ISFR 2026

Proceedings of the 14th International Symposium on Feedstock Recycling of Polymeric Materials

Sunday, September 6th – Wednesday, September 9th 2026

NTI Hörsaal, Karlsruhe Institute of Technology

Engesserstraße 5, 76131 Karlsruhe, Germany

Keynote Speakers



Keynote: Advancing Material Circularity through Chemical Recycling and Industrial Integration

Prof. Toshiaki Yoshioka

Tohoku University, Japan

Dean, Graduate School of Environmental Studies
President of the Research Association for Feedstock Recycling of Japan (FSRJ)

Toshiaki Yoshioka has been a full professor in Tohoku University's Graduate School of Environmental Studies since 2005. He currently serves as Dean of the school and as President of the Research Association for Feedstock Recycling of Japan. He studied applied chemistry at Tohoku University and later held research appointments at Eindhoven University of Technology and the University of Hamburg. His work explores resource recovery from waste plastics, including PET conversion, catalytic pyrolysis, and the removal and recovery of halogens from PVC and flame retardant plastics. He also studies the recovery of metals and polymers from complex waste streams and the use of layered double hydroxides in water and gas treatment. He received the Honda Award for Recycling Technology Development in 2007, a MEXT Commendation for Science and Technology in 2014, and a commendation from Japan's Minister of the Environment in 2019.



Keynote: Process Intensification of Plastic Waste to Olefins

Prof. Kevin M. Van Geem

Ghent University, Belgium

Director of the Board of the Laboratory for Chemical Technology
Director of the Centre for Sustainable Chemistry

Kevin M. Van Geem joined the Laboratory for Chemical Technology at Ghent University as an assistant professor in 2010 and became a full professor in 2017. He is now a senior full professor and directs the Centre for Sustainable Chemistry at Ghent University. His international experience includes a period at MIT as a Fulbright Visiting Scholar in 2009. His research centers on thermochemical reaction engineering and olefin production, with applications in the chemical recycling of plastic waste. This work draws on detailed kinetic modelling with automated reaction mechanism generation, machine learning, reactor scale up, coke formation studies, and comprehensive two dimensional gas chromatography. He also led the ERC funded OPTIMA project and is managing director of AVGI, a Ghent University company that develops the COILSIM1D simulator.



Keynote: The Ecosystem of Thermochemical Recycling

Prof. Martin Seemann

Chalmers University of Technology, Sweden

Department of Environmental and Energy Sciences, Division of Energy Technology

Martin Seemann is full professor of Energy Technology at Chalmers University of Technology. His research career began with doctoral work at ETH Zurich on the methanation of synthesis gas in fluidized bed reactors. He joined Chalmers as associate professor in 2008 and was appointed full professor there in 2024. At Chalmers he has worked with the 2 to 4 MW research gasifier and the GoBiGas demonstration plant. His research addresses dual fluidized bed gasification, catalytic effects of bed materials, tar conversion, oxygen transport, and chemical looping, while recent studies extend this work to steam cracking and thermochemical recycling of mixed plastics, cable residues, textiles, and medical products. This work also considers how existing industrial plants can be adapted for recycled chemical feedstock production.



Keynote: Garbage in, Feedstock out: Plastic Pyrolysis for Solving the Mess We Made?

Prof. Henning Bockhorn

Karlsruhe Institute of Technology, Germany

Professor emeritus, Engler Bunte Institute, Combustion Technology

Henning Bockhorn is professor emeritus at Karlsruhe Institute of Technology. Following academic positions in Heidelberg and Kaiserslautern, he moved to Karlsruhe, where he directed the Institute for Chemical Technology from 1995 to 2009 and the Combustion Technology Division of the Engler Bunte Institute from 1998 to 2013. He was among the first to work on the feedstock recovery of plastics, publishing on the recycling of polyolefin waste by partial oxidation in 1985 and on a submerged flame process for the same purpose in 1989. His group went on to establish the thermal decomposition kinetics of polyethylene, polypropylene, PVC and polyamides and staged pyrolysis processes for feedstock recovery and chlorine removal. His parallel work on combustion science, in particular soot formation and oxidation, was recognized with the Jürgen Warnatz Gold Medal in 2016 and election as a Fellow of the Combustion Institute in 2018.

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Proceedings Information

Title

Proceedings of the 14th International Symposium on Feedstock Recycling of Polymeric Materials (ISFR 2026)
Karlsruhe, Germany, 6–9 September 2026

DOI: https://doi.org/10.5445/IR/1000198914

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Direct Catalytic Cracking of Crude Waste Plastic Pyrolysis Oil for High-Yield Light Olefin Production: From Catalyst Design to Pilot-Scale Circulating Fluidized Bed Operation

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Introduction

The rapid accumulation of plastic waste has emerged as one of the most critical challenges for modern industrial societies. While mechanical recycling remains effective for clean and well-sorted streams, its applicability is limited for contaminated, mixed, or degraded plastics. Thermochemical recycling, particularly the conversion of waste plastics into base chemicals, offers a promising pathway to close the carbon loop and establish a circular plastics economy [1,2]. Among potential target products, light olefins (ethylene, propylene, and butenes) are of particular interest due to their central role in the petrochemical industry.

Current commercial recycling routes typically rely on a multistep strategy consisting of plastic pyrolysis, extensive post-treatment of the resulting waste plastic pyrolysis oil (WPPO), and subsequent thermal steam cracking [2,3]. However, crude WPPO differs substantially from fossil-based naphtha in terms of carbon number distribution, olefin content, and impurity levels, necessitating dilution with fossil feedstocks or hydrogen-intensive hydroprocessing [3,4]. These additional steps significantly reduce the economic and environmental benefits of plastic recycling.

Catalytic cracking has the potential to overcome these limitations by enabling direct conversion of heavier, olefin-rich feedstocks at lower temperatures while offering higher olefin selectivity [3]. In particular, circulating fluidized bed reactor (CFBR) technology, widely established in fluid catalytic cracking (FCC), provides inherent advantages such as continuous catalyst regeneration, efficient heat integration, and scalability [4]. In this context, the direct catalytic cracking of crude WPPO in a CFBR represents a promising alternative to state-of-the-art recycling schemes.

Experimental

A microspherical phosphorus-modified steam-treated ZSM-5 catalyst (ms-P-HZSM5-S) was developed to withstand the severe hydrothermal conditions associated with continuous reaction-regeneration cycles [3]. Phosphorus modification has been shown to stabilize framework aluminum species and preserve acidity during high-temperature steam exposure, while steam pretreatment enables realistic assessment of long-term catalyst stability [1,3].

Initial performance evaluation was conducted in a micro-activity test (MAT) unit to compare catalytic cracking of crude WPPO with conventional naphtha under identical conditions [3]. Catalyst deactivation behavior was examined through repeated short-contact-time runs, followed by oxidative regeneration to evaluate activity recovery [3].

Subsequently, the process was demonstrated in a pilot-scale circulating fluidized bed reactor with a WPPO throughput of 1000 $g \cdot h^{-1}$. The CFBR system operates enabling continuous catalyst circulation, coke combustion in a dedicated regenerator, and stable heat supply to the riser reactor [4].

Results and Discussion

Catalytic cracking of crude WPPO over ms-P-HZSM5-S in the MAT unit resulted in markedly higher C_2-C_4 olefin yields compared to thermal cracking of hydrotreated WPPO fractions and both catalytic and thermal cracking of fossil-based naphtha [3]. Under optimized conditions, total C_2-C_4 olefin yields exceeded 55 wt %, highlighting the superior crackability of WPPO. This enhanced performance is attributed to the intrinsic properties of WPPO, which contains a high fraction of olefins and long-chain paraffins over a broad carbon number range (C_5-C_{24}) [3]. During time-on-stream operation, catalyst deactivation was primarily caused by coke deposition; however, complete recovery of catalytic activity was achieved through regeneration in air, confirming the robustness of the catalyst and the feasibility of cyclic operation [3].

Based on the laboratory findings, continuous catalytic cracking of crude WPPO was successfully demonstrated in a pilot-scale CFBR [4]. Compared to fossil-based naphtha, WPPO consistently yielded higher C_2–C_4 olefin production, with typical values of 44–46 wt % under optimized conditions [4]. Stable operation was maintained over a 24 h durability test, during which product yields and selectivities remained constant within narrow deviations [4] (**Figure 1**). Continuous coke removal in the regenerator effectively prevented irreversible catalyst deactivation, while the circulating catalyst provided the primary heat input for the endothermic cracking reactions. Importantly, the CFBR configuration enabled complete utilization of crude WPPO without prior fractionation or hydroprocessing, operating at temperatures significantly lower than those required for conventional steam cracking [4].

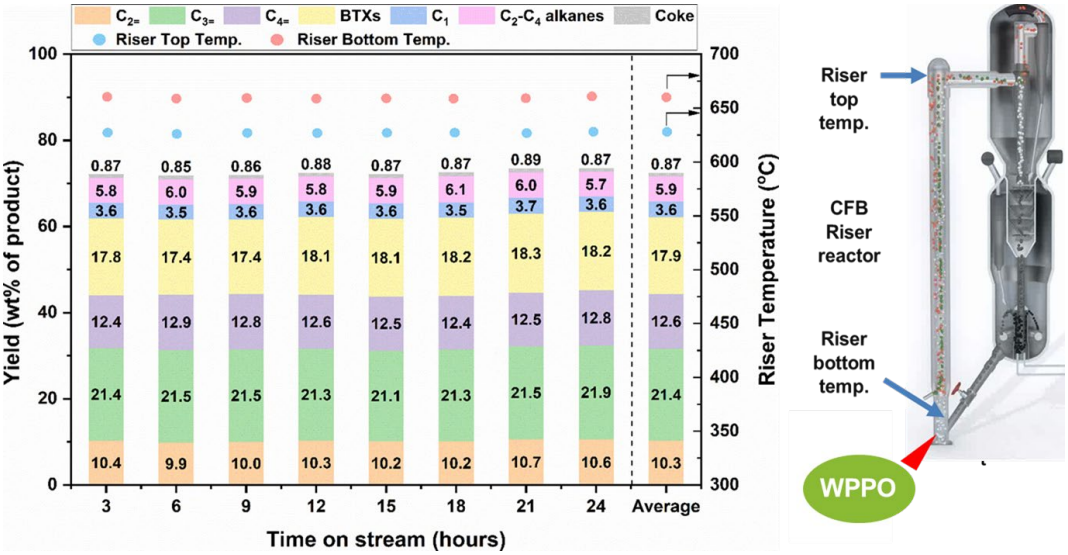


Figure 1. Product yields obtained through catalytic cracking in the pilot-scale CFBR system for 24 h (feed: crude WPPO; catalyst: ms-P-HZSM5-S; CCR = 20,000 g·h–1; feed rate = 1000 g·h–1; and COR = 20).

Conclusions and Outlook

This study demonstrates that direct catalytic cracking of crude waste plastic pyrolysis oil in a circulating fluidized bed reactor is a technically viable and scalable route for light olefin production [3,4]. The combination of hydrothermally stable P-modified ZSM-5 catalysts and CFBR reactor operation enables high olefin yields, continuous regeneration, and robust long-term performance.

Compared to state-of-the-art recycling schemes, the proposed approach offers complete utilization of crude WPPO, higher C_2-C_4 olefin yields, reduced energy demand, and elimination of hydrogen-intensive

post-treatment [3,4]. These features position catalytic WPPO cracking in CFBR systems as a promising cornerstone technology for circular petrochemical value chains (**Figure 2**).

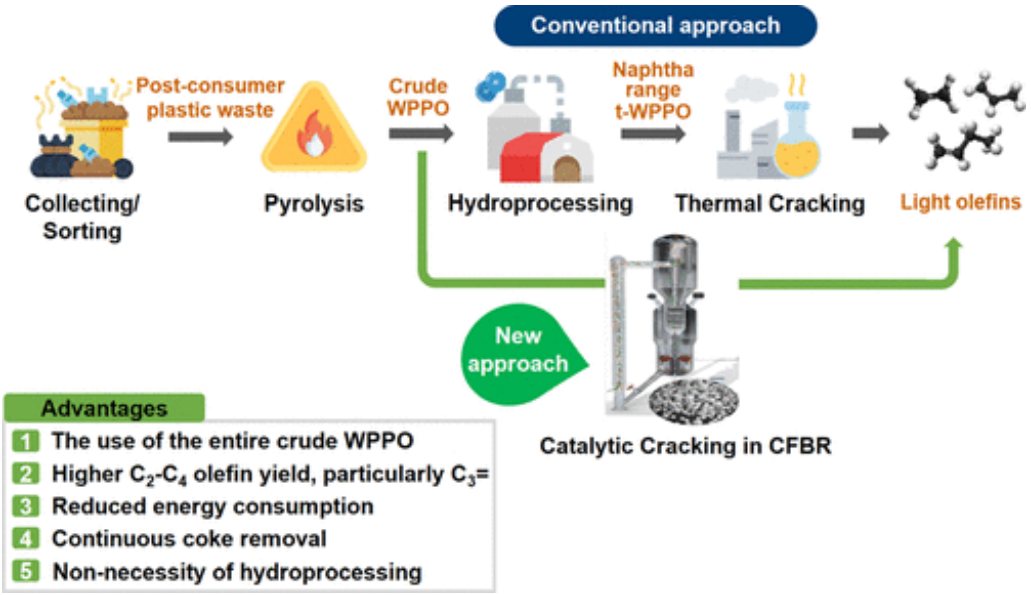


Figure 2. Thermochemical recycling of polyolefinic plastic waste using commercial schemes and our novel approach.

References

[1] Bockhorn, H.; Hornung, A.; Hornung, U.; Schawaller, D. J. Anal. Appl. Pyrolysis 1999, 48, 93–109.
[2] Scheirs, J.; Kaminsky, W. Feedstock Recycling and Pyrolysis of Waste Plastics; Wiley: Chichester, 2006.
[3] Tran, Xuan Tin; Mun, Dae Hun; Shin, Jiho; Kang, Na Young; Park, Dae Sung; Park, Yong-Ki; Choi, Jungkyu; Kim, Do Kyoung. Fuel 2024, 361, 130703.
[4] Tran, Xuan Tin; Kim, Eun Sang; Mun, Dae Hun; Jung, Taeyoung; Shin, Jiho; Kang, Na Young; Park, Yong-Ki; Kim, Do Kyoung. ACS Sustainable Chem. Eng. 2024, 12, 12493–12503.

Pyrolysis and catalytic upgrading of thermoplastic and thermoset polymers and composites

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Introduction

The rapid increase of plastic during the last decades led to the development of new technologies for their efficient end-of-life management. Traditional recycling methods, such as mechanical recycling proved to be inefficient due to the complex composition of commercial plastics as well as the low quality of the recycled products [1]. This limitation becomes even more critical in the case of thermosetting polymers, such as epoxy resins and phenol-formaldehyde (P-F) based resins, which form highly crosslinked 3D networks that cannot be remelted or reshaped. These materials are extensively used in coatings, adhesives, composites and engineered wood products, contributing significantly to the growing waste furniture stream, for which viable recycling routes remain limited.

