastic containers and packaging by 2030, complete utilization of waste plastics through reuse and recycling by 2035, and the introduction of $\sim2$ Mt of bio-based plastics by 2030. To maximize resource utilization, the strategy stipulates the necessity of the optimal combination of mechanical recycling, feedstock recycling, and energy recovery. In general, plastic products contain several additives, paints, and fillers to achieve desired performance. In the domestic market, over 150 and 230 types of resins and additives have been manufactured, respectively\textsuperscript{21}). Thus, the combination of resins and additives is uncountable, and several types of plastic products are often combinedly wasted at the recycling stage, which cannot be fully recycled by only mechanical recycling. Therefore, adequate recycling technologies according to the waste plastics quality and compatibility with the recycling technology must be discussed. China’s decision to ban waste plastics import increased the amount of domestically recyclable plastic\textsuperscript{4,22}). More stringent controls on waste plastics import have spread throughout Asian countries such as Thailand, Vietnam, and Malaysia\textsuperscript{23}). Thus, research and development of plastic waste recycling technology and creation of social and legislative frameworks accelerating plastic recycling are in high demand.

Polyolefinic plastics such as high density polyethylene (HDPE), low density PE (LDPE), and polypropylene (PP) are the most common plastics and account for half of the total plastics (Fig. 1)\textsuperscript{5}). These plastics are used in a wide variety of products and industries, such as packaging, electrical and electronic equipment (EEE), automotive, building and construc-

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Global Primary Plastics Waste Generation According to Polymer Type\textsuperscript{5})}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Current Status of the Plastic Waste Recycling in Japan in 2018 (Values were taken from a report from Plastic Waste Management Institute\textsuperscript{4}).}
\end{figure}
tion, and agriculture. Therefore, this review focused on polyolefinic plastics as good quality carbon and hydrogen resources (86 wt% C and 14 wt% H), which must be effectively utilized and circulated in our society. Recently, feedstock recycling has been gaining considerable global attention. Recycled feedstocks from waste plastics theoretically have an equivalent value of the virgin molecules, thus, they can be blended with the virgin molecules and be circulated in the existing chemical industry. One of the recent approaches is the “mass balance approach,” which enables quantification of the amount of recycled content in each product based on the chemical value-related properties, e.g., the lower heating value (LHV). As a method allowing chemical feedstock recovery from waste plastics, we focused on pyrolysis, a method of thermal degradation of polymers at higher temperatures under non-oxidative conditions. Pyrolysis is a promising feedstock recycling technique for the conversion of waste plastics into monomers, fuels, and valuable chemicals through the cleavage of multiple chemical bonds. This provides a distinct advantage in treating heterogeneous plastic wastes consisting of several types of plastics and combined with inorganics such as metals and fillers, which are difficult to recycle using mechanical methods. Based on peer-reviewed journal publications, this review examines the recent trends and challenges in pyrolysis technologies for chemical feedstock recovery from polyolefinic plastics; these technologies include reactor design and effective catalytic pyrolysis. Furthermore, ongoing plastic recycling projects led by the authors are introduced to demonstrate recent challenges in feedstock recycling. Corrosion of treatment facilities and deterioration of product quality by halogen-containing plastics and poly(ethylene terephthalate) (PET) are well-known hurdles that must be overcome for practical feedstock recycling via pyrolysis. These challenges have been summarized and discussed in our previous review; therefore, they are not the focus of this review.

2. Reactors for Plastic Pyrolysis

Pyrolysis of plastics involves endothermic processes such as melting, cracking (production of gas and liquid), and condensation (forming carbonaceous residue). The molten polyolefinic plastics such as PE and PP have high viscosity and low thermal conductivity, which cause clogging of the feeding facility and unequal heating of plastics. Pyrolysis of PE and PP progresses via a free-radical mechanism, which leads to a wide product distribution in gases, liquids, and high viscosity waxes. Therefore, many researchers have focused on optimizing the reactor design and conditions for improving the heat transfer rate during pyrolysis. The above-mentioned drawbacks are considerable problems for operating continuous pyrolysis employing large-scale reactors. However, these are not problems for small-scale fixed-bed, batch, or semi-batch reactors, which have been commonly employed for condition tests. In fact, they generally have a simple design, easy operation, and low cost, which are important benefits for investigating pyrolysis phenomena and the effects of pyrolytic conditions on the pyrolyzates distribution. On the other hand, upscaling experiments using these reactors are challenging and limited due to the poor heat transfer rates and high viscosity of molten plastics.

In order to minimize heat transfer limitations and physicochemical problems during plastic pyrolysis, unique pyrolysis systems have been reported. Murata et al. designed a continuous flow reactor (5 L volume) employing a rotating stirrer (Fig. 3) and a stirrer coupled with catalyst (silica-alumina) cage. Neat HDPE, PP, and PS were heated and melted at 200-220 °C inside an extruder, and were then fed into the reactor at a maximum feeding rate of 1.5 kg/h. The molten plastics were pyrolyzed at 350-440 °C with stirring, which assisted heat transfer to the molten plastics. Also, this apparatus allows a constant pyrolyzates output rate by modifying the plastic feeding rate and the pyrolysis temperature, which supported the investigation of the pyrolysis mechanism of polyolefinic plastics.

Bockhorn et al. developed a cascade of three well-stirred reactors (Fig. 4), which were combined with extruders to control the plastic feed (max. 3 kg/h). The reactors have a 100 mm inner diameter (i.d.) and a 220 mm (1st and 2nd reactor) or 110 mm (3rd reactor) height. Each unit is filled with 500 stainless-steel spheres (d = 10 mm), and equipped with a conveyor screw to achieve thorough mixing of spheres and melted plastics. The conveying rate of the screw is up to 90 spheres/min. With the help of the conveyor screw, the spheres are circulated through a heating and reaction zone. Reactions take place within a thin film of melted plastics around the spheres. The advantages of this design are the effective heat transfer to the
Fluidized bed reactors (FBRs) allow high heating transfer rate, isothermicity, and effective solid mixing. A laboratory-scale FBR (48 mm i.d. and 320 mm height, silica-sand as bed material) was operated for pyrolysis of polyolefinic plastics by Mastral et al. 35) Jung et al. 38) thoroughly investigated the effects of pyrolysis temperature, plastic feeding rate, gas flow rate, and fluidizing medium on the production of benzene, toluene, and xylene (BTX) from PE and PP by employing a laboratory-scale continuous fluidized bed reactor. Milne et al. 39) used a circulating fluidized bed (152 mm i.d. and 1230 mm height) to minimize the residence time and enhance the formation of light olefins at higher temperatures. A technical-scale pyrolysis plant was designed and constructed at the University of Hamburg in 1976 40). The flow scheme of the pyrolysis plant is shown in Fig. 5. 41) The heart of the plant is a FBR with an inside diameter of 450 mm and a height of 900 mm. The height of the sand bed is 650 mm. The reactor is heated by four steel heating tubes, which use propane or the excess gas of the pyrolysis products. The capacity of the pilot plant is between 10-30 kg-plastic/h. A total of 430 kg of PE and PP rich waste plastic mixture was fed into the reactor with a feeding rate of 14.8 kg/h and was pyrolyzed at 730 °C, resulting in 35.0 wt% hydrocarbon gases, 48.4 wt% liquids (20.6 wt% BTX + 24.3 wt% other aromatics + 3.6 wt% aliphatics), 14.3 wt% distillation residue, and 2.2 wt% solids. Recently, Park et al. 42) combined an auger reactor with FBR for activating plastics prior to the main pyrolysis in the fluidized bed. A combination of activation in the auger reactor at 292 °C and the subsequent pyrolysis at 727 °C in the fluidized bed enhanced the aromatic fraction in the oil product (92 wt%) from PP.

A conical spouted bed reactor (CSBR) is an alternative technique to achieve high heat and mass transfer rates, effective solid mixing, and suitable gas-solid contact. Olazar, Lopez, and co-workers concluded that the vigorous cyclic solid circulation avoids defluidization problems and eases the handling of irregular particles, those with a wide size distribution, and sticky materials. 25), 43), 44). Figure 6 shows a diagram of CSBR established by the University of the Basque Country UPV/EHU 45), 46). In Fig. 6(b), the CSBR was combined with a multitubular reactor for conducting thermal cracking of pyrolyzates from the CSBR. Firstly, HDPE was continuously fed into a CSBR (1 g/min) and pyrolyzed at 500 °C, resulted in 93 wt% C12-C21 hydrocarbons with waxes without defluidization problem. The pyrolyzates were further thermally cracked in a multitubular reactor in the 800-950 °C range, with short residence times (0.016-0.032 s). The high temperature cracking with short residence time yielded the maximum 77 wt% of light olefins (C2-C4) and the yield of aromatics was only 6.2 wt%.

