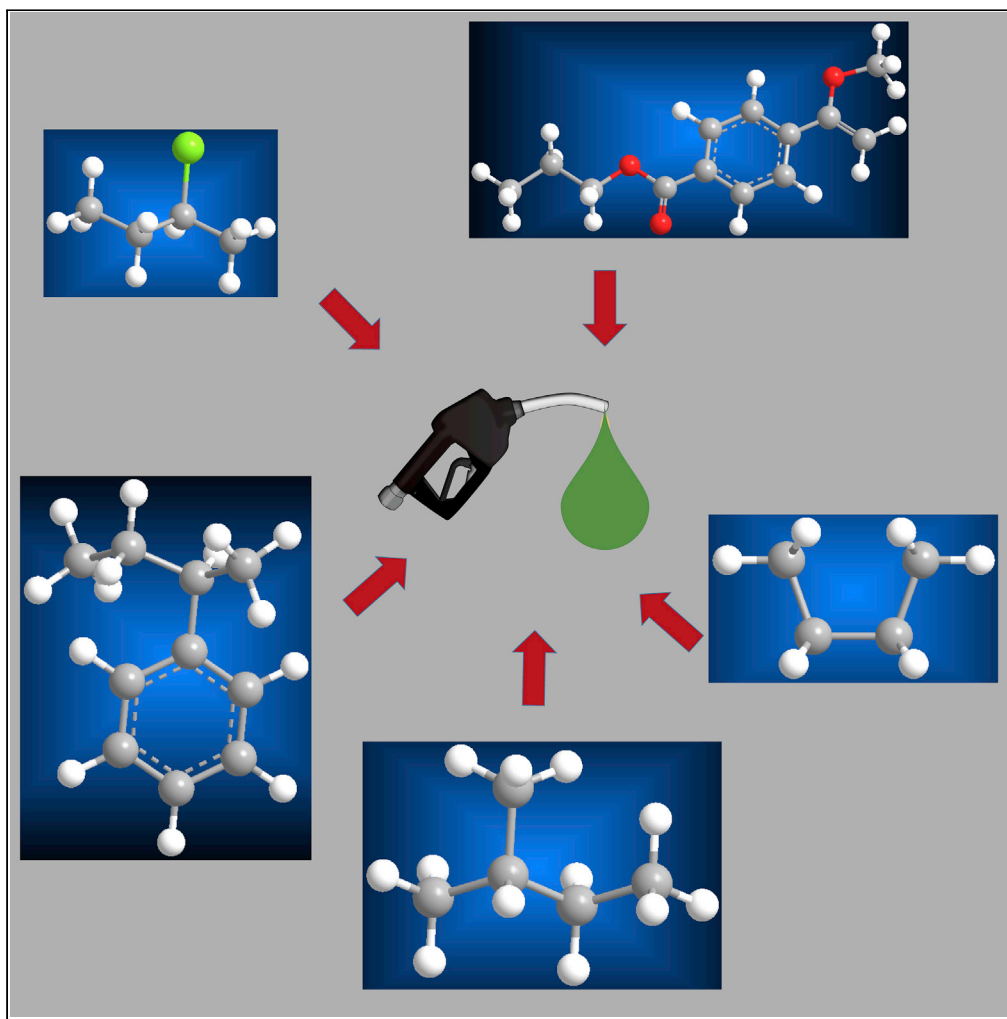


Article

Trash-to-fuel: Converting municipal waste into transportation fuels by pyrolysis



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Highlights

Development of pyrolysis reactor to convert municipal waste to transportation fuels

Studying the reaction parameters of a set of different individual polymer materials

Development of a reaction and degradation mechanism

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Article

Trash-to-fuel: Converting municipal waste into transportation fuels by pyrolysis

Yun Xu¹ and Wolfgang Schrader^{1,2,*}**SUMMARY**

In daily life humankind is producing a significant amount of garbage, creating a great environmental concern. However, garbage consists of high amounts of carbon based materials, making it a very useful resource. An easy way to use it is to produce transport fuels obtained through pyrolysis. Multiple plastic waste materials were investigated here. Thermogravimetric analysis (TGA) of individual polymers shows that almost complete conversion could be achieved. More than 70% liquid fuels were derived from pyrolysis of polypropylene, polystyrene at 450°C, and low-/high-density polyethylene at 500°C. Using gas chromatography/high-resolution mass spectrometry (GC/HR-MS) allows studying the thermal transformation and proposing a mechanism. An examination of carbon number distribution reveals the potential of plastic liquid fuels, which can be used as an alternative to partial substitution of fossil-fuel-derived gasoline and diesel fuel and also provides a final use of polymer materials, which otherwise would be deposited on waste dumps.

INTRODUCTION

Humankind is producing a large amount of municipal waste ranging from biomass over nonrecycled plastic materials to metals, wood, minerals, and a large number of different and diverse materials. Some are more environmentally malignant than others but all combine one feature, that there is a high amount produced every single day. Because more sustainable processes need to be developed, we still need a strategy that especially deals with important and necessary polymer materials to find a final use after all recycling steps are concluded. Here, something better than dumping these waste materials on waste dumps or even in the environment is needed. Especially, carbon-containing materials such as polymers can find another use when they are converted into some type of fuel.

Plastics have a wide impact on human lifestyle, being utilized for producing packages, soft bottles, textiles, toys, electronic devices, and numerous other important or less important products; this is attributed to general plastic properties that they are light, durable, resistant to corrosion by most chemicals, and easy to be processed and that they have low production cost on a large-scale level (Andrady and Rajapakse, 2016; Ibeh, 2011). Since the invention of plastic products, commercial plastic production has surged from 1.5 million tons in 1950 to 348 million tons in 2018 (Bellas and Gil, 2020; Zhang et al., 2020). The most commonly used plastics in our daily life are polyethylene terephthalate (PET), high-density polyethylene (HDPE), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) with plastic identification code from 1 to 6, respectively, accounting for around 81% of the total European plastic demand in 2016 (Yu et al., 2016; Strungaru et al., 2019).

The major problem behind using plastics is that most of them are not easily degradable, taking decades to hundreds of years for natural degradation (Shah et al., 2008; Hoàng and Lowe, 2008; Barnes and Milner, 2005). Homogenous plastic is a valuable resource, thus, it is of tremendous importance to recycle and transform them back into custom products. The plastic recycling process can be categorized into two major pathways: (1) mechanical recycling, where plastic is sorted, cleaned, and regenerated; (2) chemical recycling, where plastic is degraded into basic components (Garcia-Nunez et al., 2017; Ragaert et al., 2017; Rozenstein et al., 2017). Nowadays plastic recycling is still in strong need of improvement. Roland Geyer et al. reported in 2015 that an estimated 79% of the global plastic waste was discarded into dumpsites, 12% was incinerated, and only 9% was reused from recycling. Discarded plastic either goes into landfilling or gets dumped into the ocean, which subsequently forms microplastic and has a negative impact on environment,

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wildlife, and human health (Andrady, 2017; Thompson et al., 2009; Corcoran et al., 2009; Halden, 2010; Teuten et al., 2009; Rochman et al., 2013). On the other hand, even when plastics are properly recycled, each recycling cycle shortens the lifespan of the plastics due to additional heating and alternation of the polymer chain. After several rounds of recycling, plastic quality significantly decreases, leaving the material useless for reproduction. This means that the final end-use of the material is important where still high amounts of the plastic waste go into landfilling or ends up as trash in the oceans (Geyer et al., 2017).