Consequently, chemical recycling/upcycling emerges as an alternative approach for the conversion of both thermoplastic and thermosetting polymers into monomers, platform chemicals (phenolic/aromatic intermediates) and hydrocarbon fuels. Within this context, the most widely studied thermochemical (catalytic) depolymerization processes of polyolefins (most abundant polymer types in mixed plastic waste) are fast pyrolysis and hydrogenolysis [2]. Fast pyrolysis can provide py-oils enriched in olefins with a wide range of molecular weight. The use of appropriate catalysts, along with tuning of process conditions may reduce the molecular weight and narrow hydrocarbon distribution of derived oils, facilitating the downstream upgrading via hydrotreatment towards high quality fuels. In addition, via in situ catalytic pyrolysis upgrading, valuable light (C_2-C_4) olefins can be recovered along with the useful naphtha range (C_5-C_{12}) fractions [1, 2]. In parallel, thermochemical depolymerization of thermosetting polymers enables complementary pathways either toward closed-loop recycling through recovery of original monomers or precursors (e.g., bisphenol-A from epoxy-based systems) or toward catalytic upgrading into mono-aromatics suitable for re-integration into the petrochemical cycle. This work presents recent results on thermochemical conversion of both thermoplastic and thermosetting polymers and investigates the effect of catalysts physicochemical properties on depolymerization efficiency, monomer recovery and total composition of the produced hydrocarbon and oxygenated streams.

Experimental

Regarding thermoplastics, pristine polymers (LDPE, etc.) and real consumer plastics were used as feedstocks for the pyrolysis study. The plastics products were characterized by proximate and ultimate analysis (CHNS/O), ATR spectroscopy, SEM/EDS and TGA/DSC to determine their structural, compositional and thermal properties, as well as the presence of additives. The thermosets used comprised of epoxy and phenol-formaldehyde (PF) based resins/polymers. Lignin-modified epoxy

polymers were synthesized using BPA-based epoxy resin (EPON828, DGEBA) partially replaced by glycidylized Kraft lignin (GKL) and were thermally cured with a polyether diamine (Jeffamine D230) [3]. The Lignin-Phenol-Formaldehyde (LPF) resin was prepared by reacting phenol, formaldehyde and organosolv lignin (extracted from vine pruning) under basic conditions. Particle boards (being the main component of a wide variety of modern furniture) were prepared using the PF/LPF phenolic resins and vine pruning chips by mechanical mixing and standard hot pressing procedures. Representative pictures of the materials used as feedstocks for the pyrolysis experiments are shown in Figure 1.

Fast pyrolysis experiments were conducted in a bench-scale fixed-bed reactor under continuous N_2 flow. Thermal runs employed inert silica sand (heat carrier), whereas in-situ catalytic upgrading was performed using a plastic/catalyst mass ratio of 10/1. Pristine LDPE was used as reference polyolefin feedstock, along with real plastic products such as packaging films or garbage bags. Non-condensable gases were analyzed offline via GC-FID/TCD, while the liquid products were analyzed by GC-MS/FID, PIONA and SIM-DIS. The catalysts studied for the in-situ upgrading of plastic waste py-oils were aluminosilicate materials, mainly zeolitic, with different porous and acidic properties.



Figure 1. Thermoplastic and thermosetting feedstocks: Pristine PE and PE-based consumer plastics, lignin-epoxy composites, cured LFP resins, and PF-based particle board.

Results & Discussion

Real PE based streams exhibited negligible moisture (<0.8 wt.%), confirming suitability for direct thermochemical processing. Ash content varied significantly, reaching 6-8 wt.% in LDPE garbage bags due to $CaCO_3$ fillers and minor Ti-containing residues, as confirmed by SEM/EDS. Elemental analysis showed a typical hydrocarbon composition (C:85-92 wt.%, H:8-15 wt.%) with nitrogen and sulfur below detection limits, favorable for clean thermochemical conversion. ATR spectra deviations were attributed to additives. TGA revealed melting in the 112-135 ºC range and a primary degradation window between 420-480ºC, consistent with the radical chain scission of polyolefins.

The non-catalytic (thermal) fast pyrolysis of LDPE at 450ºC was kinetically limited, leading to the formation of heavy waxes (90 wt.%), minor liquid oil (6.5 wt.%) and low gases (3.5 wt.%, mainly C_2-C_4 olefins). The liquid fractions contained mainly (di-, α-)olefins and fewer paraffins (C_5-C_{23}), whereas the waxes contained long-chain hydrocarbons extending up to C_{100}. In-situ catalytic upgrading experiments altered product distribution by decreasing heavy residues (up to ca. 90%) and increasing both condensable liquids (up to ca. 70 wt.%) and gases (up to ca. 40 wt.%), depending on catalyst properties and the pyrolysis temperature. The resulting oils exhibited narrower MW distribution, mainly within the C_5-C_{12} range. Catalyst structure dictated product selectivity, with medium-pore ZSM-5 promoting deep cracking and gases production, increasing total C_2-C_4 (monomers) yields to 35-40 wt.% on feed. In contrast, large-pore BEA topologies favored selective formation of gasoline-range hydrocarbons, with C_5-C_{12} species accounting for up to 60 wt.% of total products. USY zeolite exhibited noticeable hydrogen transfer activity, slightly enhancing n-/iso-paraffins formation along with substituted aromatics, yet without fully suppressing the high olefinicity of the derived oils. Therefore, a subsequent hydrotreatment is required to convert olefins to (iso-)paraffins when fuel fractions or light olefins (via downstream steam cracking) are aimed.

Pyrolysis of thermosets, P(lignin)-F resins related to furniture waste for example, yielded phenolic-rich liquid streams the composition of which has a strong dependence on temperature. Non-catalytic fast

pyrolysis at 400-600°C produced 30-55 wt.% bio-oil, 10-25 wt.% gases and 22-37 wt.% char, with the liquid fraction dominated by alkyl-phenols (52-75%), along with minor alkoxy-phenolic compounds (lignin derived) and limited oxygenates.

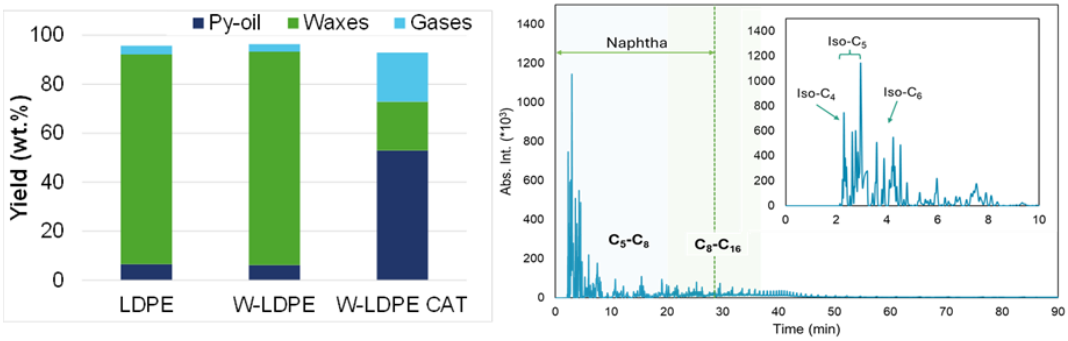


Figure 2. Non-catalytic (thermal) and catalytic (upgrading) pyrolysis of pristine LDPE polymer and real consumer plastic (LDPE based garbage bags). The chromatogram (right side) refers to the catalytic upgrading of pyrolysis vapors with ZSM-5 zeolite catalyst.

In-situ catalytic upgrading over acidic zeolites (e.g., ZSM-5) shifted bio-oil's chemical profile toward mono-aromatics (BTX) and napthalenes via transalkylation and deoxygenation, thus favoring upcycling into petrochemical intermediates rather than phenol recovery.

On the other hand, fast pyrolysis of lignin/epoxy composites (e.g., GKL-DGEBA epoxy materials) at 550 °C yielded up to 82 wt.% liquid, with limited gas formation (6 wt.%) and solid residue below 10 wt.%. Remarkably, the condensable fraction was strongly enriched in bisphenol-A (BPA), reaching concentrations up to 60%, along with lower amounts of phenolic monomers (~25%), confirming the efficient thermal cleavage of ether linkages within the epoxy network. In-situ catalytic upgrading over the same reference ZSM-5 catalyst (Feed/cat ratio=1/1) shifted selectivity toward simpler alkyl-phenols (45% conc.) and BTX aromatics (~20%) by cracking/deoxygenating the thermally formed BPA monomer. At the same time, py-oil yield was slightly reduced to 65 wt.% and gas production was mildly increased to ~12 wt.% (primarily CO, CO_2).

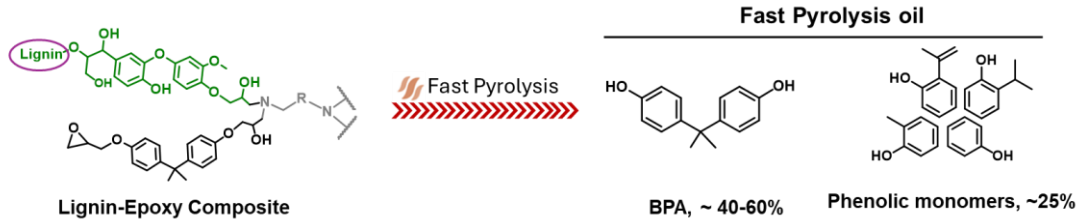


Figure 3. Non-catalytic (thermal) pyrolysis of lignin-modified epoxy polymer, based on DEGBA and diamine curing agents.

References

[1] Ragaert, K., Delva, L., Van Geem, K.: *Mechanical and chemical recycling of solid plastic waste*, Waste Management, 69, 24-58, 2017.

[2] Hu, K., Yang, Y., Wang, Y., Xiaoguang Duan, X., Wang, S.: *Catalytic carbon and hydrogen cycles in plastics chemistry*, Chem Catalysis, 4, 724-761, 2022.

[3] Pappa, C.P., Cailotto, S., Gigli, M., Crestini, C., Triantafyllidis, K.S.: *Kraft (Nano)Lignin as Reactive Additive in Epoxy Polymer Bio-Composites*, Polymers, 16(4), 553, 2024.

Acknowledgments. This project was carried out within the framework of the National Recovery and Resilience Plan Greece 2.0, funded by the European Union NextGenerationEU (Implementation Body HFRI). K.T., A.T., N.M. and N.S. would also like to acknowledge the support from King Fahd University of Petroleum and Minerals, Deanship of Research via project CUP24201.

Base-mediated degradation of epoxy thermosetting resins to form monomeric products

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Efficient technologies for achieving organic resource circularity to ensure a sustainable supply are essential. Nowadays, intense efforts are devoted to material and chemical recycling of plastics. Chemical recycling can convert plastics to raw materials via the chemical reactions involving main chain cleavages of plastics. This method is effective for plastics that are difficult to perform material recycling such as thermosetting resins and composite plastic materials, and whose main chains are easily cleaved. For this reason, many engineering plastics such as polyesters, polycarbonates, and polyamides have been focused on the reprocessing into raw organic materials and monomers.

Epoxy thermosetting resins, that are durable and light weight resin materials with excellent adhesive properties, have been widely used in various industrial products such as adhesives, electronic devices, automobiles, and wind turbine blades. In fact that the epoxy thermosetting resin materials usually contain valuable materials such as copper wires, magnets including rare metals, and carbon fiber, the development of chemical recycling methods for epoxy thermosetting resins attracts considerable attention to recover such valuable sources. , low-molecular-weight components were able to be reproduced from epoxy thermosetting resins using stoichiometric amounts of bases, Lewis or Brønsted acids, or transition metal catalysts. The base-mediated degradation method has been studied as a straightforward means of fluidifying and degrading them.[1] Beckham's group and Skrydstrup's group reported that this method was applicable to the production of organic raw compounds of monomers such as bisphenols.[2,3]

Herein we report recent studies for the base-mediated degradation of epoxy thermosetting resins. First is that the NaO*t*Bu-mediated degradation of thermosetting epoxy resins in amide solvents at 150 °C to obtain bisphenols as the monomer precursors, which are components of the polymer chains. The conditions could be applied to various epoxy thermosetting resins synthesized with a variety of curing agents, such as diamino arenes, ethylene diamine, dithiols, and acid anhydrides (Figure 1 upper).[4] This method was promoted by amide solvents. In other words, other solvents such as toluene and water are difficult to be used for the base-mediated degradation. To overcome this limitation, an effective

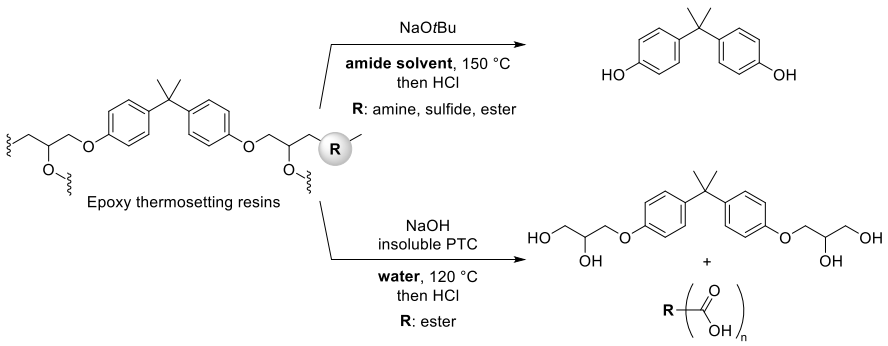


Figure 1. Degradation of epoxy thermosetting resins

promoter for epoxy thermosetting resins seems to be required. Based on this idea, second is the degradation of anhydride-cured epoxy thermosetting resins via simple de-esterification using water–lipophilic trioctylmethylammonium salt mixtures and NaOH 120 °C proceeded to form 3,3'-((propane-2,2-diylbis(4,1-phenylene))bis(oxy))bis(propane-1,2-diol) and dicarboxylic acid sodium salt (Figure 1 lower).[5]

Many epoxy thermosetting resins are prepared by the polycondensation of BADGE (bisphenol A diglycidyl ether) with various curing agents. For this reason, epoxy thermosetting resins usually have hydroxy group on the main chain and ether bonds at β position to the hydroxy group. Thus, activation of this hydroxy group by a base followed by the intramolecular attack to the ether moiety generates arenoxide products. So, we examined the degradation of a densely networked epoxy thermosetting resin prepared by BADGE and 4,4'-diaminodiphenylsulfone (DDS). As a result, use of NaO*t*Bu as a soluble strong sodium base and DMI solvent effectively underwent the degradation at 150 ℃ followed by the filtration and HCl treatment to obtain bisphenol A in a high yield (Figure 2). DMI solvent was effective for the degradation whereas non-polar xylene and water were not effective. In fact, mass of the resin increased via the swelling at 150 ℃ in DMI solvent. This effect as well as the solvation probably brings a soluble base to inside the resin and promotes the cleavage of the main chains. In the conditions, various curing agents such as imidazole, dithiols, and acid anhydrides were applicable to this degradation. Moreover, carbon fiber- or glass fiber-reinforced epoxy resins were used in the degradation to from bisphenols with recovering carbon or glass fibers.