Microwave radiation allow high temperatures and high heating rates. Plastic is known to have a very high transparency to microwaves. Therefore, plastic is mixed with highly microwave-absorbent materials, such as carbon, which can reach temperatures of up to 1000 °C in a few minutes when carbon is exposed to a
microwave field. Ludlow-Palafox and Chase\textsuperscript{47} conducted microwave-assisted pyrolysis of HDPE and aluminum laminated film (50 g) with 1000 g carbon as a microwave absorbent in a stirring batch reactor at 500-700 °C. The maximum 81.0 wt% oil/wax was collected at 500 °C within a few minutes from the initiation of microwave radiation. The microwave-assisted pyrolysis was also available for the aluminum laminated film and both pyrolyzates and aluminum were recovered.

Guddeti \textit{et al.} reported plasma pyrolysis of PE\textsuperscript{48} and PP\textsuperscript{49}, which allowed extremely high heating rates of
106 °C/s. Under these conditions, flash depolymerization occurs to yield mainly gaseous products such as ethylene and propylene. The plasma-induced pyrolysis could almost fully crack the oil fraction and significantly enhance gas production. A continuous plasma gasification process (Fig. 7) has been established by Hlina et al.\textsuperscript{50} with the feeding of a HDPE/PP mixture (11 kg/h). A DC plasma torch was employed as the energy source for gasification. Water is injected tangentially to the arc chamber of the torch and forms a vortex that surrounds the electric arc. The anode is a water-cooled rotating copper disc. Produced plasma features extreme parameters such as very high bulk temperature (17727 °C). Hlina et al.\textsuperscript{50} concluded that this new process leads to the production of high quality synthetic gas (CO + H\textsubscript{2}: over 90 vol% in the product gas) and negligible content of tars, whereas higher electricity demand could be raised as a drawback.

3. Catalytic Pyrolysis

As mentioned previously, PE and PP pyrolysis progresses via a free-radical mechanism\textsuperscript{30,31}, which leads to a wide product distribution of gases, liquids, and high viscosity waxes, unlike other plastics such as polystyrene (PS)\textsuperscript{51−54}, poly(ethylene terephthalate) (PET)\textsuperscript{27,55,56}, other polyesters\textsuperscript{52,56}, poly(methyl methacrylate) (PMMA)\textsuperscript{52,57}, and polyurethane\textsuperscript{58−60} which lead to the production of comparatively high monomer yields. Therefore, catalytic pyrolysis of polyolefinic plastics has been extensively investigated for improving the yield and selectivity of desired petrochemical feedstocks such as aromatics (BTX), light olefins, gasoline, diesel, H\textsubscript{2}, syngas, and carbon materials. We have summarized selected works regarding catalytic pyrolysis of polyolefinic plastics for oil recovery in Table 1 and catalytic pyrolysis of those at comparatively higher temperatures for H\textsubscript{2}-rich gas, syngas, and carbon materials recovery in Table 2. However, this review did not target pyrolysis works focusing on kinetic studies based on thermogravimetric analysis, analytical pyrolysis employing pyrolyzer-gas chromatography, or characterization of oil properties as an alternative fuel. Also, co-pyrolysis with other feedstocks such as coal, petroleum fraction, and biomass were not included. Tables 1 and 2 present the summaries of the selected works fitting the scope of this review, and, therefore, are not the full publication lists of the related works.

3.1. Catalytic Pyrolysis for Liquefaction

The majority of works investigated acid catalysts such as activated carbon (AC), silica-alumina (SA), and zeolites for improving oil yield and selectivity of the desired fraction from polyolefinic plastics (Table 1). The distinct feature of the catalytic pyrolysis for liquefaction is a use of comparable or lower temperatures of PE and PP pyrolysis. Uemichi et al. (Entries 1-3; Table 1)\textsuperscript{61−63} extensively investigated AC impregnated with metals such as Pt, Fe, Mo, Zn, Co, Ni, and Cu for enhancing production of aromatic hydrocarbons such as BTX from polyolefinic plastics. The aromatic hydrocarbon yield was substantially enhanced to a maximum of 45% at 526 °C using Pt/AC (Pt = 3 wt%).
whereas normal pyrolysis of PE and PP produced negligible aromatic hydrocarbons at this temperature. They concluded that Pt and Fe were the most effective metals for converting PE and PP into aromatic hydrocarbons. They also noted that in place of the enhanced aromatic hydrocarbons, there was significant coke deposition on the metal containing catalysts. Nakamura and Fujimoto (Entry 4; Table 1) reported liquefaction of PP at a lower reaction temperature of 380 °C under 3.0 MPa H2 with 0.3 wt% CS2 and employing an autoclave filled with a coal-derived disposable Fe/AC catalyst, and resulting in 98 wt% oil recovery. The effects of AC acidity on product recovery and coke deposition during LDPE pyrolysis was investigated by Zhang et al. (Entry 34; Table 1)65. They recovered 72.0 wt% C8-C16 hydrocarbons, mainly consisting of paraffins, at 500 °C using weak acidity AC (0.012 mmol-NH3/g), whereas strong acidity AC (0.436 mmol-NH3/g) produced a comparable yield of 65.1 wt% C8-C16 hydrocarbons with an improved aromatics content. Coke deposition on these AC catalysts was not significant as the latter were metal-free. Thus, these results revealed that metals such as Pt and Fe loaded on AC strongly enhance aromatic production by catalyzing desorption of hydrogen atoms, which accelerated the dehydrocyclization of pyrolyzates63. Although the production of aromatics by metal-free AC is limited, it has the potential to simultaneously recover aromatic hydrocarbons and prevent coke deposition on the catalysts.

SA, which is generally known as a moderate acidity catalyst, has been tested for PE and PP pyrolysis33,61,66,69. For example, Sakata and co-workers investigated catalytic effects of SA with different Si/Al ratios on extensively used PEs such as LLDPE, LDPE, HDPE, and XLPE (Entries 5, 6, 9, 17; Table 1)33,66,67,69. Both HDPE and XLPE produced significant amounts of waxes and yielded 58-63 wt% oils at 430 °C in the absence of a catalyst. On the other hand, LDPE and LLDPE produced higher oil yields (76-77 wt%) with very small amounts of waxes. The carbon number distribution of the product oil from these PEs was broad (C5-C25: B.P. range 36-405 °C). In contrast, SA catalysts enhanced oil yields from all PEs, with a maximum of 82.5 wt% from LLDPE, and it was confirmed that no wax was produced from any of the PEs using SA (Si/Al = 0.3 molar ratio). The oil with the broad carbon number distribution was drastically changed to the gasoline range C5-C12 (B.P. range 36-216 °C) and the products have a higher degree of unsaturation. Thus, it can be concluded that SA is a promising catalyst with moderate acidity that can lighten product oil without significant aromatization; moreover, its large pore structure prevents significant overcracking and reforming.

Amongst the acid catalysts, zeolite-based catalysts have been most extensively investigated because they exhibit a wide range of acid strengths, which determine their catalytic performance on pyrolyzates cracking. Also, morphology is an important factor because it directly relates to the accessibility of polymers or long-chain pyrolyzates to the acid sites of the catalyst. Sakata et al. (Entry 9; Table 1)69 compared the effects of zeolite, silica-alumina, and non-acidic silica on the pyrolysis of polyolefinic plastics. They selected SA with different Si/Al ratios (SA1 [Si/Al = 5] and SA2 [Si/Al = 0.3]), ZSM-5, and non-acidic mesoporous folded silica (FSM) which has a large hexagonal pore structure, for the pyrolysis of HDPE. The order of the catalyst acidity is SA2 > ZSM-5 > SA1, and FSM has no acidity. SA1 and SA2 have only weak acid sites, whereas ZSM-5 has both weak and strong acid sites. The order of the BET surface area is FSM > SA1 > ZSM-5 > SA2. The cumulative volume of oils from HDPE at 430 °C and the carbon number distribution of those oils are summarized in Figs. 6 and 7, respectively. Interestingly, over non-acidic FSM, the rate of HDPE degradation at 430 °C was faster than that of pyrolysis without a catalyst and is comparable to that over SAs and ZSM-5 catalysts (Fig. 8). For thermal degradation, the liquid products were distributed in a wide range of carbon numbers (C5-C22) equivalent to boiling point ranges of 36-370 °C (Fig. 9). In the cases of catalytic degradation over SA1, SA2, and ZSM-5, the weight fraction of lighter hydrocarbons (C4-C10) increased and that of heavier hydrocarbons decreased, which is due to the acidity of the catalysts. The liquid products from the degradation over FSM were much lighter than the thermal degradation products, but were heavier than the solid acid catalytic degradation products. The carbon number distribution of oils from catalytic pyrolysis over SA1 was very similar to commercial automobile gasoline, whereas the oil from catalytic pyrolysis over FSM contained mainly kerosene and diesel fraction oil. Furthermore, life tests performed on the acid catalyst SA1 and non-acidic FSM catalyst resulted in the rapid deactivation of SA1 by coke deposition on the catalyst, whereas FSM deactivated much more slowly. Sakata et al.69 concluded that the accelerated degradation with inhibited coke deposition over FSM was due to the large hexagonal pore structures, allowing pyrolyzates long-lived in the pores, which enhanced deep pyrolysis. Thus, both the acidity and morphology of the catalyst strongly influence the pyrolysis rate and product distribution.