Aside from the recycling and micro plastic issues, the conflict between uprising energy demand and depletion of conventional fossil energy sources raises a big concern and keeps crude oil prices high. Nowadays, 85% of the total world energy consumption is attributed to consumption of fossil fuels (Coady et al., 2019). The depletion of fossil fuel, especially for the reservation of natural gas and oil, happens in a foreseeable future, and therefore, measures have to be taken before it becomes a reality (Shafiee and Topal, 2009; Bardi, 2019). Using renewable energy resources (e.g., solar, wind, hydro power) is a solution, but is still in a developing stage and requires a massive infrastructure input (Jacobson and Delucchi, 2011; Eleftheriadis and Anagnostopoulou, 2015; Pickard et al., 2009). An alternative strategy is to use municipal carbon containing waste, especially at current situation of insufficient waste management. One example could be plastic waste, which is derived from fossil fuel and has a comparable calorific value to that of hydrocarbon fuel, thus providing a better opportunity as an alternative to dumpsites (Wong et al., 2015; Panda et al., 2010).

Therefore, energy recovery is a necessary step for those recycled low-quality plastics or improper treated plastic waste. This process can also be viewed as a thermochemical recycling process. Conventional incineration of plastic waste is a simple but disputable process to generate heat and electricity, raising a great environmental issue of producing dioxin and heavy metal in the smoke (Wang et al., 1999; Verma et al., 2016; Abad et al., 2000). One way to thermally crack polymer materials is by using pyrolysis. This is not without drawbacks, as pyrolysis needs a high input of energies, which is conducted at a high temperature under an inert condition. Although a large pyrolysis reactor is available in the industry, increasing pyrolysis capacity of plastic waste is still a challenging process because of extreme sample complexity it has to deal with (Venderbosch and Prins, 2010; Garcia-Nunez et al., 2017; Butler et al., 2011).

Because this is an easy way to crack polymers into fuels, we used pyrolysis as a tool in this *trash-to-fuel* setup. In this study, general plastic types such as PET, HDPE, PVC, LDPE, PP, and PS are used to investigate the pyrolysis process. The objective of this study is to transform plastic waste into valuable fuels and to achieve a good understanding of the conversion process. For a better understanding of the process, it is necessary to use analytical methods with high resolution and accuracy such as high-resolution mass spectrometry, which has shown to be an excellent tool for studying complex mixtures, both for low and high volatile energy mixtures (Neumann et al., 2020; Schwemer et al., 2015; Miettinen et al., 2017; Hertzog et al., 2017; Headley et al., 2016; Cao et al., 2021; Panda et al., 2009; Qi et al., 2017). In this case, the pyrolysis products are volatile and therefore they were studied by using a combination of gas chromatographic separation with high-resolution mass spectrometry (GC-EI-HRMS) to examine the detailed compound information (Kondyli and Schrader, 2019). A high resolving separation method coupled to a high resolving detection method allows a detailed characterization of the complex and diverse product mixture.

RESULTS AND DISCUSSION

TG analysis

For a better understanding of the thermal degradation of polymers, initial studies were carried out using thermogravimetric analysis to determine the optimum reaction parameters. The graphs are summarized in Figure 1; of the six different polymer materials, only one shows a different course. The results show that PVC has two major degradation steps, whereas all other curves only show a single degradation step. The T_p of first degradation stage of PVC occurs at 299°C with a loss of 72.5% (see Table 1). The second degradation T_p is located at 457°C with a degradation loss of 14.7%. In comparison, other types of polymers such as PET, PP, PS, LDPE, and HDPE only show a single degradation step, mainly observed at a high temperature range from 350 to 500°C. The TG curve of HDPE, LDPE, PP, and PS presents a high weight loss with less than 5% residue in the TG sample plates, whereas there is still a high amount of residue (22.1%) for degradation curve of PET. A high weight loss during degradation indicates a high potential to obtain an efficient transformation of plastic waste into fuels when pyrolysis is applied. Among the plastic materials, thermal degradation temperature follows the order of PS < PP < HDPE ≈ LDPE. The difference could be attributed to the

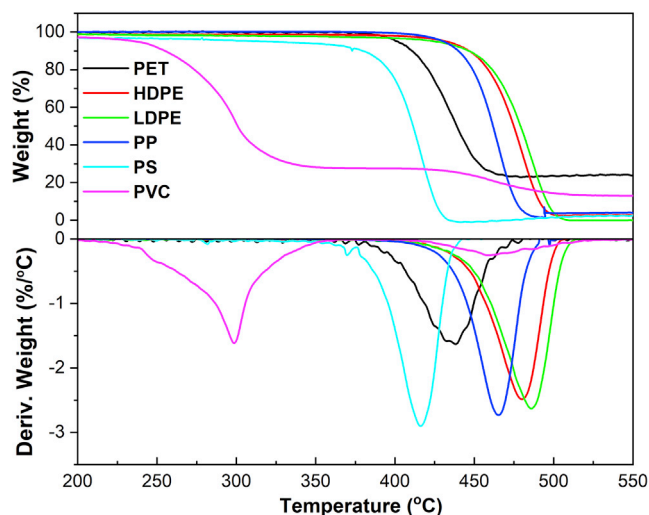


Figure 1. Thermogravimetric results

Zoom in thermogravimetric (TG) and differential thermogravimetric (DTG) profiles of individual plastics in a temperature range from 200 to 550°C.

stability of radical intermediates formed during heating process. Direct single point C-C cleavage of plastic PE, PP, and PS at a high temperature leads to the formation of single radical $R\cdot$, $R\cdot$ and $R\cdot C_6H_5$, respectively, which shows a decreasing order of radical stability.

These thermogravimetric experiments for different types of plastic waste provide insights into the temperature dependency and indicate that a temperature higher than 400°C is required for an efficient pyrolysis process. But it still does not give any indication about the reaction time that is needed for complete degradation. Therefore, TG analysis was further carried out for plastic PP by increasing the temperature to a certain temperature of either 400 or 450°C followed by maintaining at this constant temperature for 1 h reaction time. As shown in Figure 2, there is still 27% residue left after 1 h degradation at 400°C. However, when increasing temperature to 450°C, the degradation efficiency was significantly improved. There is only less than 1% residue left after 10 min degradation time at 450°C.