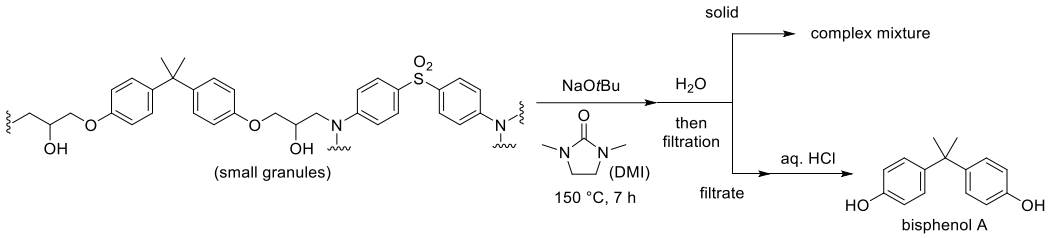


Figure 2. Degradation of amine-cured epoxy thermosetting resin prepared from BADGE and DDS

Chemical recycling ideally requires simple and environmentally friendly reaction conditions while reducing the use of petrochemicals. From this perspective, water is a preferred medium for chemical recycling. Traditionally, epoxy thermosetting resins have been degraded in water solvent under acid-mediated or hydrothermal conditions. However, the lack of methods for a precise and uniform main-chain cleavage hampers the selective recovery of low-molar-mass species; accordingly, these approaches have been primarily used for recovering fibers from fiber reinforced plastics rather than for a selective organic chemical production. Under these circumstances, Connon and co-workers reported that ammonium and phosphonium salts having long-chain alkyl groups are shown to be effective phase transfer catalysts (PTCs) for alkaline (sodium hydroxide) hydrolysis of poly(ethylene terephthalate) in water.[6] Based on the above, we found that two-phase water–lipophilic trioctylmethylammonium salt mixtures conditions are suitable for the degradation of anhydride-cured epoxy thermosetting resins with NaOH at 120 ℃ via simple de-esterification. After the degradation, PTC-based organic layer contained a corresponding tetraol product and water layer have dicarboxylic acid sodium salt, which was treated with HCl to form the corresponding dicarboxylic acid.

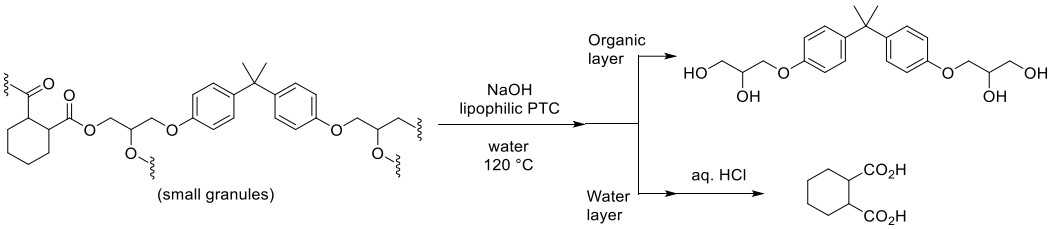


Figure 3. Degradation of anhydride-cured epoxy thermosetting resin prepared from BADGE and acid anhydrides

References

[1] For a example, see: Japanese patent JP 2002-363339.
[2] DiPucchio, R. C., Stevenson, K. R., Lahive, C. W., Michener, W. E., Beckham, G. T.: *Base-Mediated Depolymerization of Amine-Cured Epoxy Resins*, *ACS Sustain. Chem. Eng. 11*, 16946 (2023).
[3] Sun, H., Ahrens, A., Batista, G. M. F., Donslund, B. S., Ravn, A. K., Schwibinger, E. V., Nova, A., Skrydstrup, T.: *Solvent–Base Mismatch Enables the Deconstruction of Epoxy Polymers and Bisphenol A Recovery*, *Green Chem. 26*, 815 (2024).
[4] Minami, Y., Tsuyuki, T., Ishikawa, H., Shimoyama, Y., Sato, K., Yoshida, M.: *Degradation of Stable Thermosetting Epoxy Resins Mediated by Bases in Amide Solvents*, *Polym. J. 57*, 149 (2025).
[5] Minami, Y., Kato, T., Hungwe, D., Yamasaki, Y., Sato, K., Yoshida, M.: *Degradation of Anhydride-Cured Epoxy Thermosetting Resins Promoted by Two-Phase Water–Ionic Liquid Mixtures*, *ChemSusChem in press*.
[6] Anderson, L. B., Molloy, C., Pedrini, L., Martin, I. L., Connon, S. J.: *Effect of a phase transfer catalyst structure on the alkaline hydrolysis of poly(ethylene terephthalate)*, *Green Chem. 26*, 11125 (2024).

Strategies to Prevent Nitrogen-Induced Catalyst Deactivation in Catalytic Plastic Pyrolysis

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Introduction

To increase the recycling rates of plastic waste, thermochemical recycling processes have been investigated for decades as a complement to mechanical recycling. Previous studies at the KIT have demonstrated that catalytic pyrolysis of polyolefin-rich plastic waste over microporous zeolites presents a promising pathway, as it yields high amounts of C_2 to C_4 olefins and valuable by-products such as benzene, toluene, ethyl benzene and xylenes (BTEX) [1]. However, when heterogeneous plastic waste streams containing nitrogen-bearing polymers such as polyamides are pyrolyzed, the catalytic pyrolysis products begin to resemble those of non-catalytic pyrolysis, accompanied by a pronounced increase in coke formation. This behaviour is attributed to catalyst deactivation [1]. The nitrogen-induced deactivation represents a critical bottleneck for the scale-up of catalytic plastic pyrolysis, because feedstock variability cannot always be avoided in industrial recycling streams. Addressing the deactivation mechanism therefore requires a strategy that either removes the nitrogen species before they encounter the catalyst or supplies a sufficient amount of catalyst to offset the loss of active sites during catalytic pyrolysis.

Objectives

In this study, nitrogen-induced catalyst deactivation was mitigated through two complementary strategies. First, bentonite and calcium hydroxide were evaluated as a reactive sorbent minerals for their ability to capture and convert basic organic nitrogen species into less deactivating forms in pyrolysis conditions. Second, additional catalyst was introduced to counteract the fraction of active sites deactivated during the catalytic pyrolysis. The dual-approach hypothesis assumes that sorbents will lower the concentration of strongly deactivating nitrogen-containing compounds reaching the catalyst, and a calculated addition of catalyst, based on the measured deactivation rate, will maintain stable enable stable C_2 to C_4 olefin yields during the catalytic cracking of nitrogen-containing pyrolysis vapors at pilot scale.

Methodology

Systematic catalytic pyrolysis experiments were conducted on a kilogram scale screw pyrolysis reactor with an integrated fixed or moving bed reactor. Low-density polyethylene (LDPE) blended with 5 wt% polyamide-6 (PA-6) as a model feedstock was pyrolyzed in the screw reactor at a temperature between 450 to 550 °C. The resulting pyrolysis vapor was subsequently catalytically cracked in a downstream fixed bed loaded with a microporous zeolite with a catalyst-to-plastic ratio of 0.02 wt/wt at a temperature between 450 to 550 °C, and gaseous and liquid products were separated in a condenser. The sorbent was either introduced into the screw reactor along with the feedstock or in the fixed bed prior to the catalytic fixed bed. The amount of zeolite added beyond the baseline loading was calculated from the observed drop in C_2 to C_4 olefin selectivity, which served as a proxy for active-site loss. The gaseous products were identified and quantified using a gas chromatograph (GC) coupled with thermal conductivity (TCD) and flame ionization detector (FID), as well as a mass spectrometer (MS), while the liquid products were identified and quantified using proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) and a two-dimensional-GC coupled with a FID and MS.

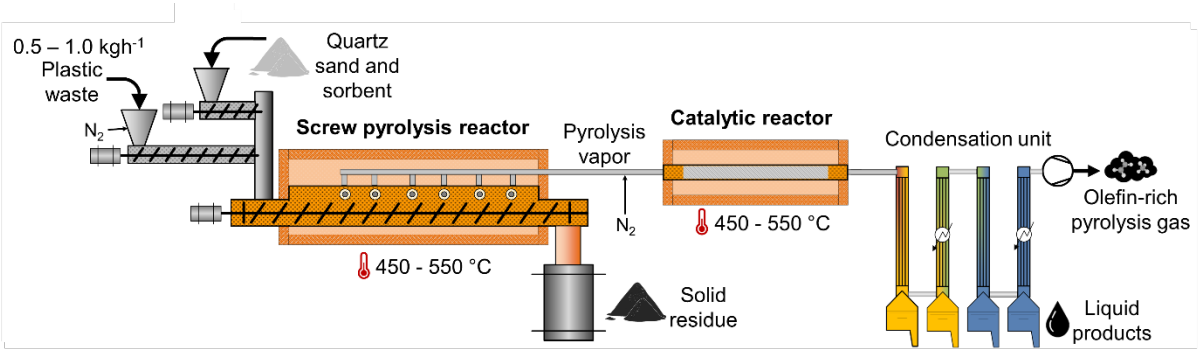


Figure 1. Schematic of the two-stage catalytic pyrolysis plant in kg-scale.

New results in sorption of nitrogen species and catalyst deactivation counteracting

The resulting mass balances and detailed gas and liquid product compositions reveal that adding 5 wt% PA-6 to LDPE led to rapid catalyst deactivation, visible in a decline in C_2 to C_4 olefin yield as well as in typical catalytic pyrolysis products such as BTEX over time on stream. In contrast, the application of bentonite or calcium hydroxide as sorbents in the pyrolysis reactor showed less catalyst deactivation, maintaining C_2 to C_4 olefin yields at a level closer to operation without nitrogen-containing species in the feedstock.

Analytical characterization of the gas and condensable fractions indicates that the sorbents not only adsorbed nitrogen-containing compounds but actively converted them into nitrogen species that exhibited less deactivating effect on the catalyst.

Based on the measured deactivation over time, the required supplementary catalyst mass to restore the original C_2 to C_4 olefin output was determined. Applying this calculated supplement restored C_2 to C_4 olefin yields to levels indistinguishable from the nitrogen-free case, while maintaining the same product distribution for BTEX aromatics and reducing coke formation.

Conclusion

This work demonstrates that nitrogen-induced catalyst deactivation, a current key limitation in the catalytic pyrolysis of mixed plastic waste, can be effectively mitigated by sorbents placed in the pyrolysis reactor, which bind and convert basic organic nitrogen species before they interact with the catalyst. By implementing additional catalyst compensating for the active-site loss caused by the nitrogen-containing compounds, the catalytic performance was maintained over the experiment. These findings contribute to the development of more flexible and feedstock-tolerant catalytic pyrolysis processes, which are essential for advancing plastic waste recycling technologies toward industrial implementation.

References

[1] Netsch et al.: *Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis,* Chemie Ingenieur Technik, 95(8), 1305-1313, 2023

Effect of impurities on Ru catalysis in hydrogenolysis of polyethylene

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General Information

Plastics are produced in large quantities worldwide; however, most of them are discarded after a single use and are not recycled. The accumulation and dispersion of such waste plastics lead to severe environmental pollution, prompting growing interest in technologies that chemically transform them into valuable chemicals. Among various plastics, polyolefins such as PE and PP comprise a large share of them. Therefore, their conversion to valuable chemicals is expected to have a significant impact. Pyrolysis is commonly used as a transformation method for the chemical recycling of polyolefins. However, it typically requires harsh conditions, such as high temperatures above 673 K, which provide high gas products and produce a mixture of various compounds, including aromatic compounds. On the other hand, hydrogenolysis of the C-C bonds in polyolefins offers a promising method for the transformation of polyolefins into valuable saturated hydrocarbons under mild conditions. Our group has reported that heterogeneous Ru-based catalysts, such as Ru/CeO_2 [1,2], Ru/ZrO_2 [2] and Cu-Ru/CeO_2 [3] catalysts, exhibit high activity for the hydrogenolysis of polyolefin, providing high yields of valuable chemicals such as liquid chemicals (C5-C21) and waxes (C≥22) by suppressing the formation of gas (C1-C4) products. However, some additives commonly incorporated to enhance plastic performance, such as fillers, pigments, and stabilizers, as well as impurities introduced during manufacturing and recycling processes are inevitably included in waste plastics. However, the effect of these impurities has not been sufficiently investigated in the hydrogenolysis of polyolefins over Ru-based catalysts. In this study, we investigated the poisoning effects of various potential impurities on the hydrogenolysis of polyethylene over a Ru/ZrO_2 catalyst. Moreover, we examined the introduction of second metal oxides into ZrO_2 to improve tolerance to model impurities [4].

Experimental

Ru/ZrO_2 catalysts were prepared by impregnating a $Ru(NO)(NO_3)_3$ in diluted nitric acid onto ZrO_2 (DAIICHI KIGENSO KAGAKU KOGYO) calcined at 1073 K for 3 h. Ru/MO_x-ZrO_2 catalysts were also prepared by the same method using various supports (M = Al, La, Ce and W). The obtained catalyst was heated at 573 K under N_2 for 1 h before the reaction. The Ru loading is 5 wt%. The reaction was conducted in an autoclave containing 3.4 g of low-density polyethylene (LDPE, M_n = 1700, M_w = 4000) and the catalyst under 6 MPa H_2 and 513 K. The products were analyzed by GC-FID, and conversion was calculated based on the weight of the solid residue.

Results and discussion

We examined the poisoning effects of model organic compounds such as ethyl sulfide, pyridine and butyl amide, and inorganic compounds such as TiO_2, ZnO, NaCl, and $CaCO_3$ on the hydrogenolysis of LDPE over a Ru-supported ZrO_2 (Ru/ZrO_2) catalyst (Figure 1). Ethyl sulfide strongly inhibited the hydrogenolysis of LDPE even at the ethyl sulfide/Ru ratio of 4. On the other hand, pyridine, TiO_2, ZnO, NaCl, and $CaCO_3$ showed almost no influence on the conversion and selectivity, although the conversion decreased with the introduction of a large amount of butyl amide (the ratio of 20 to Ru).

To develop catalysts resistant to sulfur-containing compounds, we prepared Ru catalysts supported on ZrO_2-based metal oxides mixed with various metal oxides. Ru/Al_2O_3–ZrO_2 catalyst showed no significant decrease in conversion even when ethyl sulfide was introduced at four times the Ru loading amount. The spent catalysts were recovered and characterized by various methods such as XRD, ICP-AES, and XPS, revealing that ethyl sulfide converted metallic Ru on the Ru/ZrO_2 catalyst to RuS_2 during the reaction, thereby deactivating the catalyst for polyethylene hydrogenolysis. In contrast, Al_2O_3–ZrO_2

support in the Ru/Al2O3–ZrO2 catalyst suppressed the formation of RuS_2 from Ru metal and ethyl sulfide, which accounts for the high resistance.