In zeolite catalysts, ZSM-560,68,69, Y74,84,85, beta41,76,86, and USY70,87 have been commonly investigated. For example, Huang et al. (Entry 18; Table 1)76 compared the effects of HZSM-5, H-mordenite (HMOR), and HUSY on the product distribution from PE- and PP-rich mixed plastic waste by employing a fluidized-bed reactor. They reported that the yields of volatile hydrocarbons (C1-C9 including BTX) were
Table 1 Catalytic Pyrolysis of Polyolefinic Plastics for Liquefaction Recovery

| Entry | Year | Plastics (values: wt%) | Reactor | React. mode | Catalyst | Temperatures (pyro. and catal. reactors) | References |
|-------|------|------------------------|---------|-------------|----------|----------------------------------------|------------|
| 1     | 1984 | LDPE                   | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | HNO₃-treated AC³⁶, Pt/Al₂O₃ (Pt = 1 wt%), Pt/SA¹⁵ | Pyro. and catal.: 526 °C | Uemichi et al.⁶¹ |
| 2     | 1989 | PP                     | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | M/AC (M = Pt (1 wt%), Fe (3 wt%)) | Pyro. and catal.: 502 °C | Uemichi et al.⁶² |
| 3     | 1989 | LDPE                   | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | M/AC (M = Pt (0.5, 1, 3 wt%), Fe (1, 3, 10 wt%), Mo (3 wt%), Zn (3 wt%), Co (3 wt%), Ni (3 wt%), Cu (1 wt%)) | Pyro. and catal.: 526 °C | Uemichi et al.⁶³ |
| 4     | 1996 | PP                     | Autoclave | Batch | Fe/AC (Fe = 3 wt%) | Pyro. and catal.: 380 °C (introduced 3.0 MPa H₂) | Nakamura and Fujimoto⁶⁴ |
| 5     | 1997 | HDPE                   | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | SA (SiO₂/Al₂O₃ = 5, 0.3, mol. ratio), ZSM-5 (SiO₂/Al₂O₃ = 75, mol. ratio), KFS-16 | Pyro. and catal.: 3 °C/min → 430 °C | Sakata et al.⁶⁵ |
| 6     | 1997 | HDPE, LDPE, LLDPE, XLPE | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | SA (SiO₂/Al₂O₃ = 5, mol. ratio) | Pyro. and catal.: 400-525 °C | Uemichi et al.⁶⁶ |
| 7     | 1998 | LDPE                   | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | H-Ga-silicate (Si/Ga = 25 at. ratio), HZSM-5 (Si/Al = 15 at. ratio), SA (Si/Al = 5.4 at. ratio) | Pyro. and catal.: 400-515 °C | Meritinkat et al.⁶⁷ |
| 8     | 1999 | PE                     | FBR      | Cont. | Spent FCC | Pyro. and catal.: 3 °C/min → 430 °C | Sakata et al.⁶⁸ |
| 9     | 1999 | HDPE, PP               | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | SA (SiO₂/Al₂O₃ = 5, 0.3, mol. ratio), ZSM-5 (SiO₂/Al₂O₃ = 75, mol. ratio), KFS-16, silicalte, silica-gel, mesoporous silica (FSM) | Pyro. and catal.: 3 °C/min → 430 °C | Uemichi et al.⁶⁹ |
| 10    | 1999 | PE                     | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | SA (13.5 wt % Al₂O₃), HZSM-5 (Si/Al = 11, at. ratio) | Pyro. and catal.: 375-425 °C | Uemichi et al.⁷⁰ |
| 11    | 2001 | HDPE, LDPE, PP         | Two-stage FxBR (1st: plastic melter, 2nd: catal. bed) | Cont. | H-galllosilicate (Si/Al = 25, at. ratio) | Pyro. and catal.: 375-550 °C | Takuma et al.⁷¹ |
| 12    | 2007 | HDPE                   | Two-stage FxBR (1st: plastic pyro., 2nd: catal. bed) | Semi. | Nanocrystalline HZSM-5 (Si/Al = 36, at. ratio), Al-MCM⁹⁴,41 (Si/Al = 38, at. ratio) | Pyro.: 425-475 °C | Aguado et al.⁷² |
| 13    | 2007 | HDPE                   | CSBR    | Cont. | CBV600⁶⁹ | Pyro. and catal.: 500 °C | Elordi et al.⁷³ |
| 14    | 2008 | wMP (PE > 36), wMP (60 PE, 34 PP) | Rotary kiln (pyro.) + FxBR (catal.) | Cont. | Ga-ZSM-5 (Si/Ga = 35, at. ratio) | Pyro.: 450-510 °C | Nissan et al.⁷⁴ |
| 15    | 2009 | HDPE                   | CSBR    | Cont. | CBV600, CBV302⁴⁹, CPS1E-75⁹⁰ | Pyro. and catal.: 500 °C | Elordi et al.⁷⁵ |
| 16    | 2009 | wHDPE, wPP             | Cont.⁵⁰ reactor (plastic/catal. simultaneously feed) | Cont. | ZSM-5 (Si/Al = 24.1, at. ratio) | Pyro. and catal.: 520 °C | Miskolczi et al.⁷⁶ |
| 17    | 2009 | PE                     | Stirring reactor (catal. loaded stirrer) | Cont. | SA (SiO₂/Al₂O₃ = 5, mol. ratio) | Pyro. and catal.: 420 °C | Murata and Sakata⁷⁷ |
| 18    | 2010 | wMP (37 HDPE, 25 LDPE, 33 PP, 5 PS) | FBR      | Cont. | HZSM-5 (Si/Al = 25, at. ratio), H-mordenite (Si/Al = 63, at. ratio), HUSY (Si/Al = 6.0, at. ratio), MCM-41 (Si/Al = 17.5, at. ratio), Synchlyst 25⁴⁹ (Si/Al = 2.6, at. ratio) | Pyro. and catal.: 290-420 °C | Huang et al.⁷⁸ |
| 19    | 2011 | HDPE, LDPE, PP         | CSBR    | Cont. | CBV302⁴⁹ | Pyro. and catal.: 500 °C | Elordi et al.⁷⁹ |
| 20    | 2011 | LDPE                   | Autoclave | Batch | Ni/β-ZSM-5 (Si/Al = 32, at. ratio, Ni = 5.7 wt%), Ni/β-beta zeolite (Si/Al = 25, at. ratio, Ni = 6.2 wt%), Ni/Al-MCM-41 (Si/Al = 32, at. ratio, Ni = 6.6 wt%), Ni/Al-SBA-15 (Si/Al = 56, at. ratio, Ni = 6.7 wt%) | Pyro. and catal.: 450-570 °C | Escola et al.⁸⁰ |