Pyrolysis of PP

Generally, during the pyrolysis process materials are converted into three major components, char, gas, and a pyrolysis oil. Liquid fuel is easier to be stored, whereas gas is more efficient to be used for producing energy. The distribution of pyrolysis products is highly dependent on the reaction conditions. In this study, different reaction conditions such as temperature and reaction time were investigated. First, the pyrolysis was carried out at temperatures of 400, 450, 500, and 550°C, respectively, using polypropylene as an example.

Table 1. Summary of decomposition temperatures (e.g., onset temperature T_o , peak temperature T_p , and end point temperature T_e) and weight losses of individual plastic

Plastic	$T_o/^\circ\text{C}$	$T_p/^\circ\text{C}$	$T_e/^\circ\text{C}$	Loss/%	
PET	413	438	454	77.9	
HDPE	446	481	498	97.3	
LDPE	448	485	505	>99	
PP	436	465	482	95.9	
PS	396	416	428	97.2	
PVC	237	299	351	72.5	87.2
	414	457	509	14.7	

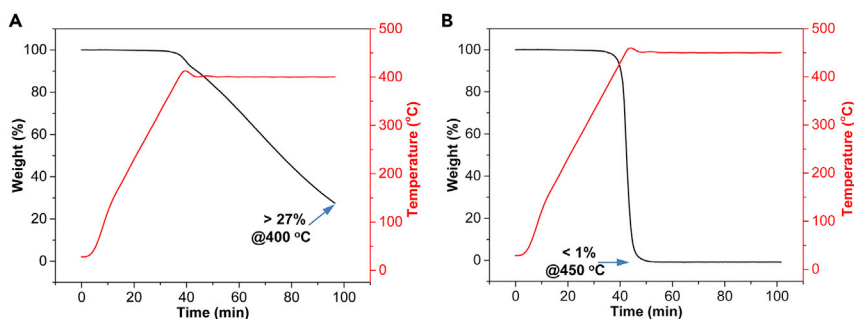


Figure 2. Studying pyrolysis temperature

TG curve of PP at a heating rate of $10^{\circ}\text{C min}^{-1}$ up to (A) 400 or (B) 450°C and then hold at this max temperature for 1 h.

All the experiments were performed on a mass of 20 g, and each reaction condition was performed by altering the temperature. Yields of liquid fuel and pyrolysis residue were determined on a mass basis, and the remaining part was calculated as gas. The results show that only a small part of PP, around 20%, is transformed into oil and gas at 400°C (Figure 3A). A significant increase of gas and oil yields (>99%) was observed by increasing the pyrolysis temperature to 450°C, whereas there is almost no difference of product yield distribution when increasing the temperature to 500°C. Further increasing the temperature from 500 to 550°C, the yield of gas increases from 21.4% to 31.8%, whereas the yield of oil decreases from 78.1% to 67.6%. The oil to gas ratio is shown in Figure 3D. A slight increase of oil to gas ratio from 3.0 to 3.7 was observed when increasing temperature from 400 to 450°C, and it then stays flat between 450 and 500°C. Later it significantly drops from 3.7 to 2.2.

As low transformation efficiency happens at a low temperature of 400°C with 1 h pyrolysis time, the effect of reaction time was examined for products yield, shown in Figures 3B and 3E. It can be observed that a linear increase of liquid and gas yields accompanies with the increase of reaction time. Compared with product yield with a reaction time of 1 h, the residue inside the reactor almost disappears after 4 h pyrolysis. The liquid yield increases from 16.0% to 74.3%, and the gas yield increases from 5.3% to 20.9%. The gas to liquid ratio is also calculated, and no significant change is observed among different reaction times.

A third reaction condition was investigated by increasing the temperature step wise. The pyrolysis was carried out at 400°C with a reaction time of 20 min, followed by a step by step temperature increasing procedure. At each temperature, the products were collected, weighed, and the residue in the reactor was acting as a starting material for the next temperature step. The results are shown in Figures 3C and 3F. Increasing temperature from 400 to 420°C, the degradation rate is relatively slow, with liquid yield increasing from 3.9% to 17.5% and gas yield increasing from 1.3% to 5.4%, respectively. In comparison, the degradation rate is more than two times higher when increasing the temperature from 420 to 440°C. For the liquid to gas ratio, there is almost no change.

Pyrolysis of individual plastic waste materials

The pyrolysis was further extended to other plastic materials, such as PET, PS, PVC, LDPE, and HDPE, and the product distribution is shown in Figure 4. Based on information from TG and DTG analysis, a temperature higher than 450°C is required to shorten the reaction time and to achieve an efficient transformation. After the pyrolysis at 450°C for 1 h, a minor difference (2.3%, 2.0%, 4.7% and 2.7% for PET, PP, PS and PVC, respectively) between pyrolysis residue and TG residue was observed. However, still a big part of LDPE and HDPE (51.7% and 36.9%, respectively) was not transformed at 450°C. This result correlates well with TG weight loss analysis, as the TG curve shows that complete degradation of LDPE and HDPE occurs at a higher temperature. Increasing the pyrolysis temperature from 450 to 500°C leads to complete degradation as well (1.5% and 1.1% residue, respectively).

The pyrolysis volatiles were cooled down by using cooling steps with two-step ice/water baths (4°C), followed by one-step dry ice/acetone bath (−78°C). Different fractions were collected. The heavy fraction with heavy compounds can be obtained from ice/water bath, and the light fraction with light compounds can be collected from dry ice-saturated acetone bath. Condensed products of PET and HDPE appear to be