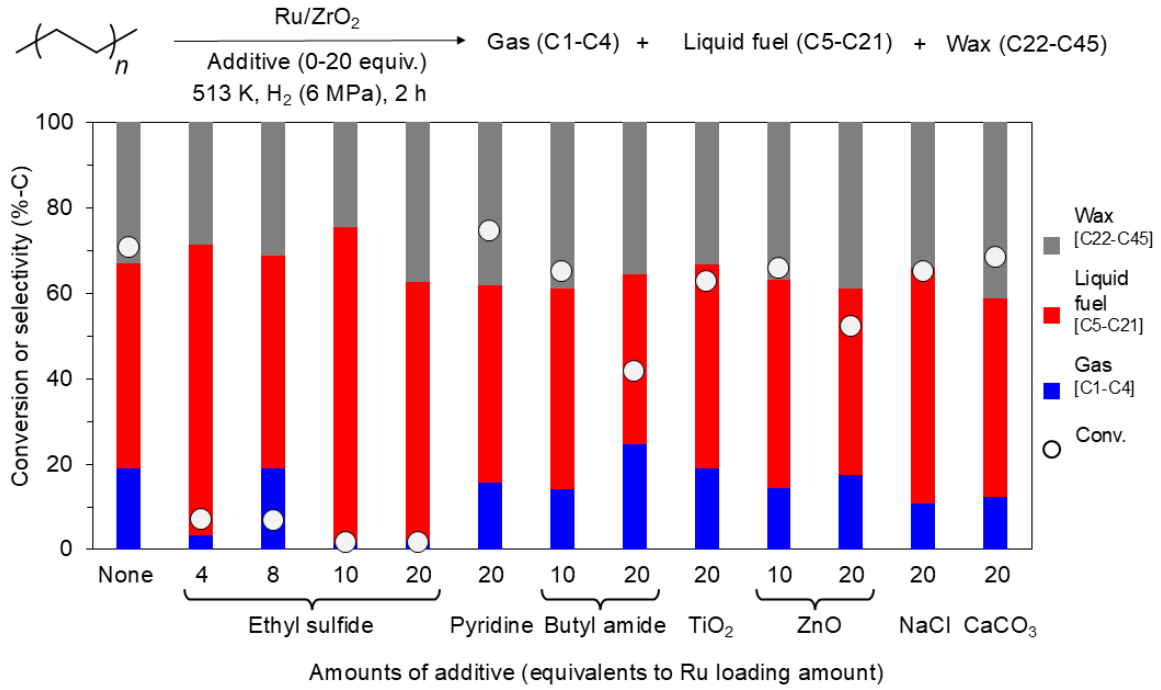


Figure 1. Effects of impurities on hydrogenolysis of LDPE over Ru/ZrO_2 catalyst. Reaction conditions: Ru/ZrO_2 (Ru: 5 wt%) 0.05 g, LDPE 3.4 g, additive 0-0.1 mmol (0-20 equiv. to Ru loading amount), P_{H2} 6 MPa (at 513 K), 513 K, 2 h.

Conclusion

The poisoning effects of ethyl sulfide, pyridine, butylamide, TiO_2, ZnO, NaCl, and $CaCO_3$ were evaluated in the hydrogenolysis of LDPE over Ru/ZrO_2 catalyst. Pyridine, butylamide, TiO_2, ZnO, NaCl, and $CaCO_3$ do not have a significant influence on the catalysis of the Ru/ZrO_2 catalyst; however, ethyl sulfide has a significant poisoning effect. Al_2O_3 and ZrO_2 composite is a beneficial support for the Ru catalyst, and the Ru/Al_2O_3-ZrO_2 catalyst has higher resistance to ethyl sulfide than Ru/ZrO_2. Based on catalyst characterizations, the poisoning effect is attributed to the formation of RuS_2 from Ru metal and ethyl sulfide, and the Al_2O_3-ZrO_2 support can suppress its formation.

Acknowledgement

This work was supported by the Environment Research and Technology Development Fund (JPMEERF20223002) of the Environmental Restoration and Conservation Agency of Japan.

References

[1] Nakaji, Y., Tamura, M., Miyaoka, S., Kumagai, S., Tanji, M., Nakagawa, Y., Yoshioka, T., Tomishige, K.: *Low-temperature catalytic upgrading of waste polyolefinic plastics into liquid fuels and waxes*, Applied Catalysis B: Environmental, 285, 119805, 2021.

[2] Tamura, M., Miyaoka, S., Nakaji, Y., Tanji, M., Kumagai, S., Nakagawa, Y., Yoshioka, T., Tomishige, K.: *Structure-activity relationship in hydrogenolysis of polyolefins over Ru/support catalysts,* Applied Catalysis B: Environmental, 318, 121870, 2022.

[3] Tamura, M., Sasano, Y., Hakim Siddiki, S.M.A., Akatsuka, M., Chen, P., Kita, Y.: *Chemical recycling of polyethylenes with low gas products by catalytic hydrogenolysis with heterogeneous CeO_2-supported Cu-doped Ru catalyst*, Journal of Catalysis, 452, 116417, 2025.

[4] Kita, Y., Fukuda, A., Chen, P., Tamura, M.: *Poisoning Effects of Impurities on Hydrogenolysis of Polyethylenes over Supported Ru Catalysts*, Catalysis Today, 461, 115492, 2025.

Catalytic Cracking of Polyolefins with Supported Catalysts in a Continuous Scale

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Introduction

Catalytic Cracking of Polyolefins is mentioned as a efficient way to improve pyrolysis. [1–5]. Gas and olefin yield can be enhanced. Nevertheless, in technical plants, recovery and regeneration of the used catalyst is difficult. Usually, catalysts as cheap powders are used in small amount. The residuals of the catalyst remain in the solid waste fraction. In stationary fluidized-beds, were the catalyst remains in the reactor, the use of solid catalyst is difficult when solids (e.g. fillers, pigments, dirt, etc.) are used, which also leads to a necessary removal of the solids and the catalyst out of the reactor system.

In this work, the catalyst was fixed on a carrier, which can be separated later from solid residues to be regenerated. However, the challenge is to remain a high activity of the supported catalyst compared to the powder. Pore size engineering is essentially required to reduce limiting effects of pore diffusion .

A second advantage of catalytic cracking is the possibility to produce high gas yield with high fractions of ethylene, propylene, butenes and aromatic compounds [3; 4]. Instead of cleaning and refining pyrolysis oil by hydrogenation and further steam cracking to monomers, these gases can easily be cleaned by absorption techniques and directly feed into the steamcracker downstream. Pyrolysis oils have to be stabilized with additives, metals, ash and heteroatoms (e.g. N, O, Cl, S) have to be removed and olefins have to be hydrogenated to hit steam cracker specifications [6]. In contrast, catalytic cracking mostly leads to light weight molecules, which can be cleaned by absorption techniques.

To get this idea run, the catalytic conversion of real plastic waste streams was examined in a continuous reactor. The correlation of catalyst, waste quality and process conditions (catalyst ratio, temperature) to gas yield and their composition was investigated.

Experimental Setup

For this work different types of polyolefinic plastic waste and different catalysts were used. As waste sorting residues from foil separation (M) - this was set as standard, RDF and 3D-mixed polyolefins (MPO) from municipal waste collection in Germany were used **(Figure 1)**. The proximate and ultimate feedstock analysis of the different feedstocks are listed in **Table 1**. As catalyst zeolite powder (MFI) fixed on two different carrier materials was used. The particle size of the supported catalysts was between 2 to 5 mm. The supports were commercial samples to guarantee low cost. Coating of the carriers was developed using specialized designed binders with additives. The loading of the carrier material with MFI was about 10 wt.-%. The catalyst formulation was done in a pilot scale. The formulation was tested in batch scale described elsewhere [7].

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Table 1. Proximate and ultimate feedstock analysis of the plastic waste used.

	MPO	E1	AC6	AC7	KoRe	**M**
water [ma.%]	0.58	18.12	28.39	22.85	12.72	**1.29**
C_{total} [ma.%]	64.9	65.2	54.5	56.9	50.0	**61.9**
C_{biogen} [ma.%]	2.53	12.9	16.8	22.2	45.0	**22.8**
H [ma.%]	12.8	10.84	n.b.	8.72	7.64	**9.25**
N [ma.%]	0.23	0.22	0.45	0.36	0.47	**0.7**
S [ma.%]	0.06	0.06	0.14	0.13	0.36	**0.12**
Cl [ma.%]	0.05	0.27	0.78	3.64	0.66	**1.1**
ash [ma.%]	2.42	9.81	22.00	11.98	15.05	**10.20**
LHV [kJ/kg]	42,273	34,246	30,068	28,605	24,162	**26,975**

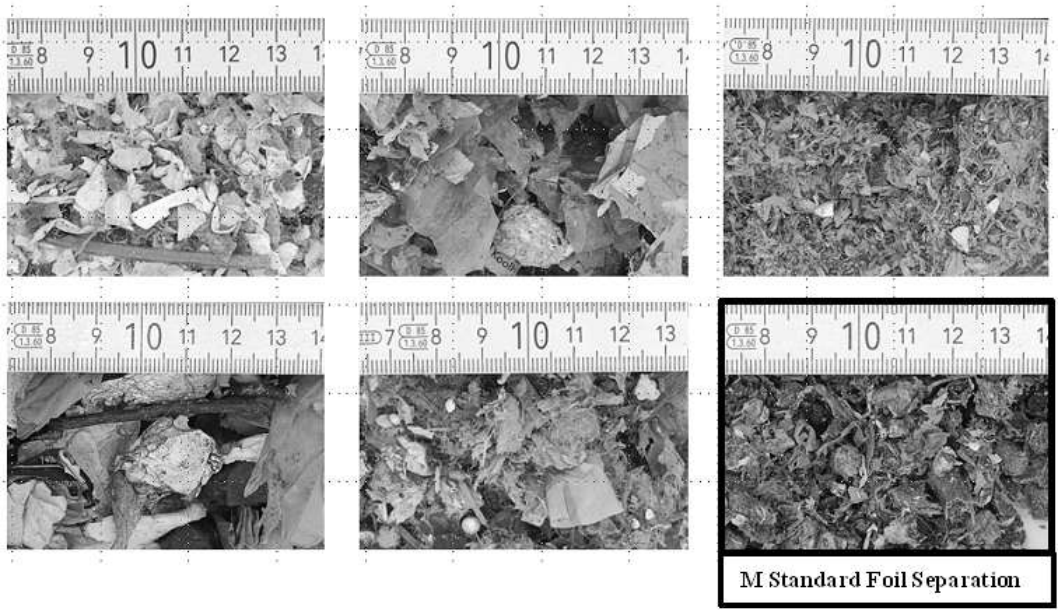


Figure 1. Different waste samples containing polyolefins (MPO, E1, AC6, AC7, KoRe, M)

For continuous catalytic cracking, the mentioned plastic waste was fed into a paddle reactor at temperatures between 430 and 600 °C. The catalyst-to-feed-ratio was between of 1:5 and 1:40. Inert gas was used to change the gas residence time. The feed rate was between 0.25 and 0.75 kg_{RDF}/h and the residence time of the solid phase between 15 and 30 minutes. The products were analyzed by GC, IR and elementary analysis. For process simulation ASPENPLUS® was used.

Results

In a first step different catalyst were developed and tested in a batch rotary kiln reactor. The binders and additives have to be designed according to the activity of catalytic cracking and the availability to penetrate the pores. **Figure 2** shows two different supported catalysts compared to a reference, the original MFI in powder form. The first formulation differs from the behaviour of the powder. At screening conditions at 430°C - these were chosen at unideal parameters to make the differences of the catalyst more obvious - the product spectra obtain high wax contents of about 20 %, while the desired fraction of olefins (ethene, propene, butenes) was 28%. Other light fractions are at about 46%. The rest are residues. Using an alternative support with similar catalyst content, the product yield is similar to the powder form with 35% olefins, 54% light products and 8% waxes. This means that the second supported catalyst is able to crack down the polymers and waxes like the powder form. He has nearly the same activity and it seems that no limiting of macro pore diffusion occurs.

Using this two catalyst at different conditions in the continuous reactor **(Figure 3)**, the results look similar to the batch reactor. At 480°C and the same conditions, the second catalyst shows higher amount of propene and butenes at a gas yield of 40% than the first catalyst (gas yield 35% gas) while pentenes and hexenes were decreasing. At temperatures at about 600°C the amount of methane, ethane and ethene is rising, while products with higher molecular weight were unfavoured (gas yield > 90%). In this case thermal cracking occurs more dominantly compared to catalytic cracking. Nevertheless, the catalytic influence to produce propene and butenes still exists, as pyrolysis without catalyst - results are difficult to obtain in this setup - leads to undesirable waxes, oils and coke formation. At higher throughput (250g/h to 750 g/h) less aromatic compounds were observed which may due to higher gas velocities (gas yield 78%) . Using other waste streams at standard conditions, it can be shown that depending on the heating value the gas yield has an optimum of about 80% at 34 MJ/kg. Higher and lower heating values lead to lower gas yields which is due to uncomplete conversion of hydrocarbons to olefins and coking of the catalyst. Especially, nitrogen compound (e.g. polyamide) lead to a reversible catalyst deactivation, which can be counteracted by higher temperatures and/or a higher catalyst to waste ratios.

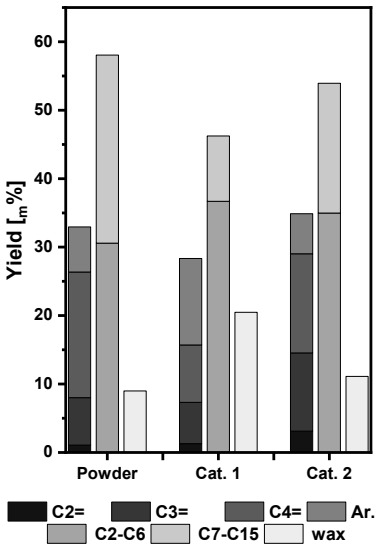


Figure 2. Product yield for different catalyst formulations at reference conditions (batch).

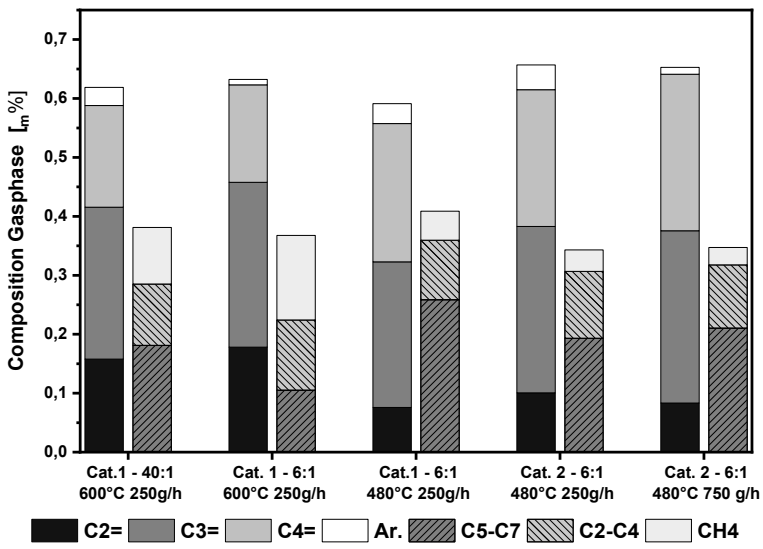


Figure 3. Product yield for different catalyst formulation (cat 1, cat 2) at different reaction conditions (continuous).

Conclusion

Catalytic cracking can lead to a better conversion of polyolefinic plastic waste streams toward monomers like ethene, propene and butenes, which can be used in steam cracker downstream directly. In contrast to pyrolysis catalytic cracking can avoid additional purification and conversion steps like hydrogenation and steam cracking of the pyrolysis oils. This leads, as calculated, to a lower energy demand and lower greenhouse gas emissions [4]. To get an optimum, for each waste stream an adaption of the process conditions have to be done. It can be shown that there exist strong correlation between catalyst demand and waste quality as well as the chosen temperature. Modelling these correlations are in progress to predict product yields, when the input waste is characterized. The results show the strong advantage of catalytic cracking in producing olefins regarding coking of pipes and apparats, the energy demand and greenhouse gases compared to pyrolysis and feeding the pyrolysis oils into steam crackers. Catalytic cracking can be suggested as a possibility of process intensification.

References

[1] Aguado, J.; Serrano, D. P.; Escola, J. M.: *Fuels from Waste Plastics by Thermal and Catalytic Processes*, Ind. Eng. Chem. Res. 47 (21), 7982–7992, 2008.