(continued on next page)
| Entry | Year | Plastics (values: wt%) | Reactor | React. mode | Catalyst | Temperatures (pyro. and catal. reactors) | References |
|-------|------|------------------------|---------|------------|----------|----------------------------------------|------------|
| 21    | 2011 | MP (40 PE, 35 PP, 18 PS, 4 PET, 3 PVC) | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | NHZSM-5 (Si/Al = 50, at. ratio), red mud⁶⁶ (Fe₂O₃, Al₂O₃, TiO₂, etc.) | Pyro. and catal.: 20 °C/min → 440-500 °C | López et al.⁷⁹ |
| 22    | 2012 | LDPE, HDPE, PP | FBR | Semi. | Commercial Ziegler-Natta (TiCl₄/MgCl₂, TiCl₄·5-16 wt%) | Pyro. and catal.: 500, 650 °C | Donaj et al.⁸⁵ |
| 23    | 2012 | LDPE | Autoclave | Batch | Ni₉₀-beta zeolite (Si/Al = 25, at. ratio, Ni = 7 wt%) | Pyro.: 250-350 °C (1.5 barr N₂) | Escola et al.⁸⁶ |
| 24    | 2013 | LDPE | Two-stage FxBR (1st: plastic pyro., 2nd: catal. bed) | Semi. | H-GaMFI (Si/Ga = 22.5, at. ratio), Ga/HZSM-5 (Si/Al = 15, at. ratio, Ga = 2 wt%) | Pyro.: 455 °C | Uemichi et al.⁸⁰ |
| 25    | 2015 | LDPE | Microwave (pyro.) + FxBR (catal.) | Semi. | ZSM-5 | Pyro.: 525 °C | |
| 26    | 2017 | HDPE | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | Fe₂O₃, CoO, ZnO, MnO₂ and NiO impregnated waste brick kiln dust (metal = 2 wt%) | Pyro.: 250-450 °C | Ahmad et al.⁹⁳ |
| 27    | 2017 | LDPE | Microwave (pyro.) + FxBR (catal.) | Semi. | MgO | Pyro.: 350-550 °C | Fan et al.⁹⁵ |
| 28    | 2017 | MP (42 HDPE, 35 PP, 18 PS, 5 PET) | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | Al₂-, Fe₂-, Ti-, and Zr-pillared bentonite | Pyro. and catal.: 40 °C/min → 300 °C → 10 °C/min → 500 °C | Li et al.⁹⁰ |
| 29    | 2017 | HDPE | Two-stage FxBR (1st: plastic pyro., 2nd: catal. bed) | Semi. | ZSM-5 (Si/Al = 20), MCM-41 (Si/Al = 4, at. ratio) | Pyro.: 40 °C/min → 500 °C | Ratnasari et al.⁹² |
| 30    | 2018 | wPE | Semi-batch (plastic was pyrolyzed with catal.) | Semi. | Fly ash catalyst (SiO₂, Al₂O₃, Fe₂O₃, etc.) | Pyro. and catal.: 500-800 °C | Gaurh and Pramanik⁹⁰ |
| 31    | 2018 | wPE, wPP, wPE PP mixtures | Cont. reactor (plastic/catal. simultaneously fed) | Cont. | USY zeolite (Si/Al = 15, at. ratio) | Pyro. and catal.: 500 °C | Kasergy et al.⁸⁷ |
| 32    | 2018 | LDPE | Microwave (pyro.) + FxBR (catal.) | Semi. | Ni₉₀, HY zeolite (Si/Al = 5.1, at. ratio) | Pyro.: 450-600 °C | Ding et al.⁹⁷ |
| 33    | 2019 | HDPE | Microwave (pyro.) + FxBR (catal.) | Semi. | HZSM-5 (Si/Al = 15, at. ratio) | Pyro. and catal.: 400-500 °C | Santos et al.⁸³ |
| 34    | 2019 | LDPE, MP (40 PE, 35 PP, 18 PS, 4 PET, 3 PVC) | Two-stage FxBR (1st: plastic pyro., 2nd: catal. bed) | Semi. | Commercial ACs (PTRODARCO, 8X30, NORIT, GAC1240, MRX, NORIT GCN 1240PLUS, NORIT C GRAN, GAC 830 PLUS) | Pyro.: 430-571 °C | Zhang et al.⁸⁸ |
| 35    | 2020 | PE | Two-stage FxBR (1st: plastic pyro., 2nd: catal. bed) | Semi. | SiO₂, SA, Si-MFI, Si/Al-MFI | Pyro. and catal.: 450 °C | Klaimy et al.⁷² |

a) waste.  b) mixed plastics.  c) fixed bed reactor.  d) fluidized bed reactor.  e) conical spouted bed reactor.  f) continuous.  g) semi-batch.  h) activated carbon.  i) silica-alumina.  j) molar.  k) Kane-mite derived folded silica.  l) atomic.  m) non-precious metals on a silica-alumina support.  n) 25 wt% of HY zeolite (SiO₂/Al₂O₃ = 5.2, mol. ratio), 30 wt% bentonite, 45 wt% inert alumina.  o) 25 wt% of HZSM-5 zeolite (SiO₂/Al₂O₃ = 30), 30 wt% bentonite, 45 wt% inert alumina.  p) 25 wt% of Hβ zeolite (SiO₂/Al₂O₃ = 75), 30 wt% bentonite, 45 wt% inert alumina.  q) silica-alumina.  r) hierarchical.  s) byproduct of Bayer process.
### Table 2  Catalytic Pyrolysis of Polyolefinic Plastics at Comparatively Higher Temperatures for Recovering H₂-rich Gas, Syngas, and Carbon Materials

| Entry | Target products | Year | Plastics (values: wt%) | Reactor | React. mode | Catalyst | Temperatures (pyro. and catal. reactors) | References |
|-------|-----------------|------|------------------------|---------|-------------|----------|---------------------------------------|------------|
| 36    | H₂              | 2006 | PP                     | FBRᵇ (pyro.) + FBR (catal.) | Cont.ᵇ | C11-NKᵇ | Pyro.: 600-700 °C; Catal.: 850 °C | Czernik and French⁹⁶ |
| 37    | H₂              | 2010 | PP                     | Two-stage FsBRᵇ | Cont. | Ru/Y-Al₂O₃ (Ru: 0.5 wt% or 5.0 wt%) | Pyro.: 400-600 °C; Catal.: 580-630 °C | Park et al.⁹⁷ |
| 38    | H₂, HDPE, PP, PS, MPᵇ (56.3 HDPE, 26.9 PP, 16.8 PS) | 2010 | PP                     | Two-stage FsBR | Semiᵇ | Ni/Mg/Al (1 : 1 : 1 at. ratioᵇ) | Pyro.: 40 °C/min → 500 °C; Catal.: 800-850 °C | Wu and Williams⁹⁸ |
| 39    | H₂              | 2010 | w/MP (mainly HDPE, PET) | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 at. ratio) | Pyro.: 40 °C/min → 500 °C; Catal.: 600-900 °C | Wu and Williams⁹⁹ |
| 40    | H₂              | 2010 | PP                     | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 : 1 at. ratio) + CaO | Pyro.: 40 °C/min → 500 °C; Catal.: 700-800 °C | Wu and Williams¹⁰⁰ |
| 41    | H₂              | 2010 | PP                     | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 : 1 at. ratio) | Pyro.: 40 °C/min → 500 °C; Catal.: 700 °C | Wu and Williams¹⁰¹ |
| 42    | H₂              | 2010 | HDPE, PP, PS, MP (56.3 HDPE, 26.9 PP, 16.8 PS) | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 at. ratio) | Pyro.: 500 °C; Catal.: 700 °C | Erkiaga et al.¹¹¹ |
| 43    | H₂              | 2010 | HDPE, PP, PS, MP (48 HDPE, 35 PP, 9 PS, and 8 PET) | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 : 1 at. ratio) | Pyro.: 500 °C; Catal.: 700 °C | Barbarias et al.¹¹² |
| 44    | H₂              | 2010 | w/PE                   | Two-stage FsBR | Semi | Ni/zeolites (zeolites = HZSM-5 (Si/Al = 30-80), β-zeolite (Si/Al = 25), Y-zeolite (Si/Al = 30)) | Pyro.: 40 °C/min → 500 °C; Catal.: 850 °C | Yao et al.¹⁰² |
| 45    | H₂              | 2010 | w/HDPE, w/PP, w/PS    | Two-stage FsBR | Semi | Ni/Al₂O₃ (Ni: 8-10 wt%; co-precipitation, impregnation, sol-gel) | Pyro.: 10 °C/min → 500 °C; Catal.: 800 °C | Yao et al.¹⁰³ |
| 46    | H₂              | 2010 | HDPE                   | Two-stage FsBR | Semi | Ni/Mg/Al (1 : 1 : 1 at. ratio) | Pyro.: 10 °C/min → 500 °C; Catal.: 800 °C | Saad et al.¹⁰⁹ |
| 47    | Syngas          | 2010 | PE, maleated PP        | Autoclave       | Batch | Ferrocene | Pyro. and catal.: 700 °C | Kong and Zhang¹¹⁴ |
| 48    | Syngas          | 2010 | PP, maleated PP        | Autoclave       | Batch | Ferrocene | Pyro. and catal.: 700 °C | Zhang et al.¹¹⁵ |
| 49    | CNTs            | 2012 | w/PP                   | Two-stage FsBR | Semi | Ni | Pyro.: 30 °C/min → 600-800 °C | Misha et al.¹⁶ |
| 50    | CNTs            | 2012 | Gases assumed LDPE pyrolysis | FsBR | Semi | Fe/Al₂O₃ | Pyro. and catal.: 650-750 °C | Arnaiz et al.¹¹⁷ |
| 51    | CNTs            | 2016 | HDPE, PP, PS, PA, PVC, wHDPE, wPP, wMP (93.1 PE, 4.9 PP, 0.2 PVC, 1.8 others) | TRᵇ (pyro.) + FsBR (catal.) | Cont. | Co-Fe/Silica-alumina | Pyro.: 560-570 °C; Catal.: 700 °C | Borsodi et al.¹¹⁸ |
| 52    | CNTs            | 2019 | w/PP                   | Two-stage FsBR | Semi | Ni/La₂O₃ or Ni-Ca/La₂O₃ | Pyro.: 500 °C; Catal.: 700 °C | Aboul-Enein and Awadallah¹⁹ |
| 53    | CNTs            | 2019 | LDPE, PP, PS, PET, MP (40 LDPE, 40 PP, 10 PS, 10 PET) | Two-stage FsBR | Semi | NiO/CoO₃ | Pyro.: 600 °C; Catal.: 500-800 °C | Moso et al.¹²⁰ |
| 54    | CNTs            | 2019 | PE, PP, PS, PET        | Two-stage FsBR | Semi | Commercial stainless-steel mesh (SS-304, SS-316, SS-316S) | Pyro.: 800 °C; Catal.: 800 °C | Panahi et al.¹²¹ |