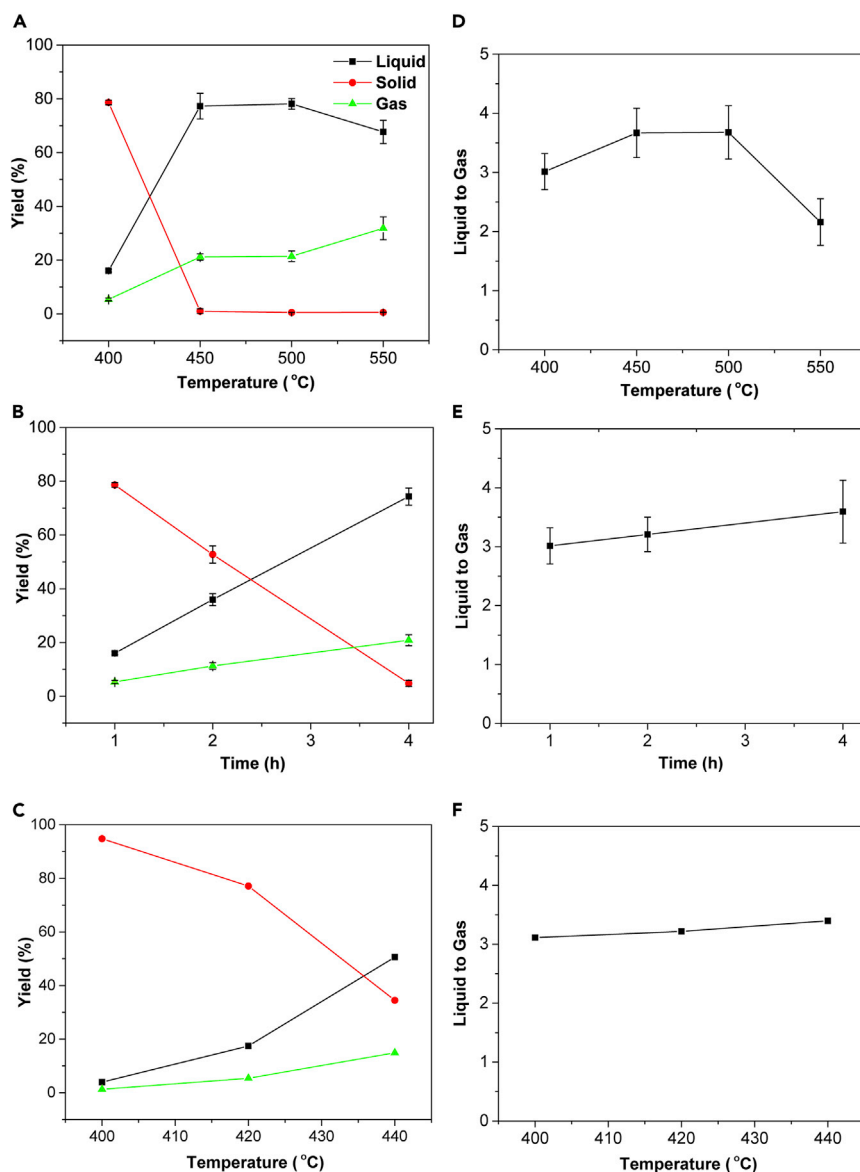


Figure 3. Results of polypropylene pyrolysis

Plots of temperature versus the pyrolysis products yield (A) or liquid to gas ratio (D) for polypropylene.

Plots of reaction time at temperature 400°C versus the pyrolysis products yield (B) or liquid to gas ratio (E).

Plots of temperature versus the products yield (C) or liquid to gas ratio (F).

solid and wax-like, respectively, whereas pyrolysis of other polymers obtained more liquid fuels. The pyrolysis reaction of PP leads to the highest amount of light oil fraction with a yield of 19.3%.

In respect of the gas distribution, the pyrolysis of PET and PVC containing a high quantity of heteroatoms (O and Cl) obtained a higher amount of noncondensable gases in comparison with hydrocarbon plastics; this might be attributed to loss of CO, CO₂, and HCl, which does not happen in hydrocarbon plastics during pyrolysis under an inert atmosphere. Theoretically, 58.7% HCl would be formed during PVC decomposition if the dehydrochlorination was complete. Miranda et al. (1999) discovered 58% gas loss was assigned to HCl and only less than 0.5% gas loss was attributed to other gases after the complete decomposition of plastics. In comparison, theoretically a 40.6%–58.3% loss for PET decomposition can be calculated at the basis of weight loss of CO and CO₂. Muhammad et al. (2015) found that nearly 35% gas loss was observed and more than 30% gas was assigned to the release of CO and CO₂. Similarly, in our study, a high amount of

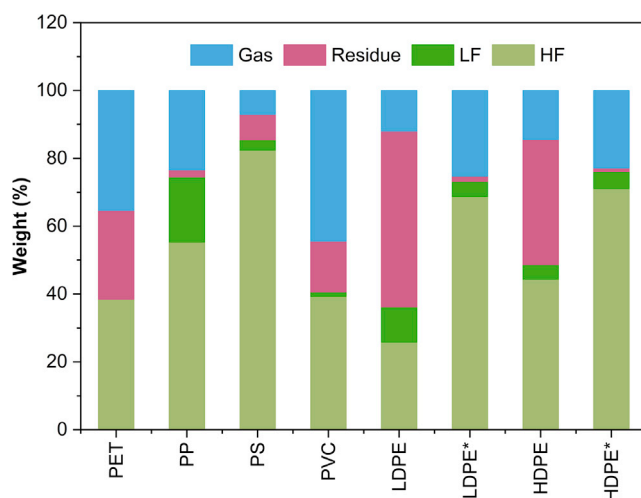


Figure 4. Product yield

Pyrolysis products yield at 450°C for individual plastics and 500°C only for LDPE and HDPE, indicated by (*) (LF stands for light fraction and HF for heavy fraction).

gas loss for PVC (44.4%) and PET (35.3%) was observed during pyrolysis. Among hydrocarbon plastics, PS has the least quantity of noncondensable gas formed after pyrolysis.

Structural characterization and mechanistic study

Pyrolysis oils including light and heavy fractions derived from plastic waste materials were analyzed by using GC-El-Orbitrap mass spectrometry. The data of four different materials are shown in Figure 5. The structural characterization was carried out by searching spectral libraries, and the results are summarized in Tables S1–S4, Schemes S1–S3, and Scheme 1 for all different polymer materials. There is a slight shift of dead volume time for GC chromatogram measured at different dates because of slight cuttings at the end of GC column. Pyrolysis of PP produces a lot propylene dimer and trimer derivatives. These derivatives contain not only linear alkenes (e.g., 2-methylpentene, 4-methyl-2-pentene) and dienes (e.g., 4-methyl-1,3-pentadiene) but also cyclic alkanes (e.g., 1,3,5-trimethylcyclohexane) and alkenes (e.g., 3,5-dimethylcyclopentene). Similar compounds can be detected from the pyrolysis oil obtained from LDPE with an emphasis on compounds derived from multiple ethylene units. A small amount of aromatics (e.g., toluene, m-xylene) can also be characterized. One significant difference is that a series of adjacent characteristic peaks can be observed, which has also been revealed before, but only with evidence of low resolution mass spectra data (Sharma et al., 2014; González-Pérez et al., 2015; Kumar and Singh, 2011). Serious attention should be placed on the identification of these heavier compounds. An alkane molecule with 12 carbon number can produce at least 355 isomers, and many of them cannot be found in mass spectral libraries, which makes the characterization of those heavier compounds extremely difficult.

But by using high-resolution Orbitrap mass spectrometry (Kondyli and Schrader, 2020), we can detect these molecular ions and their characteristic fragment ions with high mass accuracy, as the accurate mass data allow assigning elemental formulas for each detected signal. Therefore, the results presented in the table can give an indication of the types of high-molecular-weight compounds present in the pyrolysis oils. These characteristic signals are assigned to alkane and alkenes with the difference of one carbon unit.