[2] Kaminsky, W.; Zorriqueta, I.-J. N.: *Catalytical and thermal pyrolysis of polyolefins*, Journal of Analytical and Applied Pyrolysis, 79 (1-2), 368–374, 2007.

[3] Eschenbacher, A.; Varghese, R. J.; Abbas-Abadi, M. S.; van Geem, K. M.: *Maximizing light olefins and aromatics as high value base chemicals via single step catalytic conversion of plastic waste*. Chemical Engineering Journal 2022, 428, 132087. DOI: 10.1016/j.cej.2021.132087.

[4] Schröter, S.; Rothgänger, T.; Heymel, D.; Seitz, M.: *Concept of Catalytic Depolymerization of Polyolefinic Plastic Waste to High Value Chemicals*, Chemie Ingenieur Technik, 95 (8), 1297–1304, 2023.

[5] Netsch, N.; Vogt, J.; Richter, F.; Straczewski, G.; Mannebach, G.; Fraaije, V.; Tavakkol, S.; Mihan, S.; Stapf, D.: *Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis*. Chemie Ingenieur Technik, 95 (8), 1305–1313, 2023

[6] Kusenberg, M.; Eschenbacher, A.; Djokic, M. R.; Zayoud, A.; Ragaert, K.; Meester, S. de; van Geem, K. M.: *Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?* Waste management, 138, 83–115, 2022.

[7] Seitz, M.; Schröter, S. Catalytic *Depolymerization of Polyolefinic Plastic Waste*. Chemie Ingenieur Technik, 94 (5), 720–726, 2022.

[1] J. Aguado, D. P. Serrano und J. M. Escola, Ind. Eng. Chem. Res. Fuels from Waste Plastics by Thermal and Catalytic Processes 2008, 47, 7982–7992, DOI: 10.1021/ie800393w.
[2] W. Kaminsky und I.-J. N. Zorriqueta, Journal of Analytical and Applied Pyrolysis. Catalytical and thermal pyrolysis of polyolefins 2007, 79, 368–374, DOI: 10.1016/j.jaap.2006.11.005.
[3] A. Eschenbacher, R. J. Varghese, M. S. Abbas-Abadi und K. M. van Geem, Chemical Engineering Journal. Maximizing light olefins and aromatics as high value base chemicals via single step catalytic conversion of plastic waste 2022, 428, 132087, DOI: 10.1016/j.cej.2021.132087.
[4] S. Schröter, T. Rothgänger, D. Heymel und M. Seitz, Chemie Ingenieur Technik. Concept of Catalytic Depolymerization of Polyolefinic Plastic Waste to High Value Chemicals 2023, 95, 1297–1304, DOI: 10.1002/cite.202200212.
[5] N. Netsch, J. Vogt, F. Richter, G. Straczewski, G. Mannebach, V. Fraaije, S. Tavakkol, S. Mihan und D. Stapf, Chemie Ingenieur Technik. Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis 2023, 95, 1305–1313, DOI: 10.1002/cite.202300078.
[6] M. Kusenberg, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. de Meester und K. M. van Geem, Waste management (New York, N.Y.). Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? 2022, 138, 83–115, DOI: 10.1016/j.wasman.2021.11.009.

[1] J. Aguado, D. P. Serrano und J. M. Escola, *Ind. Eng. Chem. Res.* Fuels from Waste Plastics by Thermal and Catalytic Processes **2008**, *47,* 7982–7992, DOI: 10.1021/ie800393w.
[2] W. Kaminsky und I.-J. N. Zorriqueta, *Journal of Analytical and Applied Pyrolysis.* Catalytical and thermal pyrolysis of polyolefins **2007**, *79,* 368–374, DOI: 10.1016/j.jaap.2006.11.005.
[3] A. Eschenbacher, R. J. Varghese, M. S. Abbas-Abadi und K. M. van Geem, *Chemical Engineering Journal.* Maximizing light olefins and aromatics as high value base chemicals via single step catalytic conversion of plastic waste **2022**, *428,* 132087, DOI: 10.1016/j.cej.2021.132087.
[4] S. Schröter, T. Rothgänger, D. Heymel und M. Seitz, *Chemie Ingenieur Technik.* Concept of Catalytic Depolymerization of Polyolefinic Plastic Waste to High Value Chemicals **2023**, *95,* 1297–1304, DOI: 10.1002/cite.202200212.
[5] N. Netsch, J. Vogt, F. Richter, G. Straczewski, G. Mannebach, V. Fraaije, S. Tavakkol, S. Mihan und D. Stapf, *Chemie Ingenieur Technik.* Chemical Recycling of Polyolefinic Waste to Light Olefins by Catalytic Pyrolysis **2023**, *95,* 1305–1313, DOI: 10.1002/cite.202300078.
[6] M. Kusenberg, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. de Meester und K. M. van Geem, *Waste management (New York, N.Y.).* Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate? **2022**, *138,* 83–115, DOI: 10.1016/j.wasman.2021.11.009.
[7] M. Seitz und S. Schröter, *Chemie Ingenieur Technik.* Catalytic Depolymerization of Polyolefinic Plastic Waste **2022**, *94,* 720–726, DOI: 10.1002/cite.202100182.

Microwave-Assisted Selective Depolymerization for Efficient Recycling of Cotton/Polyester Blended Textiles

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Introduction

Cotton/polyester (cotton/PET) blended textiles represent one of the most widely consumed and discarded categories of apparel materials, yet their heterogeneous structure makes recycling particularly challenging. Mechanical recycling often deteriorates fiber quality, while conventional chemical recycling relies on high temperatures or strong alkaline conditions that limit practical applicability. These constraints have hindered the development of efficient, scalable recycling routes capable of recovering both cellulose and polyester in usable forms.

To address this issue, our group has established a microwave-assisted selective depolymerization method that enables rapid and controlled decomposition of the polyester component in cotton/PET blends (Figure 1). Under relatively mild reaction conditions, PET can be selectively cleaved into recoverable monomer units, while the cellulose fibers retain their structure and can be isolated with minimal damage. This approach offers a promising pathway toward material-to-material recycling compatible with large waste streams of cotton/PET textiles.

Building on our initial findings, we have further optimized reaction conditions to enhance depolymerization efficiency, improve monomer purity, and preserve cellulose fiber integrity. The present study examines the separation behaviour, component recovery, and overall performance of this microwave-assisted system for the efficient recycling of cotton/PET blended textiles.

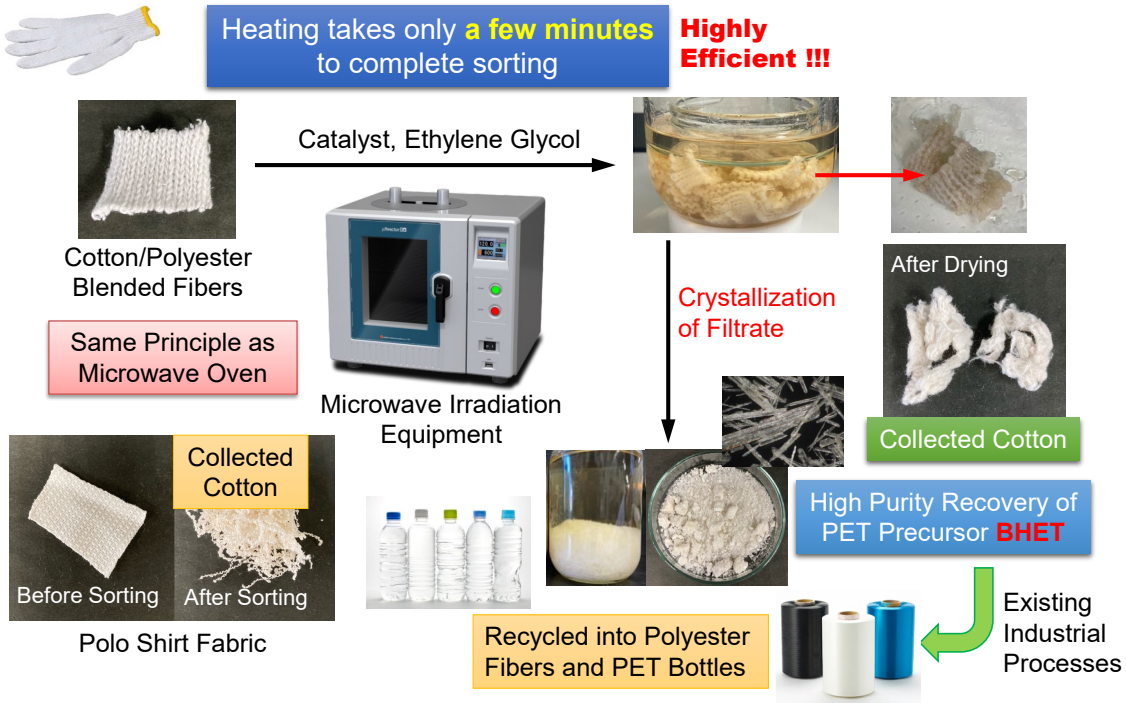


Figure 1. Sorting and Recycling Technology for Cotton/Polyester Blended Fibers

Materials and Methods

Commercial cotton/polyester blended textiles with representative blend ratios were cut into small pieces and immersed in ethylene glycol containing an organocatalyst. The samples were then subjected to microwave irradiation for several minutes under atmospheric pressure. This approach enabled rapid heating of the reaction medium, promoting selective cleavage of ester bonds in the polyester component while avoiding excessive thermal stress on the cellulose fibers.

After irradiation, the reaction mixture was cooled to ambient temperature and filtered to separate the solid cellulose fraction. The liquid phase, containing depolymerized products, was purified by recrystallization to obtain monomer-grade material suitable for re-polymerization. The recovered cellulose fibers were washed and dried prior to characterization.

Chemical structures, component purity, and morphological changes were assessed by FT-IR spectroscopy, GPC, and optical microscopy. These analyses were used to evaluate reaction selectivity, monomer recovery, and preservation of cellulose fiber integrity under various reaction conditions.

Results and Discussion

Selective depolymerization of the polyester component in cotton/PET blends proceeded efficiently under microwave irradiation, yielding high-purity monomer after recrystallization. The recovered cotton retained its fibrous morphology and showed minimal structural degradation, indicating that the reaction conditions were sufficiently mild to preserve the cellulose backbone. These results confirm that microwave-assisted processing can promote controlled depolymerization at relatively low temperatures and under atmospheric pressure.

Building upon these results, the adaptability of this system to more complex, multi-component textiles was investigated. Preliminary experiments using blended fabrics containing polyurethane (PU) demonstrated that the microwave-assisted approach can selectively cleave both ester and urethane linkages. By optimizing the choice of reagents and the reaction temperature, the PU component was successfully depolymerized alongside the PET, while the structural integrity of the cellulose fibers remained largely unaffected. This suggests that the current method is not limited to simple binary blends but can be extended to post-consumer waste containing various synthetic fibers.

The ability to recover monomer suitable for re-polymerization provides a direct chemical-recycling route back to polyester, while the preserved cellulose fibers remain available for mechanical or chemical reuse. The operational simplicity of the method—requiring neither high-pressure equipment nor strongly alkaline solutions—suggests strong potential for scale-up and practical deployment. Together, these outcomes demonstrate that the approach offers a viable pathway toward resource-circulating textile recycling systems, particularly for widely used cotton/PET and multi-component materials.

Conclusions

This study demonstrates that microwave-assisted selective depolymerization provides an effective and practical route for recycling cotton/polyester blended textiles. The method enables selective cleavage of both ester and urethane linkages under relatively mild conditions, yielding high-purity monomer units while preserving the structure of cellulose fibers. These outcomes highlight the potential of microwave-assisted processes to support material-to-material recycling and contribute to broader resource-circulation strategies in the textile sector.

Future work will focus on scaling the process, improving energy efficiency, and integrating continuous-flow operation. In addition, the approach will be extended to more complex post-consumer textiles, enabling the development of comprehensive recycling systems capable of handling a wide range of mixed-fiber waste materials.

Continuous-feed pyrolysis of waste plastics using biochar as both catalyst and adsorbent

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Purpose

One of the most promising methods for recycling waste plastics is conversion to oil through pyrolysis. This study aims to develop an innovative recycling technology that uses biochar as both a catalyst and an adsorbent in the pyrolysis process. This approach targets waste plastics that are difficult to process by conventional methods and simultaneously seeks to enhance the value of biochar. The replacement of conventional high-performance catalysts with biochar is expected to reduce processing costs and increase the yield of valuable products. Furthermore, an adsorption step by biochar is integrated to remove heavy hydrocarbons and impurities that cause operational issues and degrade product properties, enabling stable operation and efficient recovery of valuable products. In our previous studies [1], batch-scale pyrolysis experiments demonstrated that biochar exhibits catalytic effects that promote plastic decomposition, as well as adsorption capacity for heavy hydrocarbons. In this presentation, to obtain data necessary for scaling up the proposed technology, a continuous-feed pyrolysis apparatus was constructed, and the results of pyrolysis experiments conducted using this apparatus are presented.

Experiment

The experimental apparatus (Figure 1) consists of three sections: a feed unit, a furnace, and a product recovery unit. The feed unit continuously supplies a mixture of waste plastics and biochar at a constant rate of 1 kg h^{-1}. As the pyrolysis feedstock, we used waste plastics generated at an actual recycling facility that were deemed unsuitable for mechanical recycling. Biochar produced by carbonizing conifer pellets at 600 °C was employed as both the catalyst and the adsorbent. The properties of the samples are shown in Table 1. The furnace is a horizontally mounted, electrically heated tubular furnace, whose temperature is controlled at 500 °C using three independently controlled heating zones. The sample and catalyst are conveyed through the furnace by a screw, undergoing pyrolysis during transport. The residence time is controlled by the screw rotation speed and was set to 15 min in this study. Metals contained in the waste plastics and the catalytic biochar are collected in a Catalyst/Metal recovery holder, whereas the pyrolysis gases flow downstream to the product recovery section.

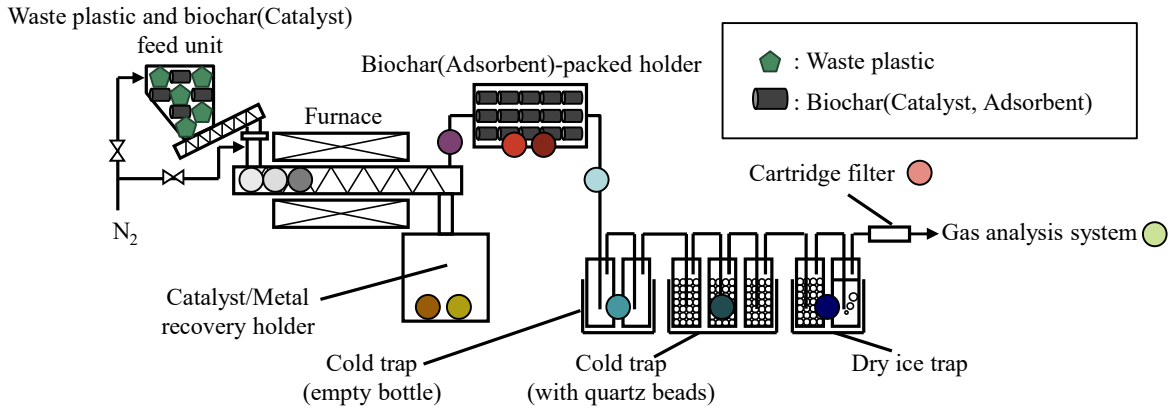


Figure 1. Schematic diagram of the experimental apparatus and product formation locations

Table 1. Properties of the samples

Sample	VM	FC	Ash	C	H	N	O(diff)	SSA*1	HHV*2
	[wt%$_{db}$]							[m^2/g]	[kJ/g]
Waste plastic	93.2	2.9	4.0	72.8	9.2	0.3	13.9	0.5	36.0
Biochar of conifer pellets	14.3	75.2	10.5	77.3	2.5	0.7	9.1	311.7	29.4

＊1　Specific Surface Area（BET（Brunauer-Emmett-Teller）method）

＊2　Higher Heating Value

The product recovery section comprises a biochar-packed holder and a cold trap. The packed holder forms a biochar adsorption bed in the gas flow path and is installed downstream of the furnace to remove solid and heavy components that would otherwise deposit in the cold trap. The holder allows heating and cooling of the packed biochar, enabling adsorption at controlled temperatures. Downstream of the adsorption bed, condensable liquids are collected in the cold trap and dry ice trap, and the remaining non-condensable gases are directly introduced into a gas chromatograph.
A mass balance was calculated based on the measured product masses and gas analysis results, and the results were discussed.