(continued on next page)
(continued from previous page)

| Entry | Target products | Year | Plastics (values: wt%) | Reactor | React. mode | Catalyst | Temperatures (pyro. and catal. reactors) | References |
|-------|-----------------|------|------------------------|---------|-------------|----------|----------------------------------------|------------|
| 57    | H₂/CNTs         | 2011 | PP                     | Screw kiln (pyro.) + moving bed (catal.) | Cont. | HZSM-5 (pyro.) NiO (catal.) | Pyro.: 550-750 °C; Catal.: 500-800 °C | Liu et al.¹²¹ |
| 58    | H₂/CNTs         | 2014 | LDPE, PP, PS           | Two-stage FxBR | Semi. | Niₓ-AlₓOᵧ (Ni: 5 wt%) | Pyro.: 50 °C/min → 600 °C; Catal.: 800 °C | Acomb et al.¹²² |
| 59    | H₂/CNTs         | 2014 | w-MP (68.3 HDPE, 13.3 LDPE, 9.5 PP, 1.1 PS, 4.8 others) | Two-stage FxBR | Semi. | Ni/Mn/Al (1 : 1 : 1 at. ratio) | Pyro.: 40 °C/min → 500 °C; Catal.: 800 °C | Wu et al.¹²³ |
| 60    | H₂/CNTs         | 2015 | w-LDPE                | Two-stage FxBR | Semi. | Feₓ-AlₓOᵧ (Fe: 10 wt%) | Pyro.: 50 °C/min → 600 °C; Catal.: 700-900 °C | Acomb et al.¹²⁴ |
| 61    | H₂/CNTs         | 2015 | w-PP                  | Two-stage FxBR | Semi. | Ni/Metal/Al (1 : 1 : 1 at. ratio; Metal = Mg, Ca, Zn, Ce, Mn) | Pyro.: 40 °C/min → 500 °C; Catal.: 800 °C | Nahl et al.¹²⁵ |
| 62    | H₂/CNTs         | 2016 | w-LDPE                | Two-stage FxBR | Semi. | Metalₓ-AlₓOᵧ (Metal: 10 wt%; Metal = Ni, Fe, Co, Cu) | Pyro.: 50 °C/min → 600 °C; Catal.: 800 °C | Acomb et al.¹²⁶ |
| 63    | H₂/CNTs         | 2017 | w-MP (40 HDPE, 35 LDPE, 20 PP, 5 PS) | Two-stage FxBR | Semi. | Niₓ-Feₓ-AlₓOᵧ (3 : 1 : 2 : 1 : 1 : 1 : 1 : 2 : 1 : 3 at. ratio) | Pyro.: 10 °C/min → 500 °C; Catal.: 800 °C | Yao et al.¹²⁷ |
| 64    | H₂/CNTs         | 2017 | w-MP (42 LDPE, 20 HDPE, 10 PP, 16 PS, 12 PET) | Two-stage FxBR | Semi. | Niₓ-Feₓ/MCM-41 (1 : 0, 3 : 1, 1 : 1, 1 : 3, 0 : 1 at. ratio) | Pyro.: 40 °C/min → 500 °C; Catal.: 800 °C | Yeshui et al.¹²⁸ |
| 65    | H₂/CNTs         | 2020 | PP                    | Two-stage FxBR | Semi. | Niₓ-Feₓ/AlₓOᵧ (Ni + Fe: ~ 9 wt%; impregnation, sol-gel, Ni: Fe = 1 : 0, 1 : 3, 0 : 1) | Pyro.: 15 °C/min → 500 °C; Catal.: 800 °C | Yao and Wang¹²⁹ |
| 66    | H₂ and CB nano-spheres | 2016 | PE, PP, PVC, ABS     | Plasma reactor | Cont. | FeₓOᵧ/ZSM-5 (Fe: 9.0 wt% (pyro.)); NiO/CaCO₃ (Ni: 0.9 wt%) (catal.) | Pyro.: 15 °C/min → 550 °C; Catal.: 400 °C or 700 °C | Mohsenian et al.¹³⁰ |
| 67    | Oil/CNTs        | 2020 | w-MP (PE, PP, PA, and PET films) | TR (pyro.) + FxBR (catal.) | Semi. | NiₓOᵧ/AlₓOᵧ (Ni: Fe: ~ 9 wt% (pyro.)); NiO/CaCO₃ (Ni: 0.9 wt%) (catal.) | Pyro.: 15 °C/min → 550 °C; Catal.: 400 °C or 700 °C | Veksha et al.¹³¹ |

a) carbon nanotubes.  b) mixed plastics.  c) waste.  d) fluidized bed reactor.  e) fixed bed reactor.  f) conical spouted bed reactor.  g) tubular reactor.  h) continuous.  i) semi-batch.  j) commercial Ni catalyst for naphtha reforming.  k) atomic ratio.  l) commercial Ni catalyst for CH₄ reforming.
higher in the presence of zeolites than that in the presence of non-zeolite catalysts such as SA. The hydrocarbons yield decreased in the order HZSM-5 (93.1 wt%) > HMOR (90.2 wt%) > HUSY (87.5 wt%) at 360 °C, which is a lower temperature than used for normal PE and PP pyrolysis. Klaimy et al. (Entry 36; Table 2) compared the effects of amorphous SiO₂ (0.045 mmol-NH₃/g), silica-alumina (0.209 mmol-NH₃/g), Si-MFI (0.017 mmol-NH₃/g), and Si/Al-MFI (0.638 mmol-NH₃/g) on PE pyrolysis at 450 °C. The increase of catalyst acidity led to a decrease in the molecular weight of pyolyzates and promoted aromatic products via cyclization. Elordi et al. (Entries 15 and 19; Table 1) studied the cracking of HDPE over CBV3024 (HZSM-5), CBV600 (HY), and CP811E-75 (Hβ), which are bed materials containing 25 wt% HZSM-5, HY, and Hβ, respectively. The use of a HZSM-5 catalyst produced a gas yield of 74 %, with a remarkable light olefin yield (70 %) at 500 °C. On the other hand, HY zeolite produced 63 % liquid with a boiling point in the gasoline range. The product distribution obtained with Hβ zeolite was evenly distributed between gases (48 %) and oil (50 %). Elordi et al. (Entries 74,77) concluded that HZSM-5 is selective to light olefins, 58 wt% once equilibrated; whereas high yields of non-aromatic C5-C11 products (around 45 wt%) are obtained with Hβ and HY zeolite-based catalysts. The main limitation on the use of these catalysts is their deactivation by coke deposition. The high gas flow rate in the CSBR reduced the residence time of pyrolyzates and enhanced the dragging of coke precursors, which contributed to preventing the formation of coke precursors.[86] Thus, continuous operation for more than 16 h (1 kg of polyolefin fed into a bed of 30 g of catalyst) was achieved when HZSM-5 was used above 450 °C.