The results for the other materials are a bit different. The data for the PS pyrolysis products only reveal monomer derivatives with the major components including toluene, ethylbenzene, and styrene. The pyrolysis products for PVC mostly consist of nonchlorinated hydrocarbons. Based on comparison with data from different databases, the spectra can be assigned to a number of different compounds, which allows proposing a corresponding mechanism, depicted in Scheme 2. Based on these data we can suggest that pyrolysis of olefinic polymers proceeds through a free radical mechanism, which corresponds well with data that have been reported about the thermal behavior of crude oil. Initially, random C-C bond

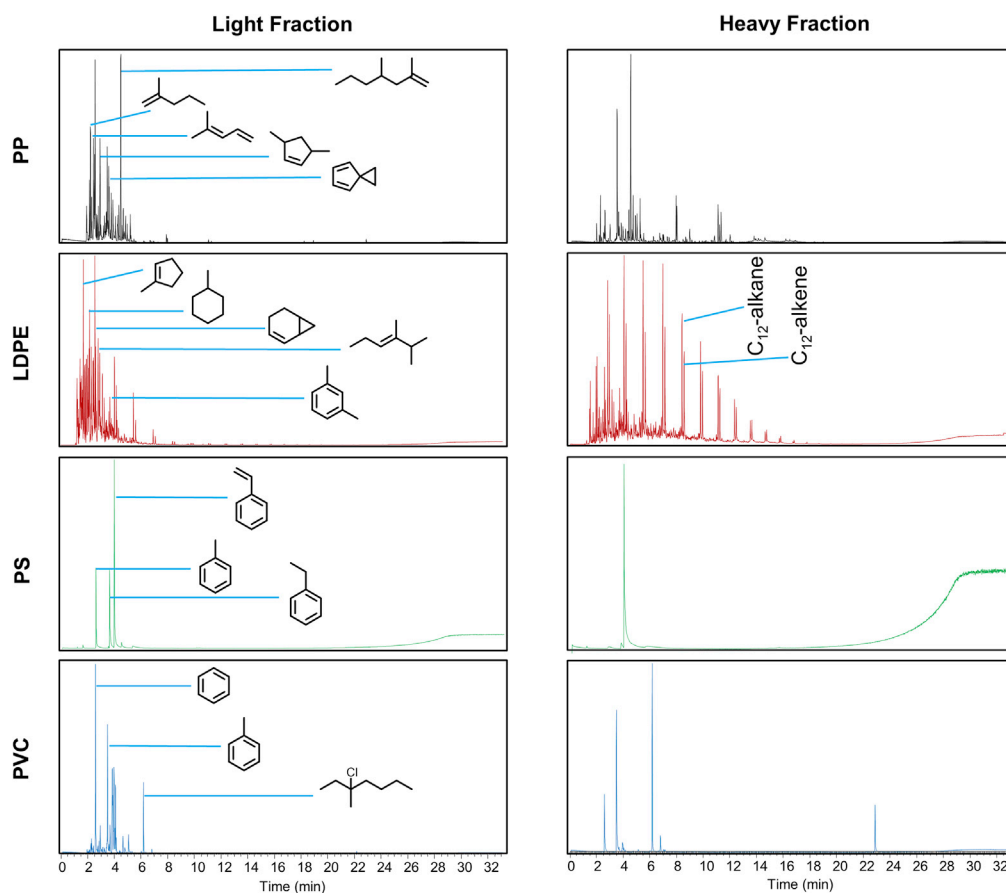


Figure 5. GC/MS results of light and heavy pyrolysis fraction

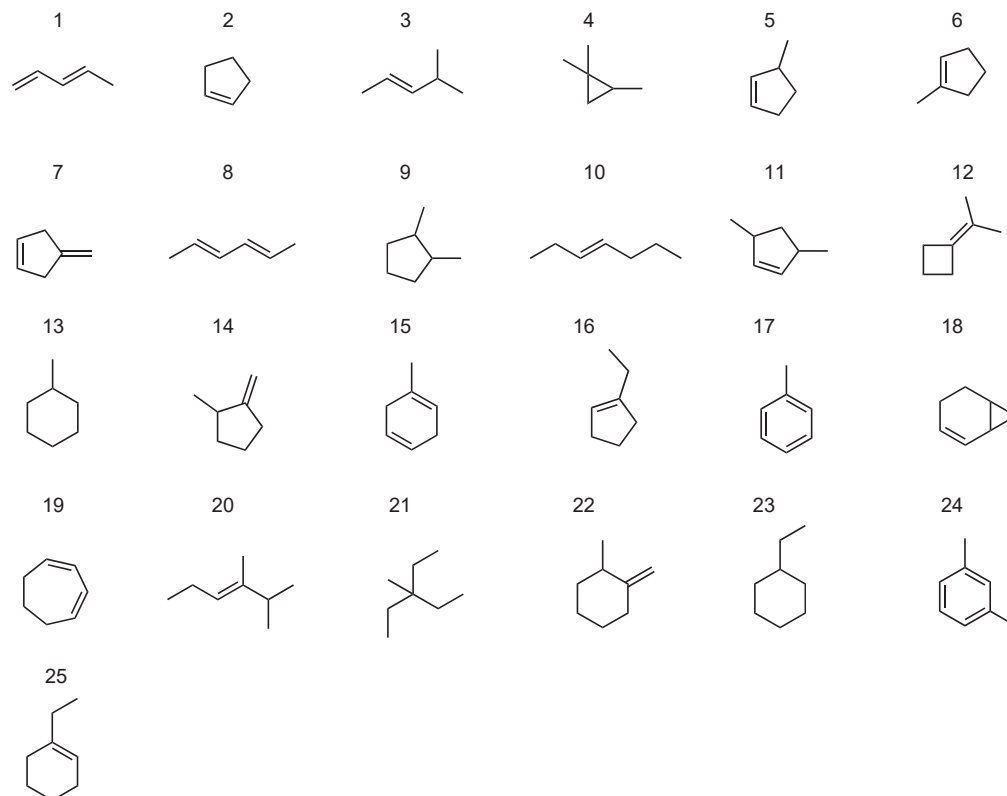
TIC signal of light (left) and heavy (right) fractions of plastics PP, LDPE, PS, and PVC pyrolysis oils obtained at 450°C. Detailed characterization of each GC/MS run is shown in the [supplemental information](#) in [Tables S1–S4](#) and [Schemes S1–S3](#).

cleavage along the polymer chain forms single radical species, followed by hydrogen re-arrangement to generate single radical isomers. Once these single radicals are formed, they can be consumed immediately by β -scission to produce smaller single radicals and alkenes or by β -H abstraction to generate alkenes. The formed alkene compound can further undergo another random C-C bond cleavage to produce a diene. A big polymer can also break at both sides to produce biradicals, followed by radical rearrangements and cyclization reactions to produce different cyclic rings. A diene and an alkene can form a cyclohexene through a Diels-Alder reaction, followed by removal of hydrogen or dealkylation to produce aromatic compounds. Two radicals can combine with each other to produce hydrocarbons with side chains of different length.