Result

The weight fractions of the pyrolysis products obtained in this study are shown in Figure 2, where the color of each product corresponds to the dots indicating the product formation locations in Figure 1. The operating conditions were set to avoid equipment clogging and ensure completion of the test. The feed mixture of waste plastics and biochar was adjusted to a mass ratio of 1:3 (waste plastics:biochar). Under a feed rate of 1 kg h^{-1}, continuous operation for 50 min was achieved without clogging. Under these conditions, the feed mass of waste plastics introduced into the furnace was 210.9 g, which was used as the basis for calculating the mass balance. As a result, 91.6 mass% of the input waste plastics was quantified as products, indicating a good overall mass balance.
The presentation will focus on the appearance of the products and their qualitative analyses. In addition, the characteristics of the data obtainable with this apparatus and future prospects will be outlined.

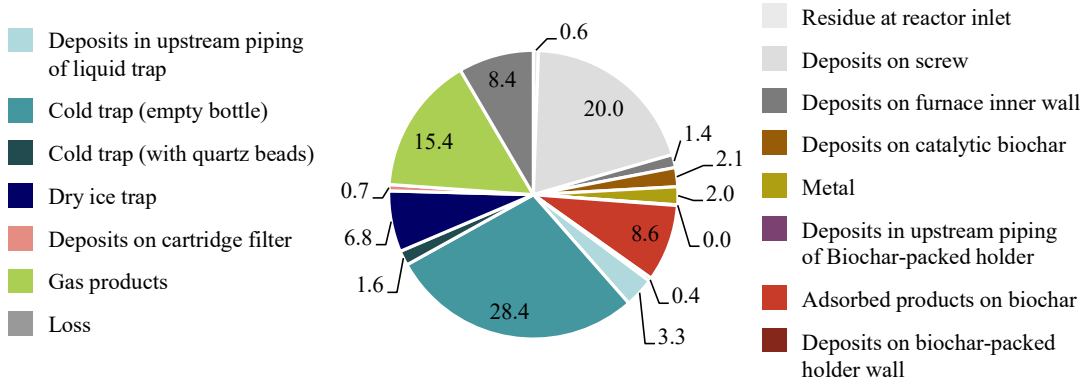


Figure 2. Weight fractions of pyrolysis products with color correspondence to Figure 1

References

[1] Kasataka, K., Umemoto, S., Ikeda, A.: *Potential Use of Biochar as a Catalyst and an Adsorbent in Plastic Pyrolysis Process*, Waste and Biomass Valorization, 16, 6559-6572,2025.

Fast and Isothermal Hydrothermal Liquefaction of High-density Polyethylene: Process Optimization and Intensification

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Introduction

Every year, nearly 130 million tonnes of plastic wastes pollutes the land, air, and water bodies [1]. This number is expected to double by 2040, owing to the rapid urbanisation and lack of adequate waste management systems for supporting this growth. Pollution from plastic packaging is the largest source of plastic waste. In fact, in 2025, nearly 150 million tonnes of plastics were used in the packaging industry, of which more than 80 million tonnes belong to the polyethylene (PE) category, mainly linear / low-density polyethylene (LLDPE / LDPE) and high-density polyethylene (HDPE) [1]. HDPE is a versatile, durable and chemically resistant thermoplastic, widely used in rigid packaging such as milk jugs, shampoo bottles, detergent containers, as well as in automotive parts, toys, and outdoor furniture. Although HDPE is generally recyclable, only 1.75 million tonnes of HDPE was recycled in 2024, representing 13% of its total recycling capacities. Clearly, there is a need for alternative methods to support recycling initiatives.

Chemical recycling of plastic waste via hydrothermal liquefaction (HTL) has gained interest in recent years, primarily due to the versatility of the hydrothermal process [2]. HTL uses water at near-critical conditions to decompose plastic wastes to monomers, fuels and chemicals. At near-critical conditions, water undergoes significant changes in its density, dielectric constant, and ionic product, which makes it behave as a non-polar solvent [3]. HTL exploits this change in property of water to carry out the decomposition and depolymerization of plastics. Depending on the heating rate, HTL can be classified as fast HTL (with very high heating rate) and isothermal HTL (with low-moderate heating rate). Generally, condensation polymers such as polycarbonate and polyethylene terephthalate require sub-critical conditions (≤350 ºC, 15-20 MPa), while addition polymers like LDPE and HDPE require supercritical conditions (>400 ºC, 25MPa) [4].

HTL of PE generally yields hydrocarbon-rich oil as the major product, which is analogous to petroleum crude, and can be used as a source of alternative fuel [5]. The efficiency of HTL decomposition of HDPE is primarily influenced by the operating conditions, such as temperature, pressure, reaction times, heating rate, and plastic loading. For the first time, the present study aims to understand the combined impact of operating temperature, pressure, residence time, and plastic loading, on the decomposition of HDPE, under both fast and isothermal supercritical HTL conditions. The study aims to optimize the conditions to produce high oil yield, preferably rich in aliphatic hydrocarbons, with high calorific value, through systematic experimentation and product analysis. Following the optimization of operating variables, process intensification techniques such as two-stage HTL or catalytic HTL may be explored.

Experimental methods

HDPE pellets used for the study was supplied by Shenzhen Junchi Plastify Limited, China. Supercritical HTL experiments were performed using a custom-made bomb type 316 SS reactors made using HyLok 1'' parts with a total capacity of ~26 mL. In a typical experiment, 0.8 – 4g of HDPE was loaded Millipore water was loaded into the reactors. The water loading was determined by the required temperature and pressure inside the reactor, and the corresponding water densities based on NIST water physical

properties database. The study employed a Box-Behnken response surface design, and the parameters were varied as 425 – 475 ºC temperature, 19 – 25 MPa pressure, 60 – 120 min residence time, and 30 – 60 wt.% plastic loading. After loading, the reactors were then immersed in a fluidized sand bath. For fast HTL experiments, the sand bath was first heated to a predetermined temperature, and then the reactors were submerged. For isothermal HTL, the reactors were first submerged in the sand bath at room temperature, and then they were heated to the reaction temperature. After the desired residence time was reached, the reactors were taken out of the sand bath, and then quenched in a water bath, followed by an ice bath to prevent volatile components from escaping. The reactors were vented, and the gas yields were determined by weight difference. The components of the reactors were decanted, and the reactor insides were washed using dichloromethane to extract residual oil. The wash solvent and the decanted components were collected in a 15 mL tube and centrifuged to separate them into aqueous phase (AP), oil, and solid residues. The yield of the product phases are given by:

$$Yield_{Product}(wt.\%) = \frac{Mass\ of\ the\ product}{Mass\ of\ HDPE} \times 100 \quad (1)$$

Organic composition of the oils from the HTL experiments were then semi-quantitatively analysed using a gas chromatograph mass spectrometer (GC/MS, Agilent 7890A). Proton nuclear magnetic resonance (NMR) spectra were acquired using a Bruker Ascend Evo spectrometer. Elemental composition of the oils were determined using Elemental Vario Macro Cube (Langenselbold). With the data from experiments, a simplified model equation predicting the oil yield and aliphatic hydrocarbon yield from fast and isothermal HTL was constructed using a second-degree polynomial. Using the GC/MS data, the variation of carbon distribution in the oils are also mapped.

Results and Discussion

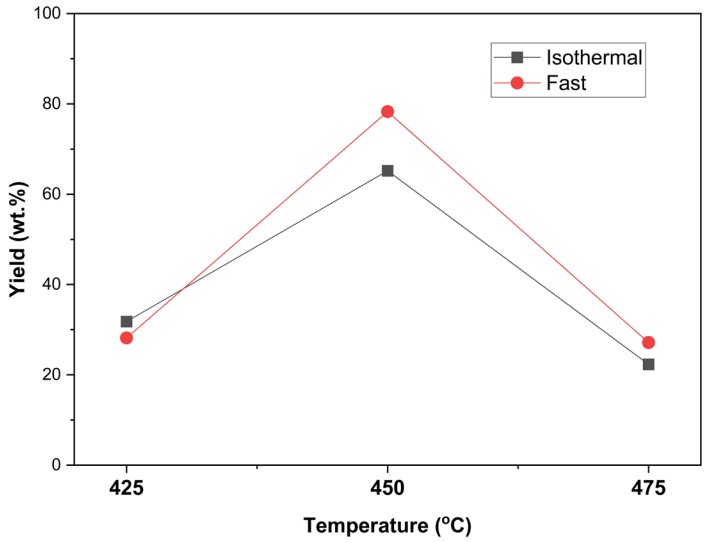


Figure 1. Variation of yield of synthetic oil from fast HTL

From the experiments, it was clear that HDPE started to decompose at 425 ºC. However, the extent of depolymerization was not significant, and the major product at this condition was solid residue, for both fast and isothermal conditions. Increasing the operating temperature from 425 ºC to 450 ºC clearly increased the yield of oils (Figure 1). However, further increasing the temperature to 475 ºC decreased the oil yield, while significantly increasing the gas yields. This was the case for both fast and isothermal HTL. It is clear that HDPE just starts to depolymerize into synthetic hydrocarbon oil at 425 ºC, while at 450 ºC, conversion of HDPE to synthetic oil is nearly complete. At 475 ºC, secondary reactions start to dominate, leading to further cracking of the oil components to form more gases. In fact, at 475 ºC, 19 MPa, 90 min and 45% plastic loading, the gas yield reached up to 50.7 wt.% of the initial HDPE used for the reaction, under isothermal conditions. The oil yields from fast HTL experiments at 425 ºC, 450 ºC, and 475 ºC, at 22 MPa and 90 min residence time were ~28.2 wt.%, ~78.3 wt.%, and ~27.2 wt.%, respectively. For isothermal HTL at 22 MPa, and 90 min residence time, the average oil yields at 425

ºC, 450 ºC, and 475 ºC were ~31.8 wt.%, ~65.2 wt.%, and ~22.3 wt.%. It is evident from the experiments performed so far that fast HTL has a slight edge over isothermal HTL when it comes to oil yields. Among the experiments performed till now, maximum oil yield was 78.3 wt.%, observed at 450 ºC, 22 MPa, 60 min residence time and 60% plastic loading under isothermal conditions. The oil yields corroborate with previous studies where HDPE led to similar oil yields at 425-450 ºC [4].

GC/MS analysis indicated the presence of aliphatic and aromatic hydrocarbons in all the oils. Temperatures of 425 ºC and 450 ºC mainly favoured the formation of alkanes ranging from C6 (Hexane) to C27 (Heptacosane) in the oils (Figure 2). This was the case for both fast and isothermal HTL conditions, although the individual peak area% of the alkanes varied with respect to the operating conditions. Increasing the temperature to 475 ºC led to severe cracking of the synthetic oil. This increased the presence of cyclic and aromatic hydrocarbons in the oils ranging from C5 (Cyclopentane) to C17 (1-Methylpyrene). More results will be discussed during the conference presentation.

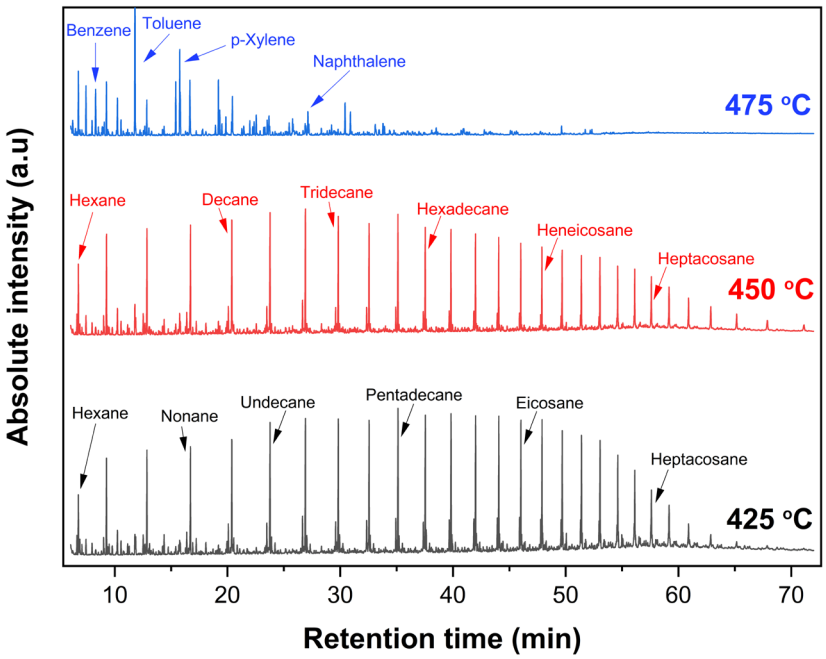


Figure 2. GC/MS composition of synthetic oils from 425, 450, and 475 ºC, 22 MPa and 90 min residence time

References

[1] Pew. *Breaking the Plastic Wave 2025*. The Pew Charitable Trusts https://www.pew.org/en/research-and-analysis/reports/2025/12/breaking-the-plastic-wave-2025, 2025.

[2] dos Passos, J. S., Glasius, M. & Biller, *P. Screening of common synthetic polymers for depolymerization by subcritical hydrothermal liquefaction*. Process Saf. Environ. Prot. 139, 371–379, 2020

[3] Peterson, A. A., Vogel F., Lachance R. P., Froling M., Antal Jr M. J. & Tester J. W. *Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies*. Energy Environ. Sci. 1, 32–65, 2008.

[4] Harisankar, S., Babu, M. V. P., Srinivasan, S. & Vinu, R. *Hydrothermal liquefaction of diverse plastics using water and seawater*. Chem. Eng. J. 501, 157365, 2024.

[5] Seshasayee, M. S. & Savage, P. E. *Oil from plastic via hydrothermal liquefaction: Production and characterization*. Appl. Energy 278, 115673, 2020.

Effects of Contamination Removal and Shear Relaxation on Mechanical Properties

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1.Introduction

Three factors commonly cited as barriers to recycling waste plastics are: ① reduced mechanical properties, ② characteristic odor, and ③ high content of contaminants. Regarding point ①, the conventional view has been that the significant deterioration in the physical properties of waste plastics, compared with virgin materials, is caused by chemical degradation involving irreversible polymer chain scission. Consequently, research on material recycling had remained largely stagnant.