Uemichi et al. (Entry 10; Table 1)[70] filled silica-alumina and HZSM-5 in series in a flow reactor. When silica-alumina and HZSM-5 were used at a weight ratio of 9 : 1 and at a temperature of 375 °C, 58.8 wt% liquid was recovered and consisted of the gasoline fraction (C5-C12) only with an octane number of 94 % and 25.2 % aromatics. Similarly, Ratnasari et al. (Entry 29; Table 1) reported effects of mesoporous MSM-41 and HZSM-5 in series on liquid recovery from HDPE. The most favorable results, i.e., >80 wt% liquid yield with 97.7 wt% C8-C12 hydrocarbons and 95.9 wt% aromatics selectivity, were observed when MCM-41 and ZSM-5 were used at a weight ratio of 1 : 1 at 500 °C.

Zeolites combined with metal promoters have been reported by several research groups. Uemichi et al. (Entries 7, 11, 14, 24; Table 1)[68,73,80,89] conducted H-gallosilicate catalyzed pyrolysis of PE and PP. In the case of HDPE pyrolysis with H-gallosilicate at 525 °C, the maximum of 71.6 wt% aromatic hydrocarbons (61.8 wt% BTX) was obtained, even under the reaction conditions that led to a major formation of wax in the absence of a catalyst. The synthesized Ga loaded HZSM-5 (Ga/HZSM-5) showed better resistance against the Cl compounds that caused catalyst deactivation than other gallosilicates, implying that the catalyst can treat polyolefinic plastics with a small amount of PVC. Escola et al. (Entries 20 and 23; Table 1) synthesized hierarchical ZSM-5 (h-ZSM-5) and beta zeolites (h-Beta) catalysts in order to improve the accessibility of bulky plastic to the acid sites, because plastics usually lead toward steric hindrances or diffusion constraints e.g. in zeolite micropores. Furthermore, the shortened diffusion path lengths may have...
reduced the secondary reactions, resulting in a higher resistance to catalyst deactivation. Escola et al.\textsuperscript{78,86} further synthesized Ni supported \textit{h-}ZSM-5 (Ni/\textit{h-}ZSM-5, Ni = 7 wt%) and \textit{h-}Beta (Ni/\textit{h-}Beta, Ni = 7 wt%) for hydrotreating of LDPE pyrolyzates. The product from LDPE pyrolysis at 400 °C under 1.5 bar of N\textsubscript{2} using a batch reactor produced oil with 48 % gasoline range, 35 % light diesel, and 15 % heavy diesel, whereas it contained a high proportion of olefins (54 g-Br/100 g-sample). Complete hydrogenation of the olefins was observed over Ni/\textit{h-}Beta, whereas there always remained approximately 30 % of olefins over Ni/\textit{h-}ZSM-5 due to an imbalance in the acid and metal function. Ni/\textit{h-}ZSM-5 led towards significant amounts of gases (~18 %) while gasoline range hydrocarbons were the main products (55 %) over Ni/\textit{h-}Beta, at the expense of diesel fractions. Higher hydrogen pressures also suppressed the occurrence of secondary reactions such as aromatization and, presumably, coke formation.

The spent fluid catalytic cracking (FCC) catalyst is of great interest because it is inexpensive and active for cracking polyolefinic plastics (Entry 8; Table 1\textsuperscript{90}, and enhanced the catalytic pyrolysis of polyethylene even at low temperatures (450-515 °C), resulting in gases (48-52 wt%) and low boiling aliphatic oils (38-39 wt%) instead of waxes (~90 wt%) in non-catalytic experiments. Donaj et al. (Entry 23; Table 1)\textsuperscript{91} employed a commercial Ziegler-Natta catalyst (TiCl\textsubscript{4}/MgCl\textsubscript{2}) in the pyrolysis of a mixed polyolefinic plastics at 650 °C, improving the gas fraction (54.3 %), and, especially, the ethylene and propylene yields (22.3 % and 21.1 %, respectively). Li et al. (Entry 28; Table 1)\textsuperscript{92} conducted catalytic pyrolysis of PE- and PP-rich mixed plastics at 500 °C using Fe-, Ti-, Zr-, and Al-pillared clays (PILC), which are known as mild acidity catalysts. Fe-PILC enhanced the oil product yield (79.3 wt%) with 80.5 wt% diesel fraction selectivity. Simultaneously, a high yield of H\textsubscript{2} gas (47.7 vol%) was obtained. The superior catalytic performance of Fe-PILC was most likely attributed to its moderate total acidity, relatively high BET surface area, and uniformly dispersed iron oxide particles on montmorillonite support. Its mild acidity was also effective at suppressing coke deposition on the surface of the catalyst.

Potentials of inexpensive secondary materials such as red mud (byproduct of the Bayer process; 36.5 wt% Fe\textsubscript{2}O\textsubscript{3}, 23.8 wt% Al\textsubscript{2}O\textsubscript{3}, 13.5 wt% TiO\textsubscript{2}, 8.5 wt%, etc.) (Entry 21; Table 1)\textsuperscript{93}, waste brick kiln dust (WBKD, 19.7 wt% Si, 6.1 wt% Al, 5.5 wt% Ca, 5.4 wt% Fe, etc.) (Entry 26; Table 1)\textsuperscript{93}, and fly ash (53.6 wt% SiO\textsubscript{2}, 27.7 wt% Al\textsubscript{2}O\textsubscript{3}, 5.5 wt% Fe\textsubscript{2}O\textsubscript{3}, etc.) (Entry 30; Table 1)\textsuperscript{93} as catalysts have been investigated. Red mud increased gas yield and promoted aromatization from PE- and PP-rich mixed plastics, whereas it required higher temperatures (>500 °C) to become active in the pyrolysis\textsuperscript{79}. W BKD has a comparatively high BET surface area (300 m\textsuperscript{2}/g) and was a suitable metal support. ZnO-impregnated W BKD improved the oil yield from HDPE and the product oil satisfied the fuel grade quality and was suggested to be a blend of gasoline and diesel range hydrocarbons\textsuperscript{93}. Fly ash calcined at 800 °C (BE surface area: 310 m\textsuperscript{2}/g; Si/Al = 16) showed the best performance on the liquid recovery from waste PE at 700 °C, and resulted in >80 wt% oil with 22.1 wt% BTX selectivity.

Microwave-assisted pyrolysis and the subsequent catalytic upgrading using MgO, ZSM-5, NiO, and HY zeolite have been reported (Entries 25, 27, 32; Table 1)\textsuperscript{81,85,95}. As mentioned in the previous section, microwave radiation allows high temperatures and high heating rates. As an example, Ding et al. (Entry 32; Table 1)\textsuperscript{95} conducted catalytic microwave-assisted pyrolysis of LDPE. NiO and HY zeolite were used as \textit{in-situ} and \textit{ex-situ} catalysts, respectively, in a two-stage pyrolysis-catalysis system. The optimum oil yield (56.5 wt%) and oil quality were achieved at the pyrolysis temperature of 500 °C, and the catalysis temperature of 450 °C. The addition of NiO further increased the yield of high octane number compounds without obvious effects on the oil yield. The hydrogen abstraction from alkanes by NiO produced numerous alkenes, which were further converted by HY into aromatics and cyclo-alkenes.

The Hamburg process shown in Fig. 5 is a well-known pilot-scale process which allows catalytic pyrolysis employing a wide variety of catalysts\textsuperscript{41}. Nishino et al. (Entry 14; Table 1)\textsuperscript{73} achieved continuous Ga-ZSM-5 catalyzed pyrolysis of waste PE- and PP-rich mixed plastics for 460 h with catalytic cracking under alternating degradation and regeneration conditions, which retained >50 % of the oil yield with 80 % of the aromatics selectivity. Miskolczi et al. (Entry 16; Table 1)\textsuperscript{75} investigated the effects of feeding HZSM-5 in a pilot-scale continuous tube reactor at 520 °C and achieved a gas yield of 11 % and an oil yield of 89 % from waste HDPE and PP. Kassargy et al. (Entry 31; Table 1)\textsuperscript{77} conducted catalytic pyrolysis of PE, PP, and their mixtures (50/5, 80/20, and 20/80) using USY zeolite in a continuous pilot plant at a temperature of 500 °C, resulting in ~20 wt% gas and ~80 wt% oil.