Fuel application

Gasoline and diesel are the most commonly used transport fuels, which are mainly produced by fractional distillation from petroleum oil. Gasoline generally consists of low-molecular-weight compounds with C_{5-11} , and diesel fuel is composed of molecules with C_{12-20} . This criterion can be used for evaluating the potential application of plastic fuels.

Comparison of the chromatograms obtained from light and heavy fraction of LDPE pyrolysis fuel shows that a good separation was achieved. The chromatogram of the light fraction shows compounds with a short retention time, eluting mainly within the first 7 min. After 7 min, the chromatogram contains a few heavier compounds (C_{12-20}) in very low intensity, which only contributes to 1.1% of the TIC (see [Figure 6](#)). In comparison, the chromatogram of the heavy fraction shows signals with high intensity in the retention time



Scheme 1. Structural motifs of pyrolysis products

The assigned structural motifs resulting from pyrolysis of LDPE.

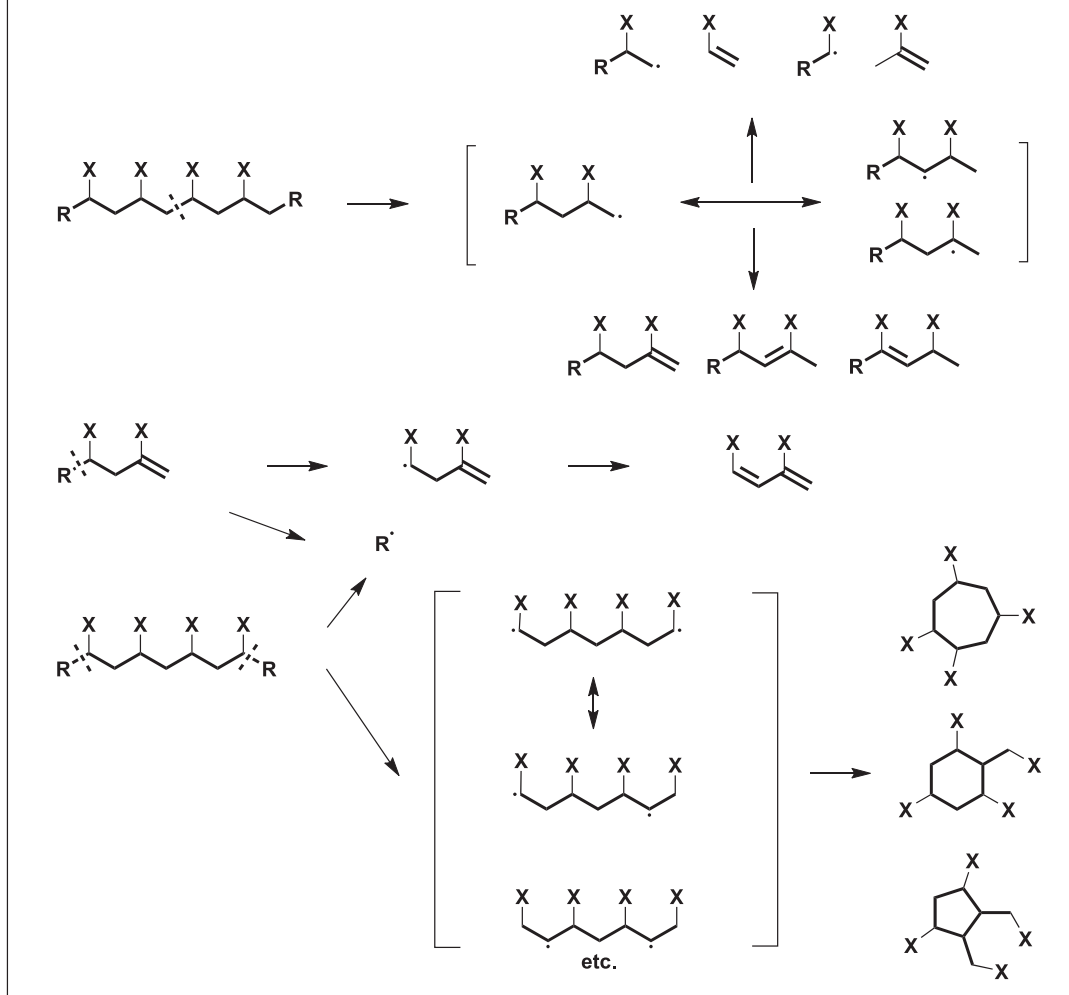
range 1–17 min. Heavy compounds with $C_{>20}$ can be detected. Semiquantification of this fraction shows that light compounds with $C_{\leq 11}$ (73.7%) have a higher amount than heavy compounds with C_{12-20} (26.2%).

For other plastic fuels light and heavy fractions, a slight (PP) or almost no clear (PS and PVC) separation was observed. The heavy fraction from PP also contains only a slight amount of heavy compounds (C_{12-20}) with 16.6%. Both light and heavy fractions of PS and PVC pyrolysis fuels display a low retention time in GC chromatography. Based on these analyses, the separation process using different cooling traps did not go well in our current experimental setup, which needs a better trapping efficiency, but it shows a potential to be used as alternative to fossil-fuel-derived gasoline and diesel range fuel, as both heavy and light fractions contain mainly compounds with $C_{\leq 20}$. To further improve the quality of those pyrolysis fuels, a clean-up step is required.

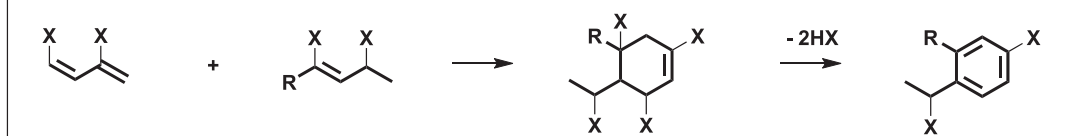
Conclusion

The large amount of different types of municipal waste materials can still be a valuable resource. Here, we could show that plastic waste is a valuable material and can be converted easily into a fuel. Different polymer waste materials such as PET, HDPE, PVC, LDPE, PP, and PS were investigated for their behavior during pyrolysis degradation. Thermogravimetric analysis for individual polymers was conducted to study the potential degradation behavior and to optimize the reaction conditions. Thermogravimetric analysis of PVC shows two degradation steps, whereas thermogravimetric analysis for other plastics gives a single degradation step with a degradation temperature order of $PS < PET < PP < HDPE \approx LDPE$. For the pyrolysis process, temperature and reaction time are two important pyrolysis parameters. A high temperature can significantly decrease the reaction time required for the pyrolysis process. The type of material also has a significant impact on the pyrolysis product distribution. The pyrolysis of PVC and PET produces a high amount of gaseous compounds, whereas the pyrolysis of PS produces the least amount of gas. Instead, the pyrolysis of PS produces the highest liquid yield. The pyrolysis liquid fuels derived from different plastic types were further studied by high-resolution GC-EI-Orbitrap, revealing the structural information about different fuels. A free radical mechanism was suggested, involving a series of reactions such as chain