In contrast, we were the first to propose the Physical Deterioration and Physical Regeneration Theory, illustrated in Fig. 1, which posits that the primary cause of property degradation is a physical phenomenon arising from internal structural changes retained from prior molding histories, and that complete regeneration is achievable through sufficient melt-relaxation treatment.

Based on this theoretical framework, we designed an extruder equipped with a molten-resin-reservoir and experimentally verified its functionality. The validity of both the theory and the extruder has been substantiated through fundamental investigations as well as collaborative research with industrial partners[1]~[8]. Furthermore, the extruder with the molten-resin-reservoir has been commercialized by the Research Laboratory of Plastics Technology Co., Ltd. and was exhibited at the 2025 K Show.

Regarding factor ②, it has been confirmed that odors can be reduced through high-temperature processing, including pelletization, and the application of steam or subcritical carbon dioxide.

For factor ③, while pretreatment steps like washing before pelletization are necessary, challenges such as cost and wastewater treatment pose significant barriers to practical implementation. Furthermore, there are no clear standards for setting cleaning criteria. Additionally, ambiguity remains regarding the particle size threshold for classifying materials as contaminants. For example, inorganic/organic filler-

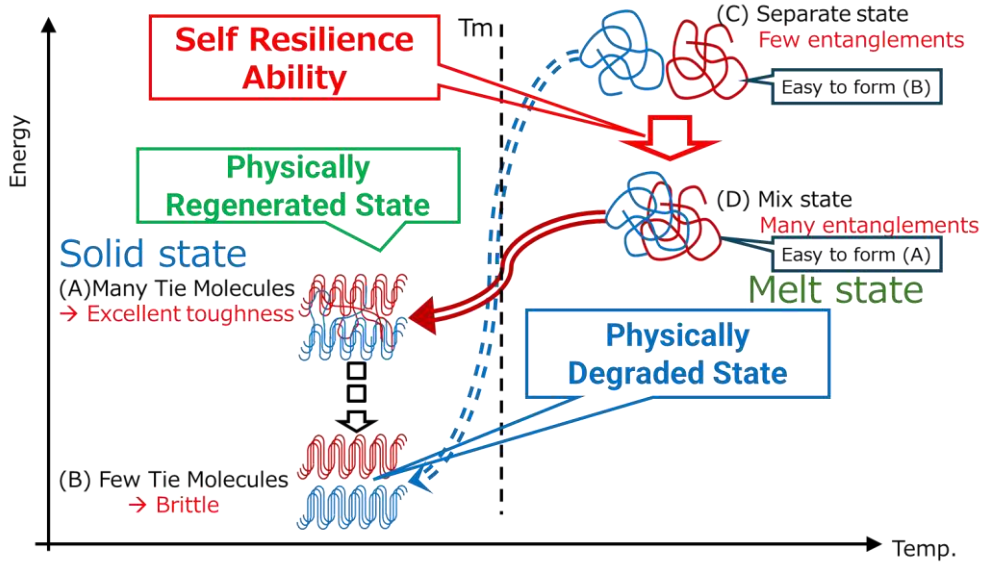


Fig.1 The concept of Physical degradation and Physical regeneration Theory

filled composites are already in practical use, and in such materials, the fillers are typically not treated as contaminants. This ambiguity suggests the need to establish clear guidelines.
On the other hand, mesh filtration has been used as a method for removing contaminants from resin. This report presents the results of verifying changes in material properties when using this mesh filtration.

2. Experiments and Results

As the experimental material, we used a PP mix purchased from Toyama Environmental Improvement Co. Ltd. This material had been processed using an optical sorting system to isolate the polypropylene (PP) fraction, resulting in an approximate composition of 80% PP with about 20% polyethylene (PE) contamination. In addition, during pelletization, contaminations were removed using an 80 mesh laser filter.
We re pelletized the sample using a two stage filtering process. In the first stage, an 80 mesh laser filter was employed, followed by a second stage filtration using a 100 mesh metal filter to remove residual contaminants. All processing zones were maintained at a set temperature of 220 °C. The extrusion throughput during re pelletization was 250 kg/h.
The results of the tensile property measurements before and after contaminant removal are shown in Fig. 2(a). Despite the implementation of a second stage filtration through a 100 mesh screen, no improvement in the mechanical properties was observed. This results are attributed to physical deterioration of the resin caused by shear stresses generated at the final 100 mesh filtration which was positioned immediately upstream of the die exit.
Next, the sample was re pelletized using the twin screw extruder equipped with a molten-resin reservoir. The barrel temperature was set to 230 °C, and two conditions were applied for the molten-resin reservoir temperature: 180 °C and 230 °C. In both cases, the throughput was maintained at 10 kg/h, with a screw rotation speed of 100 rpm. Figure 2(b) presents the tensile test results of these samples, showing a substantial improvement in elongation properties.

3. Summary

It was found that although contaminant removal was performed using a 100 mesh filter, no improvement in mechanical properties was observed; rather, the shear history introduced during the filtration process appears to have hindered property enhancement as predicted by the Physical Degradation and Physical Regeneration Theory. In contrast, re pelletization using the extruder equipped with a molten-resin reservoir resulted in effective physical regeneration. These findings indicate that contaminant removal alone is insufficient to improve material properties, and that shear control or melt relaxation treatment during processing is essential. Additional case studies will be discussed in the presentation.

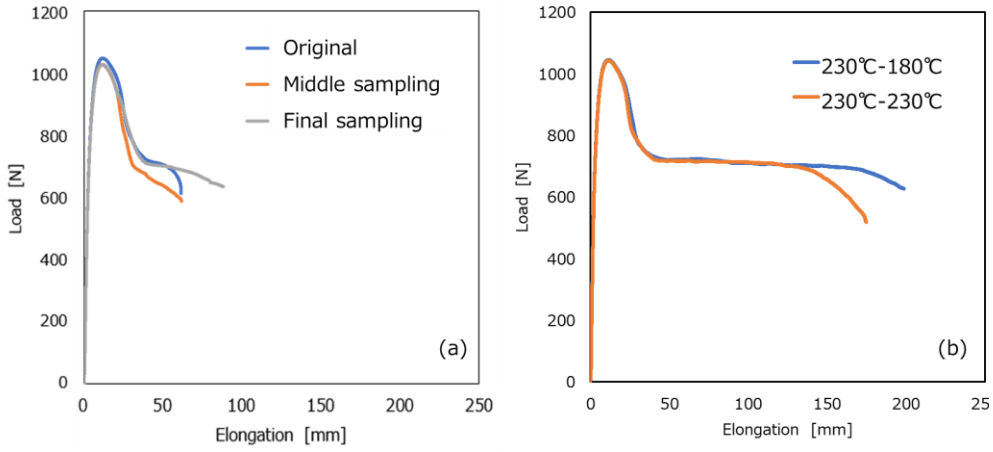


Fig.2 Comparison of mechanical properties of various samples.
(a):Samples before and after filtering process.
(b):Samples after repalletize with molten resin reservoir process, the front temperature is the cylinder temperature, and the rear is the reservoir temperature.

References

Literature sources are identified in the text with numbers in square brackets. References to journals [1], books [2], conference proceedings [3] and dissertations [4] are to be formatted as shown below.

[1] Yao S., Tominaga A., Fujkawa Y., Sekiguchi H., Takatori E.: *Inner Structure and Mechanical Properties of Recycled Polypropylene*, NIHON REOROJI GAKKAISHI, 41(3), 173-178, 2013.

[2] Tominaga A., Sekiguchi H., Nakano R., Yao S., Takatori E.: *Relationship between the Long Period and the Mechanical Properties of Recycled Polypropylene*, NIHON REOROJI GAKKAISHI, 45(5), 287-290, 2017.

[3] Tominaga A., Sekiguchi H., Nakano R., Yao S., Takatori E.:*Advanced recycling process for waste plastics based on physical degradation theory and its stability*, Journal of Material Cycles and Waste Management, 21, 116-124, 2019.

[4] Okubo H., Phanthong P., Yao S.,: *Effects of a Twin-Screw Extruder Equipped with a Molten Resin Reservoir on the Mechanical Properties and Microstructure of Recycled Waste Plastic Polyethylene Pellet Moldings*, Polymers, 13(7), 1058-1069, 2021.

[5] Phanthong P., Miyoshi Y., Yao S.,: *Development of tensile properties and crystalline conformation of recycled polypropylene by re-extrusion using a twin-screw extruder with an additional molten resin reservoir unit*, Applied Sciences, 11(4), 1707-1716, 2021.

[6] Kaneyasu H., Phanthong P., Okubo H., Yao S.: *Investigation of Degradation Mechanism from Shear Deformation and the Relationship with Mechanical Properties, Lamellar Size, and Morphology of High-Density Polyethylene*, Appl. Sci., 11(18), 8436-8436, 2021.

[7] Report of NEDO Project in JAPAN : https://fukuoka-u.app.box.com/s/frwmjbq03bolcjx2b5ei5voccvival5n

[8] Report of Joint Research project of NISSAN Motor and Fukuoka University : https://www.nissan-global.com/JP/SUSTAINABILITY/ENVIRONMENT/A_RECYCLE/R_FEE/SAISHIGEN/PDF/2022_report_01.pdf

Enabling Circular Polystyrene: Reactor Influence on Styrene Yield and Process Integration in Chemical Recycling Processes

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The present study aims to systematically map the importance of reactor design on the chemical recycling of polystyrene (PS) waste with a particular focus on styrene recovery and downstream process performance. A fluidized bed reactor (FBR) [1] and a screw pyrolysis reactor (SR) [2, 3] are used operated at 500°C, but with otherwise inherent different characteristics in the main reaction parameters: The FBR shows high heating rate of the feed and short residence time of the primary cracking products, the SR implies a lower heating rate but high cracked gas residence time. A comparison is made with regard to their respective product oil yield, product distribution; the resulting implications for process integration, separation strategies, and environmental performance based on a life-cycle assessment (LCA) is displayed. To the best of the author's knowledge, literature does not provide such a systematic comparison of the reactor impact with identical feedstock and equal operating temperature, thus hindering reactor design impact analysis. Based on this, the overarching objective is to identify reactor-specific process conditions that enable high-quality styrene recovery suitable for repolymerization while also ensuring overall environmental and process efficiency.

Table 1. Feed and product characteristics obtained from elemental and proximate analysis.

Feedstock	**C** wt.-%	**H** wt.-%	**N** wt.-%	**Cl** mg kg^{-1}	**Br** mg kg^{-1}	**H/C** mol mol^{-1}	**Ashes** wt.-%
PS waste material	81.40 *± 1.82*	7.86 *± 0.24*	0.55 *± 0.10*	1910 *± 522*	427 *± 80*	1.16	4.67
EPS shredded	91.30 *± 0.76*	7.33 *± 0.15*	< 0.20		6000 *± 109*	0.96	0.56
EPS therm. compressed	91.50 *± 0.70*	7.16 *± 0.19*	< 0.20		6270 *± 132*	0.94	0.27
PS waste oil condensate (SR)	87.00 *± 1.60*	8.20 *± 0.13*	< 0.20	40 *± 6*	87 *± 3*	1.13	-
Shredded and therm. compressed EPS oil condensate (SR)	89.10 *± 0.80*	7.70 *± 0.06*	< 0.20	36 *± 2*	1040 *± 6*	1.04	-

Experiments were run utilizing two PS feed streams: virgin EPS boards and a PS waste stream obtained from industrial sorting of light-weight packaging material. Both material sources were characterized prior to pyrolysis (Table 1). The virgin EPS board material was shredded and thermally compressed, resulting in a slight enrichment of certain fractions, particularly brominated compounds. In case of the SR, the process was operated continuously with a feed stream of 0.7 kg h^{-1} and 6 kg h^{-1} of quartz sand as a carrier medium. The reactor features a heated length of 2000 mm and a screw diameter of 150 mm. Nitrogen was used as the inert gas (19 L min^{-1}), and pyrolysis was conducted at 500 °C with a residence time of the solids of 30 minutes. The hot cracked gas residence time in the reactor is widely distributed around a mean value of approximately 50s. The condensation unit consists of two double-tube

condensers operated at 60 °C and 5 °C, respectively, each followed by an electrostatic precipitator. The FBR is operated continuously with a feed rate of 1 kg h^{-1} into a bed of 9 kg of quartz sand as carrier medium. The fluidized bed reactor features a heated reaction zone of approx. 370 mm and a freeboard of 400 mm. Nitrogen is utilized as the inert gas with a flow rate of 66 L min^{-1} and the pyrolysis is conducted at a temperature of 500 °C with a residence time in the hot zone of about 1s. The condensation unit consists of one double-tube condenser and a glass coil condenser operated at temperatures of 5 °C and -30 °C, respectively, each followed by an electrostatic precipitator.

The experimental results show a high styrene yield related to the ash-free feed in the condensate oil: 51.9 wt.% in the screw pyrolysis reactor and 60.2 wt.% in the fluidized bed reactor in case of the virgin EPS boards. Notably, the PS waste stream yields a reduced styrene content of 46.5 wt.% in the screw pyrolysis reactor and increases to 64.7 wt.% in the fluidized bed (Figure 1). In addition to styrene, the condensate oil contains aromatic by-products such as toluene, ethylbenzene, and α -methyl styrene, as well as dimers, including Diels–Alder products, and trimers. Overall, the product compositions align with findings reported in literature [4–9]. The formation of the by-products not only affects the complexity of the downstream separation but also opens potential valorization pathways for co-products, depending on the intended application. Across both feed streams, toluene and ethylbenzene levels are significantly higher in the SR (by a factor of ~3–5 or up to 6–11 in the case of the PS waste stream), while α-methyl styrene levels are comparable or differ by a factor of two. Trimer and diphenyl product formation is more pronounced in the FBR. A direct comparison of same waste stream in different pyrolysis reactors appears absent although the relevance for choice of effective equipment is very high.

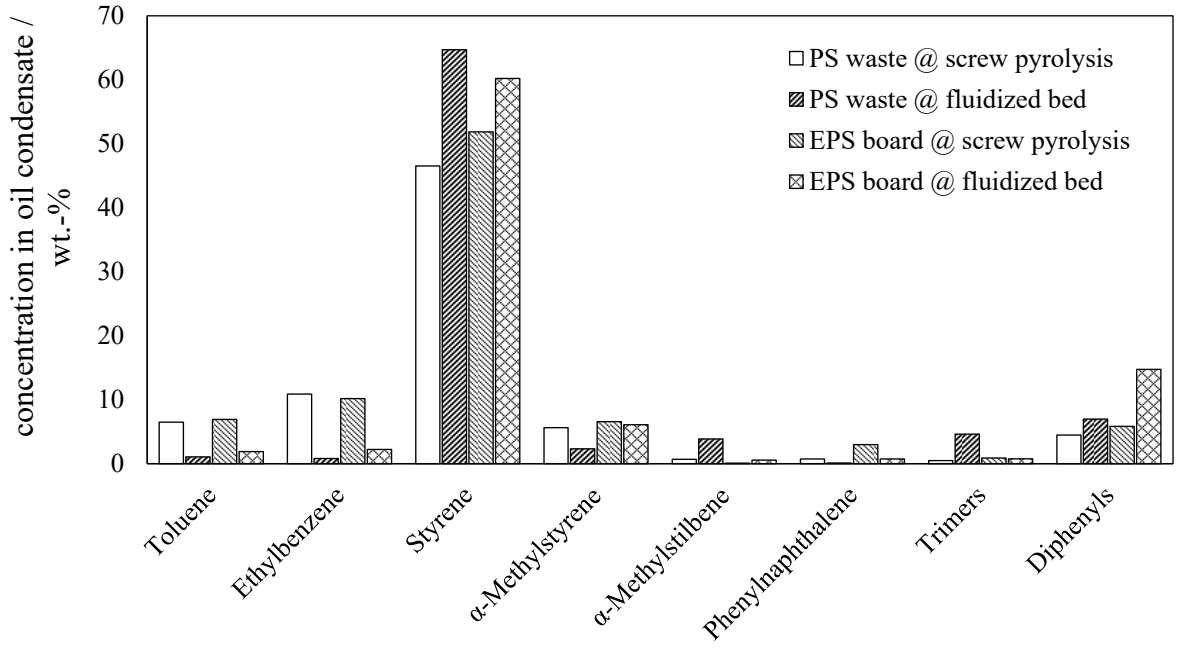


Figure 1. Condensate oil characteristics for pretreated EPS board for fluidized bed and screw pyrolysis reactor at 500°C.