3.2. Catalytic Pyrolysis for Gasification and Carbon Materials Recovery

Polyolefinic plastics are good sources for hydrogen production by catalytic steam reforming of their pyrolyzates. Selected works targeting H\textsubscript{2}-rich gas and syngas recovery from polyolefinic plastics are summarized in Entries 36-46 in Table 2. Pyrolyzates of PE and PP are hydrocarbons (C\textsubscript{n}H\textsubscript{2n+2}) and are further converted into H\textsubscript{2} and CO by reaction with steam (Eq. (1)) catalyzed by heterogeneous catalysts. The water gas shift reaction (Eq. (2)) is also enhanced by the steam gasifi-
Ni-based catalysts, as comparatively inexpensive noble metal catalysts, would be suitable candidates for steam-reforming catalysts for plastics pyrolyzates. Czernik and French (Entry 36; Table 2)\textsuperscript{96} employed a tandem fluidized-bed pyrolysis/reforming reactor (feed: 60 g-PP/h) using a commercial Ni catalyst for naphtha reforming (C11-NK) which was continuously operated for 60 h. The test resulted in the maximum yield of 20.5 g-H\textsubscript{2}/h hydrogen at 600-700 °C and 800 °C for pyrolysis and steam reforming, respectively. Park et al. (Entry 37; Table 2)\textsuperscript{97} investigated a two-stage PP pyrolysis and subsequent steam reforming using Ru/\gamma-Al\textsubscript{2}O\textsubscript{3} for supplying H\textsubscript{2} in solid oxide fuel cells. Ru is more expensive than Ni, although the former does have a higher activity and causes less coke formation. Therefore, it has a potential to more reduce steam reforming temperature and keep longer catalytic activity. They employed a continuous two-stage fixed-bed reactor and achieved continuous PP feed with 60 g-PP/h at a pyrolysis temperature of 400 °C. In addition, the experimentally obtained gas composition (70.3 vol % H\textsubscript{2}, 8.7 vol% CO, 18.7 vol% CO\textsubscript{2}, and 2.2 vol% hydrocarbons) using 5 wt% Ru content catalyst was almost the same as that predicted by chemical equilibrium laws for steam reforming. They concluded that for this system, the optimum reformer temperature and WHSV were to be 630 °C (a low temperature) and approximately 0.11 g-sample g-catalyst\textsuperscript{-1} h\textsuperscript{-1}, respectively, from the viewpoint of decreased coke formation and sufficient conversion of carbon to gaseous products. Wu and Williams investigated the effects of wide variety of Ni-based catalysts on the recovery of H\textsubscript{2}-rich gas from PE, PP, and real waste plastics employing a two-stage fixed-bed reactor (Entries 38-41, 45, 46; Table 2)\textsuperscript{98}-\textsuperscript{103}. As an example, H\textsubscript{2} yields from HDPE, PP-, and PE-rich mixed plastics were approximately 2.5, 2.6, and 2.0 L-H\textsubscript{2}/g plastic, respectively, at a gasification temperature of 800 °C using a Ni/Mg/Al catalyst (atomic ratio = 1 : 1 : 1)\textsuperscript{98}, given their well-described catalytic activity in steam reforming and because both Al\textsubscript{2}O\textsubscript{3} and MgO are well-known effective Ni supports\textsuperscript{104},105). The effectiveness of Ni-based catalysts on gasification of biomass tar has been previously validated\textsuperscript{106},107). It has been reported that even if aggregation of the metallic Ni particles lowers the catalytic activity, the presence of Mg, which is strongly interacted with Ni in the catalysts, re-disperses the metallic Ni particles through calcination and reduction\textsuperscript{108}. Therefore, the Ni/Mg/Al catalyst is recognized as a suitable candidate of steam reforming catalyst. The effectiveness of the Ni/Mg/Al and Ni/Co/Al catalyst on dry CO\textsubscript{2} reforming has also reported by Saad et al. (Entries 47, 48; Table 2)\textsuperscript{109,110}.

Prof. Olazar’s group investigated sequential processes for hydrogen production based on continuous CSBR for plastic pyrolysis and in-line steam reforming by fixed-bed (Entry 42; Table 2)\textsuperscript{111} or FBRs (Entries 43, 44; Table 2)\textsuperscript{112,113}). The CSBR allowed flash pyrolysis of plastics by improved high heat and mass transfer and solid mixing, which also avoids defluidization problems and eases the handling of sticky polyolefinic plastics. The sequential CSBR and in-line FBR steam reform using a commercial Ni catalyst (G90LDP) performed without operational problems, although it showed a constant catalyst deactivation due to the coke depositions. Under the optimum conditions (700 °C; space time 16.7 g-cat min/g-HDPE; steam/plastic ratio 5), the H\textsubscript{2} yield was 92.5 % of that corresponding to stoichiometry, which accounts for H\textsubscript{2} production of 38.1 g/100 g-HDPE in the feed. They concluded that the capability of the reforming catalyst used to regenerate will be studied in future work via reaction-regeneration cycles, and that the determining the kinetics of the reforming step is crucial for reactor design.

Because of the high carbon content in the plastics, there is considerable research regarding carbon material production from plastics (Entries 49-56; Table 2)\textsuperscript{114}-\textsuperscript{121}.

\begin{align*}
\text{C}_n\text{H}_m + n\text{H}_2\text{O} & \rightleftharpoons \text{CO} + (n + m / 2)\text{H}_2 \quad (1) \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (2)
\end{align*}

Zhang et al. (Entries 49, 50; Table 2)\textsuperscript{114,115} synthesized straight and helical carbon nanotubes (CNTs) and CNTs microspheres from PE and maleated PP in an autoclave at 700 °C using ferrocene as a catalyst. The yield of CNTs reached > 80 wt% with diameters of 20-60 nm from PE\textsuperscript{114} and 5.5-7.5 μm microspheres assembled from CNTs could be recovered from PP\textsuperscript{115}. Other works mainly employed Ni or Fe-based heterogeneous catalysts and recovered CNTs deposited on the catalyst through catalytic reaction between the catalysts and non-condensable plastic pyrolysis gases using a two-stage fixed-bed reactor. For example, Aboul-Enein and Awadallah (Entry 54; Table 2)\textsuperscript{109} recovered 51.9 wt% carbon from a Ni-Cu/La\textsubscript{2}O\textsubscript{3} (Ni, Cu, and La\textsubscript{2}O\textsubscript{3} = 40, 10, and 50 wt%, respectively) catalyst and another 38.1 wt% and 10 wt% were gaseous products and waxes, respectively at 500 °C for PP pyrolysis and 700 °C for the catalytic reaction. Moo et al. (Entry 55; Table 2)\textsuperscript{120} synthesized CNTs from non-condensable pyrolysis gases from LDPE, PP, and mixed plastics and assessed the performance of the synthesized CNTs as electrode materials for their heterogeneous electron transfer rate using a redox probe, which showed improved electrochemical behavior. Panahi et al. (Entry 56; Table 2)\textsuperscript{121} synthesized CNTs on pretreated stainless-steel mesh (SS-304, SS-316, and SS-316 L), which was beneficial to produce CNTs. Carbon deposition on Ni-based surface of the catalysts is inevitable during the gasification process although they are also used to produce CNTs. Therefore, the simultaneous recovery of H\textsubscript{2} and CNTs has
been investigated recently (Entries 57–65; Table 2). Li et al. (Entry 57; Table 2) proposed a process consisting of two stages: catalytic pyrolysis of PP over HZSM-5 zeolite in a screw kiln reactor, and subsequent catalytic decomposition of pyrolysis gases over a NiO catalyst in a moving-bed reactor for producing H₂ and CNTs, simultaneously. The product gas is mainly comprised of hydrogen, methane, and C₂-C₅ hydrocarbons. The CNTs yield (34.1 g-CNTs/100 g-PP) and hydrogen gas concentration (110 L/100 g-PP; H₂: 72.1 vol%) reached the maximum at the catalytic decomposition temperature of 700 °C. Prof. Williams’s group tested multiple combinations of Ni- and Fe-based catalysts synthesized via different methods (Entries 58–65; Table 3). Through these studies, it can be said that bimetallic Ni-Fe catalysts exhibited superior performance for simultaneous H₂ and CNTs production from waste polymers. Furthermore, improved morphology and purity of carbons could be obtained over a Ni-Fe catalyst. The yield of deposited carbon was related to the metal-support interaction, and a higher carbon yield was obtained for the catalysts with a higher Fe loading. On the other hand, CNTs with narrower diameters and uniform distributions were synthesized with a higher Ni ratio. The presence of Ni enhanced the thermal stability of the produced carbon products with fewer carbon defects and a higher graphitization degree of carbon CNTs. Veksha et al. converted waste mixed plastics into oil and CNTs through catalytic pyrolysis using Fe₂O₃/ZSM-5 (and the subsequent catalytic reactions between non-condensable gases and NiO/CaCO₃) (Entry 66; Table 2). Plasma gasification process (Entry 67; Table 2) achieved complete decomposition of PE and PP and hydrogen-rich gases recovery at an arc temperature of 10749–16070 °C. A high H₂ concentration (60–70 vol%) with a lack of CO in gas products in the absence of a catalyst is one of the main achievements of this work.