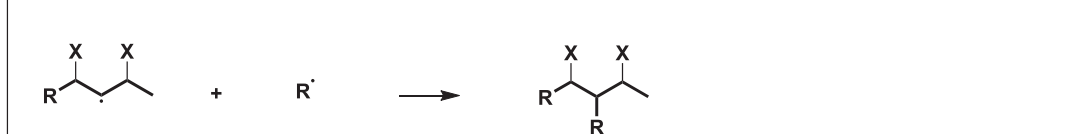
Chain scission, beta-scission, beta-H abstraction and cyclization



Diels-Alder reaction



Radical recombination



R = H or linear alkyl chain

X = H or methyl or phenyl group

Scheme 2. Proposed mechanism

Mechanism proposed for the pyrolysis of LDPE (X = H), PP (X = methyl group), and PS (X = phenyl group).

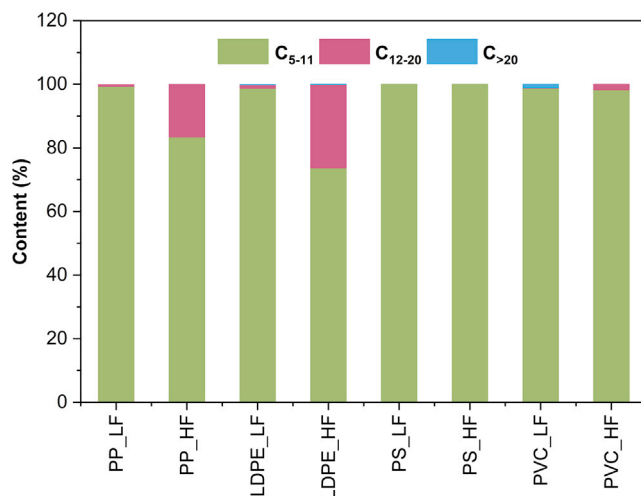


Figure 6. Fuel characterization

Semiquantification of light and heavy fraction from pyrolysis-derived plastic (PP, LDPE, PS, and PVC, respectively) fuels.

scission, beta-scission, beta-H-abstraction, cyclization, Diels-Alder reaction, and radical recombination. The fuel quality was simply evaluated for potential application of gasoline and diesel range fuels based on GC retention time. Overall, this study successfully demonstrated that pyrolysis is an efficient way to convert plastic wastes to fuels. A better understanding of the pyrolysis of plastic materials was also achieved through the systematic study of different types of plastic.

Limitations of the study

The mechanism shown here for the thermal degradation of polymers is based on analytical data and chemical understanding. Because of the fact that this is a very complex reaction mixture with multiple potential pathways, this can only be a first step in understanding such a reaction. Here, additional studies are necessary for a full understanding of the detailed mechanism.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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 - Materials availability
 - Data and code availability
- METHOD DETAILS
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 - Development of a pyrolysis reactor setup
 - Pyrolysis reactions
 - GC-EI-orbitrap mass spectrometry

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2022.104036>.

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AUTHOR CONTRIBUTIONS

Y.X. performed the experiments, analyzed the data; W.S. conceived and supervised the research; all authors participated in writing the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

Reagent or Resource	Source	Identifier
Chemicals, peptides and recombinant proteins		
polyethylene terephthalate (PET)	drinking bottles	from waste
polyvinylchloride (PVC)	shower gel bottles	from waste
high density poly ethylene (HDPE)	water tubing	from waste
low density poly ethylene (LDPE)	shampoo bottles	from waste
polypropylene (PP)	plastic pellets	
polystyrene (PS)	coffee cups	from waste
Dichloromethane	Fisher Chemicals	D/1850/17
potassium hydroxide (KOH)	JT Baker	CAS: 1310-58-3
Software and algorithms		
MassLib software	MSP Kofel, Zollikofen, Switzerland	https://www.msp.ch/
Mass spectrometer software Thermo Xcalibur 4.1	Thermo Fisher Scientific Inc	Dreieich, Germany

RESOURCE AVAILABILITY

Lead contact

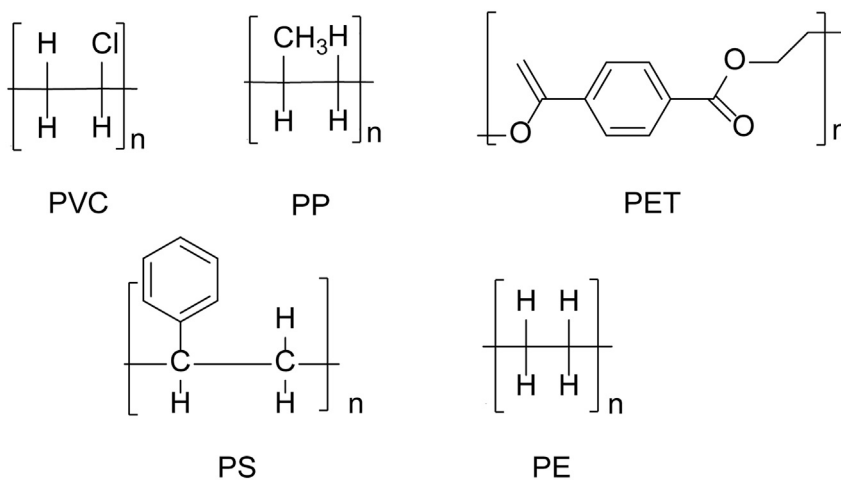
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Wolfgang Schrader (wschrader@kofo.mpg.de).

Materials availability

All materials generated in this study are available in the article and [supplemental information](#) or from the lead contact without restriction upon reasonable request.

Data and code availability

Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.



Structures of the polymers used in this study

METHOD DETAILS

Materials

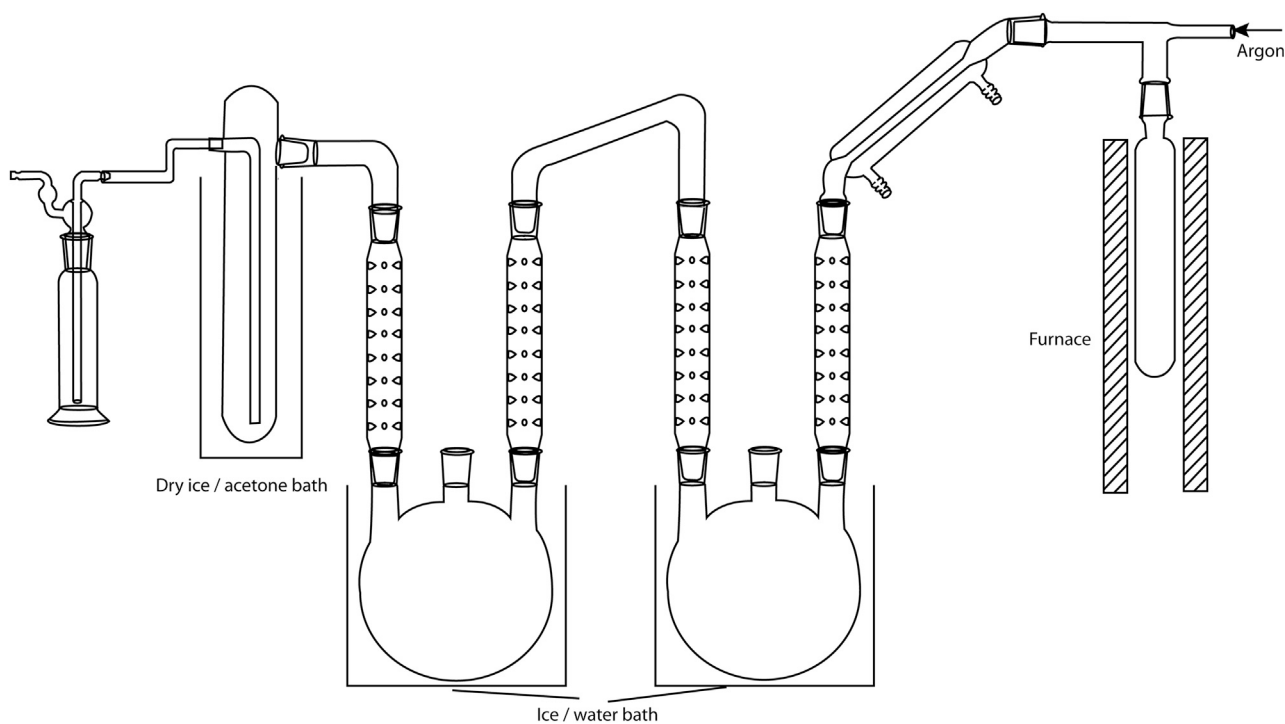
Six different polymer materials were used in this study. Household plastic waste was collected for PET (from drink bottles), HDPE (from shower gel bottles), PVC (from water tubing), PP (from shampoo bottles) and PS (from coffee cups). Labels for household plastic waste were removed, which were later washed with clean water, dried and shredded into small pieces. For LDPE, commercially available plastic pellets were used. The structures of these polymers are summarized in below figure.

Thermogravimetry

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC 1 Star System connected to data acquisition station. For each measurement, around 2 mg of sample were placed in the TGA cell at an inert gas (argon) flow rate of 40 mL min^{-1} . Each sample (plastic PP, PET, LDPE, HDPE, PS and PVC, individually) was heated from 35 to 750°C at a heating rate of $10^\circ\text{C min}^{-1}$. For plastic PP, additional experiments were carried out by heating the sample from 35 to 400 or 450°C and kept at this temperature for further 1 h reaction.

Development of a pyrolysis reactor setup

A lab scale pyrolysis system was developed as shown in below figure. The whole pyrolysis setup contains several parts: a 1480 W tube furnace (EVA 12/300 B, Carbolite Gero, Germany), a quartz tube reactor (H x W: 300 mm x 50 mm) with continuous argon supply, a cooling trap system and a waste gas cleaning part. The cooling trap system consists of a cooling water bridge that is followed by two different cooling steps. The first step consists of two consecutive ice water baths (4°C) and the second step is a single dry ice saturated acetone bath (-78°C). The waste gas cleaning container was filled with KOH saturated solution.



Setup of the pyrolysis reactor

Pyrolysis reactions

For the transformation of carbon based municipal waste a pyrolysis reactor was constructed and built. The setup is shown in Figure 1. The material is placed in a quartz tube that is then inserted into a tubular furnace (Carbolite Gero Type EVA 12/-/300/E301, Carbolite Gero, Neuhausen, Germany).

Pyrolysis of each material was carried out individually were around 20 g material each time was weighted and added into the reactor. Before starting pyrolysis reaction, the reactor was located and fluidized with argon continuously for roughly 20 min to remove air and humidity out of the system. For the reaction, the furnace was heated at a maximum heating rate of $100^{\circ}\text{C min}^{-1}$ until reaching to the desired temperature, followed by an isothermal step of 1 h. The reactor was continuously fluidized with an argon flow of 0.2 mbar during the transfer reaction process. After exiting the reactor, the pyrolysis volatiles passed through the cooling trap system consisting of two flasks using a ice/water bath for cooling and in a second stage using one cooling trap with dry ice/acetone. Inorganic gaseous halogens were removed by bubbling pyrolysis gas through KOH saturated solution. The products were collected from each cooling trap and weighted and then the two fractions from the first cooling trap were combined. Products on the surface of cooling water column were washed out with dichloromethane, dried under vacuum evaporation and weighted as well. The amount of residue left in the pyrolysis reactor was determined.

GC-EI-orbitrap mass spectrometry

GC/MS measurements were performed with a Q Exactive GC (Thermo Fisher, Bremen, Germany), consisting of a AI/AS 1310 autosampler equipped TRACE 1300 series GC coupled to a Q Exactive Orbitrap MS. The injection volume of an individual sample was 0.2 μL and dichloromethane was used as injector cleaning solvent. The sample injector was operated at 300°C and split mode was selected with a split flow of 80 mL min^{-1} , and a purge flow of 5 mL min^{-1} . High purity helium (N5.0) was used as a carrier gas at a constant flow rate of 1.2 mL min^{-1} . The GC separation was carried out on a RTX[®]-1ms capillary column (30 m \times 0.25 mm ID, 0.25 μm). The temperature program was performed with a starting temperature of 35°C , which was increased to a final temperature of 320°C at a heating rate of $10^{\circ}\text{C min}^{-1}$ and then held at 320°C for additional 5 min. Transfer line temperature was set to 320°C . The eluted compounds from GC were ionized by EI at an electron energy of 70 eV. The mass spectra were recorded in full scan mode with a mass range of 30–600 Da at a mass resolution of 120,000 (FWHM at m/z 200). Collected GC-MS data were imported and characterized against NIST and our own MPI libraries by using the MassLib software package (MSP Kofel, Zollikofen, Switzerland).