4. Feedstock Recycling of Waste Plastics Using Petroleum Refinery Processes

The authors, Toshiaki Yoshioka (project leader), Shogo Kumagai, and Yuko Saito are leading a project titled “Development of chemical recycling processes for waste plastics,” which has been commissioned by the New Energy and Industrial Technology Development Organization (NEDO) for realizing chemical feedstock recovery from waste plastics using real petroleum refinery processes. Pyrolysis reactions require heat energy and the produced hydrocarbons must be refined to become available petrochemical products. Therefore, completing all the plastic treatment processes from pyrolysis to refinery using existing petroleum plants is a highly efficient and promising approach. In this project, three routes of feedstock recycling in petroleum processes have been suggested (Fig. 10): (1) Waste plastics are mixed with vacuum residue (VR) and the mixture is directly co-pyrolyzed in the delayed coker; (2) Catalytic pretreatment of waste plastics for reducing molecular weight of polymers and influencing the undesirable compounds emission, and subsequent co-pyrolysis of the treated plastics with VR in the delayed coker; (3) Catalytic pyrolysis of waste plastics for direct recovery of target petrochemical feedstocks. In the 1st and 2nd suggested routes, we have targeted maximizing synergistic effects between plastic pyrolyzates and VR pyrolyzates during the co-pyrolysis in the delayed coker. We have confirmed the presence of positive synergistic effects such as enhanced gasification and liquefaction or suppression of coke during co-pyrolysis of plastics and lignocellulosic biomasses. Therefore, we investigated the co-pyrolysis behavior and optimized the pyrolytic conditions to maximize the recovery of high value products.

The annual amount of treated domestic crude oil was 166 million kL in 2017, which was much larger than the domestic production of waste plastics (~8.9 Mt in 2018). Therefore, treatment of waste plastics with a small percentage of crude oil has significant impacts on plastic recycling. Theoretically, all hydrocarbons derived from waste plastics are fully utilized in the existing petroleum refinery processes. Also, using the existing refinery equipment for plastic treatment drastically reduces the investment for new facilities. Thus, this project has a significant potential for drastic advancement in the feedstock recycling of waste plastics in Japan.

5. Generation Sources of Waste Polyolefinic Plastics

For developing an efficient recycling system, the quality and quantity matching between waste sources and recycling technologies is required in addition to development of individual technologies. In the case of pyrolysis of polyolefinic plastics, one of the key elements for recyclability would be to locate plastic waste which contains a high percentage of polyolefinic plastics, including PE and PP. However, regarding the quality of plastic waste including the composition of resin types, only fragmentary information such as waste composition survey data with a limited sample of waste sources are available.

Against this backdrop, we developed a material flow model using input-output tables and specified the intersectoral flow of plastics. The results for container and packaging waste, which accounts for approximately half (4.5 Mt in 2015 according to our estimation) of the total plastic waste generation in Japan, are available for 112 waste source sectors (including 108 industry sectors and 4 domestic final demand sectors) and 7 resin types.
types (LDPE, HDPE, PP, PS, PVC, PET, and other resins). As shown in Fig. 11, resin compositions of plastic waste vary between generation source sectors. According to our estimation, polyolefinic plastics (LDPE, HDPE, and PP) account for > 80% of plastic container and packaging waste (excluding PET bottles that are separately collected for recycling) in some manufacturing industry sectors, whereas plastic container and packaging waste generated from service sectors has a relatively low percentage (around 60-70%) of polyolefinic plastics. In addition, if we aim to collect PE/PP rich plastic waste, household container and packaging waste is not necessarily a good target.

6. Conclusion

This review examined global trends in waste plastic recycling and concluded that there is rapid demand in growth of feedstock recycling, both domestically and globally. Selected pyrolysis technologies for polyolefinic plastics regarding reactor design and catalytic pyrolysis were examined and summarized in this review. Although each study conducted pyrolysis using different combinations of plastic, apparatus, scale, and catalyst, it can be concluded that all researchers targeted improvements in pyrolysis efficiency and maximization of high-value feedstock recovery. It should be noted that pyrolysis of PVC, PET, nitrogen containing plastics, and halogenated flame retardant containing plastics, which were not the focus of this review, present other important challenges for broadening the targeting of waste plastics.

Feedstock recycling via pyrolysis has infinite combinations, and the optimal process is strongly dependent on the available waste plastics and the demand for products. The authors’ project which attempted pyrolysis of waste plastics in existing refinery petroleum processes is an example of highly efficient feedstock recovery. Thus, this review shows the potential of feedstock recycling of polyolefinic plastics through pyrolysis.

As a final remark, even in a report which positively discusses the introduction of feedstock recycling in Europe, it is regarded as complementary to mechanical recycling. However, we should not forget that increasing the overall effect of the plastic recycling system is the highest priority, and, therefore, we need to explore appropriate allocation of waste plastics generated from various sources to different recycling technologies beyond the stereotypical and hierarchical view of mechanical and feedstock recycling.

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References

1) Plastics Europe, The Compelling Facts About Plastics 2009, https://www.plasticseurope.org/en/resources/publications/180-compelling-facts-about-plastics-2009 (access date: June 10, 2020).
2) Plastics Europe, Plastics – the Facts (2019), https://www.plasticseurope.org/en/resources/publications/1804-plastics-facts-2019 (access date: June 10, 2020).
3) United Nations Environment Programme, Single-Use Plastics: A Roadmap for Sustainability, https://wedocs.unep.org/bitstream/handle/20.500.11822/25496/singleUsePlastic_sustainability.pdf?sequence=1&isAllowed=y (access date: June 10, 2020).
4) Plastic Waste Management Institute, Plastic Products, Plastic Waste and Resource Recovery, PWMI Newsletter, 49, (2020).
5) Geyer, R., Jambeck, J. R., Law, K. L., Sci. Adv., 3, e1700782/1 (2017).
6) Ellen Macarthur Foundation, The New Plastics Economy: Rethinking the future of plastics, https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics (access date: June 11, 2020).
7) United Nations, Transforming our world: the 2030 Agenda for Sustainable Development, https://sustainabledevelopment.un.org/post2015/transformingourworld (access date: June 11, 2020).
8) European Commission, Closing the loop: An EU Action Plan for a Circular Economy, https://ec.europa.eu/environment/circular-economy/index_en.htm (access date: June 11, 2020).
9) Global Affairs Canada, Group of Seven, Ocean plastics charter, http://publications.gc.ca/puf?vid=9.859436&sl=0 (access date: June 19, 2020).
10) Ryan, P. G., Dilley, B. J., Ronconi, R. A., Connan, M., Proc. Natl. Acad. Sci. USA, 116, 20892 (2019).
11) Kawecki, D., Nowack, B., Environ. Sci. Technol., 53, 9664.
要 旨

ポリオレフィンのケミカルリサイクルの研究開発動向とチャレンジ

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世界の廃プラスチック排出量は増加の一途をたどしており、リサイクルに対する期待や需要が大きな高まりを見せている。その背景では、Sustainable Development Goals（SDGs）、欧州のサーキュラーーエコノミー、プラスチックによる海洋汚染問題、中国を始めとするアジア各国の廃棄物輸出規制等が大きな影響を及ぼしている。国内では、2019年5月より国家戦略としてプラスチック資源循環戦略が掲げられ、マイスタイルトとして2030年までに「ワンウェイプラスチックを排出25%排出抑制すること、2030年までに容器包装プラスチックの6割をリユース・リサイクルすること、2035年までに使用済プラスチックを100%リユース・リサイクル等により有効利用することの達成を目指している。）

よって、プラスチックリサイクルを促進するための研究・技術開発およびそのための社会システムの基盤整備が極めて重要となっている。今後プラスチックのリサイクル量を大きく増大させる上で、著者らは、熱分解法により廃プラスチックを化学原料に戻すケミカルリサイクル（フィードストックリサイクル）が、有力な技術になると期待している。本総説では、まず国内外のプラスチックリサイクルを取り巻く状況について整理した。続いて、ポリオレフィンの熱分解法によるケミカルリサイクル、特に熱分解装置開発および触媒を用いた熱分解生成物の高付加価値化に関する研究に関する視点を整えて研究開発動向を整理した。