Based on the experimental data, a published distillation sequence [5, 10] is adapted to meet the purity requirements for styrene repolymerization (≥ 99.6 wt.% styrene concentration and ≥ 90% yield in the condensate oil). Prior to the simulation in Aspen Plus®, the experimental data were prepared by validating component completeness, classifying components by boiling point, and grouping them into light boiling products, the target compound styrene, and heavy boiling components. The dataset was normalized to 100 % and implemented with a unified feed stream to ensure consistency. Thermodynamic properties were modelled using NRTL-RK [11, 12] and UNIFAC [13] with binary interactions [14]. The process model allows adjustment of multiple operating and design parameters, including the distillate-to-feed ratio, reflux ratio, column stage numbers, and feed stage location across all three columns. In order to assess robustness under realistic operating conditions, parameter variations are deliberately restricted to operating variables that can be adjusted during continuous plant operation. Accordingly, configurations requiring adjustments only to the distillate-to-feed ratio were favoured, while changes in the reflux ratios were introduced only when strictly necessary; all column design

parameters were kept constant. The separation of styrene from ethylbenzene is inherently challenging due to a boiling point difference of less than 10 K and becomes critical for feed compositions with elevated ethylbenzene content, which limits overall styrene yield. Similarly, the separation from high-boiling propyl-cyclohexane is constrained by the formation of an azeotrope at approximately 25 wt.-% styrene, leading to a pronounced trade-off between recovery and product purity depending on the feed composition. By carefully adjusting operating parameters, these challenges can be mitigated, thereby enabling all evaluated configurations to meet the target product specifications. However, the use of additional degrees of freedom is associated with a reduced robustness of the column configuration.

In a final step, an LCA will be conducted based on both the experimental and simulation data to assess how differences in reactor and downstream process design affect the environmental impacts of the overall process. Preliminary findings indicate that both reactor concepts enable a high-purity styrene recovery utilizing a thermal downstream processing, while the FBR shows higher styrene monomer yield at the given temperature. The results show the importance of understanding the interplay between pyrolysis reaction kinetics, heat and mass transfer, and reactor design in order to optimize polymer-specific pyrolysis efficiency. The upcoming life cycle assessment will complement this evaluation by determining whether these technical differences also translate into environmental benefits, thus completing the assessment of reactor-specific process performance in the context of circular polystyrene.

References

[1] Matthiesen, K., Plessing, L., Luinstra, G. A.: *Fast Pyrolysis Product Analysis of Commercial Polyethylenes*, Energy & Fuels, *38 (16)*, 15543 – 15559, 2024.

[2] Netsch, N., Tauber, A., Keskin, O., Bergfeldt, B., Wehner, H., Eidam, D., Tavakkol, S., Stapf, D.: *Chemical recycling of mixed thermoplastics via pyrolysis: A comparative study of feedstock influence and reactor impact*, Journal of Analytical and Applied Pyrolysis, *194*, 107575, 2026.

[3] Zeller, M., Netsch, N., Richter, F., Leibold, H., Stapf, D.: *Chemical Recycling of Mixed Plastic Wastes by Pyrolysis – Pilot Scale Investigations*, Chemie Ingenieur Technik, *93 (11)*, 1763 – 1770, 2021.

[4] Inayat, A., Fasolini, A., Basile, F., Fridrichova, D., Lestinsky, P.: *Chemical recycling of waste polystyrene by thermo-catalytic pyrolysis: A description for different feedstocks, catalysts and operation modes*, Polymer Degradation and Stability, *201*, 109981, 2022.

[5] Holtkamp, M., Renner, M., Matthiesen, K., Wald, M., Luinstra, G. A., Biessey, P.: *Robust downstream technologies in polystyrene waste pyrolysis: Design and prospective life-cycle assessment of pyrolysis oil reintegration pathways*, Resources, Conservation and Recycling, *205*, 107558, 2024.

[6] Netsch, N., Weigel, L., Schmedding, T., Zeller, M., Bergfeldt, B., Straczewski, G., Tavakkol, S., Stapf, D.: *Chemical characterization of mixed plastic pyrolysis oils relevant for cracker reintegration by advanced two-dimensional gas chromatography*, Fuel Processing Technology, *280*, 108359, 2025.

[7] Inayat, A., Klemencova, K., Grycova, B., Sokolova, B., Lestinsky, P.: *Thermo-catalytic pyrolysis of polystyrene in batch and semi-batch reactors: A comparative study*, Waste Management & Research: The Journal for a Sustainable Circular Economy, *39 (2)*, 260 – 269, 2021.

[8] Mo, Y., Zhao, L., Chen, C.-L., Tan, G. Y. A., Wang, J.-Y.: *Comparative pyrolysis upcycling of polystyrene waste: thermodynamics, kinetics, and product evolution profile*, Journal of Thermal Analysis and Calorimetry, *111 (1)*, 781 – 788, 2013.

[9] Zayoud, A., Dao Thi, H., Kusenberg, M., Eschenbacher, A., Kresovic, U., Alderweireldt, N., Djokic, M., van Geem, K. M.: *Pyrolysis of end-of-life polystyrene in a pilot-scale reactor: Maximizing styrene production*, Waste management (New York, N.Y.), *139*, 85 – 95, 2022.

[10] Merkel, A., Plessing, L., Luinstra, G. A., Grünewald, M., Biessey, P.: *Development of a Separation Sequence for the Integration of a Styrene Recyclate into Polystyrene Production*, Chemie Ingenieur Technik, *95 (8)*, 1323 – 1331, 2023.

[11] Dahal, R., Uusi-Kyyny, P., Pokki, J.-P., Alopaeus, V.: *Isobaric Vapor–Liquid Equilibrium of the Binary Mixtures Toluene + Styrene and Styrene + α-Methylstyrene*, Journal of Chemical & Engineering Data, *68 (3)*, 654 – 663, 2023.

[12] Renon, H., Prausnitz, J. M.: *Local compositions in thermodynamic excess functions for liquid mixtures*, AIChE Journal, *14 (1)*, 135 – 144, 1968.

[13] Fredenslund, A., Jones, R. L., Prausnitz, J. M.: *Group-contribution estimation of activity coefficients in nonideal liquid mixtures*, AIChE Journal, *21 (6)*, 1086 – 1099, 1975.

[14] Seyf, J. Y., Nasiri, L., Medi, B.: *Development of the NRTL functional activity coefficient (NRTL-FAC) model using high quality and critically evaluated phase equilibria data. 2*, Fluid Phase Equilibria, *577*, 113982, 2024.

How can temperature-staged pyrolysis contribute to reaching specification-compliant petrochemical feedstock?

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Introduction

Enabling chemical recycling requires converting pyrolysis products into base chemicals for polymer synthesis. This conversion is enabled by reintegrating the generated pyrolysis products into chemical industry cracking plants. For successful reintegration, they must meet the specifications for fossil-based feedstocks. On the other hand, in pyrolysis, product yields and composition strongly depend on the waste plastic feedstock. Thermoplastic polymers dominate the waste streams relevant for chemical recycling. These are polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyamide (PA), and polyvinyl chloride (PVC). Each of these polymers yields distinct pyrolysis products because their reaction mechanisms depend on the plastic's molecular structure.

Various techniques for improving the quality of pyrolysis oil have been reported in the literature. Besides the catalytic and sorption treatment, downstream cleaning and heteroatom removal, thermochemical pretreatment of the feedstock can come into focus. This alternative can usually be carried out in a separate step, such as low-temperature torrefaction, improving the pyrolysis oil quality by reducing the heteroatom content in the pyrolyzed feedstock. However, these strategies require additional process steps or separation systems, which increase investment costs and can introduce additional technical difficulties.

Yet the polymer-specific differences in the decomposition mechanism and, thus, the decomposition kinetics allow the direct, in-situ process optimization of plastic pyrolysis. In particular, thermoplastics that contain chlorine, oxygen, nitrogen, or aromatic groups in their polymeric structure decompose at lower temperatures than polyolefins. The concept of temperature-staged pyrolysis, therefore, comes into attention, which was already investigated for mixed plastics by Bockhorn et al., conducting experiments with defined mixtures of PE, PS, PA6, and PVC [1,2]. One of the important outcomes of the work was the fact that chlorine content could be significantly minimized in the target product by selective temperature staging. Furthermore, the temperature staging for model mixtures of PVC, PS, PA6, and PE allowed the generation of a styrene- and caprolactam-rich pyrolysis oil separate from an aliphatic condensate.

Results & discussion

Thermogravimetry (TG) Experiments

The decomposition behavior of the polymers is characterized under well-controlled TG conditions. The time- and temperature-dependent sample mass change is recorded to resolve the progression of the pyrolysis reaction by the formation of gaseous and condensable products.

TG experiments with virgin polymers exhibit the conversion rate of individual polymers in the selected isothermal segments. These segments are set to 300 °C and 370 °C. The temperatures were maintained for 30 min and 60 min, respectively. The results are shown in Figure 1. A significant mass loss during the 300 °C stage is only evident for PVC. The decomposition of PVC starts even before reaching the isothermal temperature. At the end of the segment, about 61.4 ± 0.1 wt. % of volatiles are released. The results emphasize the dichlorination reactions occurring in PVC at low temperatures below 300 °C. In the second stage, the reactions of PVC pyrolysis slow down, leading to a minor volatile release of only 7.3 ± 0.1 wt.%. As the temperature rises, the polyene chains pyrolyze at temperatures above 400 °C. This results in the additional release of volatile products and coke formation. The coke amounts to 6.2 ± 0.1 w.t%. In the second stage, at 370 °C, the non-polyolefinic thermoplastics degrade according to the kinetics that were characterized in the dynamic experiments shown in Figure 1. While HDPE only

degrades to approximately 3 wt.% until the end of the second isothermal segment, the decomposition of PS, ABS, PET, and PA6 is pronounced. The PS decomposition results in nearly complete conversion at the end of the stage. Here, the formation of volatiles from ABS, PET, PA6, and PP pyrolysis reaches 77.3 ± 0.1 wt. %, 51.1 ± 0.3 wt.%, 43.6 ± 1.8 wt.%, and 16.8 ± 0.1 wt.%, respectively. This partial decomposition reflects their slower pyrolysis kinetics at 370 °C compared to PS. Only for PET and PVC, significant coke formation can be detected at the end of the experiment. The coke amounts to 12.9 ± 0.2 wt.% in the case of PET. PP features a partial decomposition in this stage. These TG results show remarkably different reaction rates, depending on the polymer type in the sample. Applying a higher temperature or extending the hold time raises the conversion rate of all thermoplastics. A distinct temperature cutoff for separating the pyrolysis of aromatic or heteroatom-containing polymers from the pyrolysis of polyolefins cannot be identified. The overlapping of decomposition ranges, especially for PP and PS, leads to a transitional effect. Instead of a clear separation, this suggests an enrichment or depletion of specific decomposition products by temperature-staging.

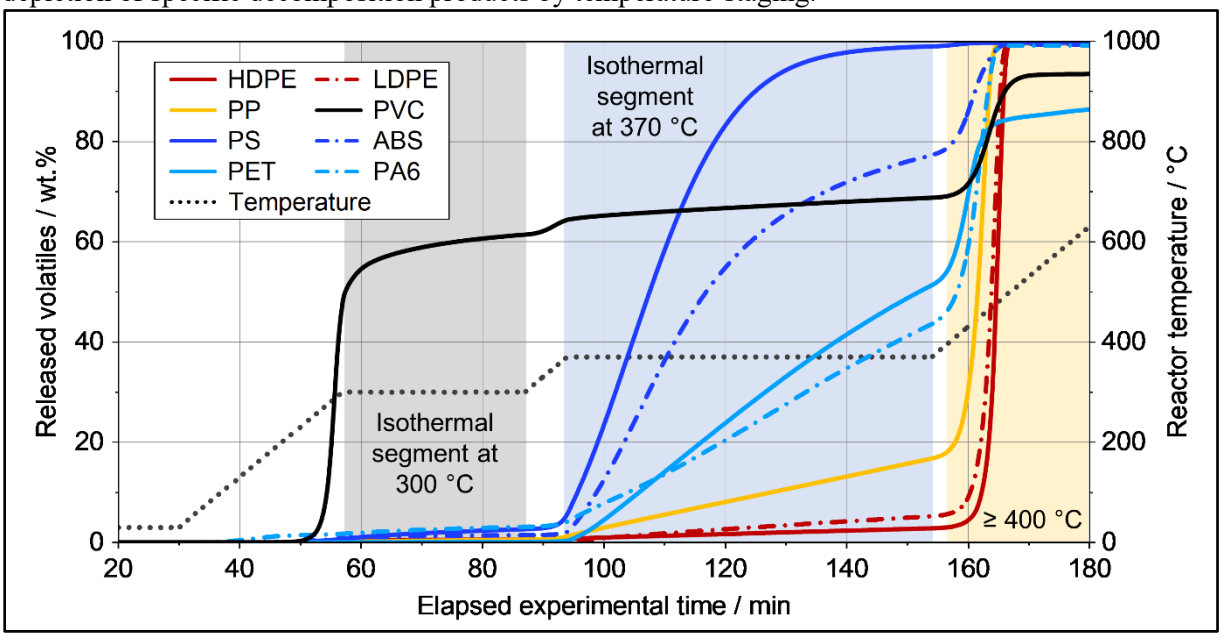


Figure 1 Individual three-staged TG experiments conducted for virgin polymers at isothermal segments for PVC dichlorination at 300 ◦C (grey), decomposition of aromatic-based and heteroatom-containing polymers at 370 ◦C (blue), and polyolefin decomposition above 400 ◦C (yellow) (adopted von [3]).

The impact of polymer-polymer interactions on the reaction rate is particularly relevant for the application of temperature-staged pyrolysis. Possible deceleration or acceleration effects during the co-pyrolysis of polymers may either reduce or widen the kinetic gap between polyolefins and other thermoplastics. To evaluate such effects, the complexity of the feedstock mixture was increased through thermogravimetric (TG) experiments using a representative multi-component mixture.

The decomposition of the “TG Mix”, a complex mixture containing 20 wt.% each of LDPE and HDPE, and 10 wt.% each of PP, PS, ABS, PET, PA6, and PVC, was investigated and is shown in Figure 2. A distinct acceleration of the decomposition is observed, consistent with the behavior previously reported in dynamic TG tests. This acceleration increases volatile formation during the first stage, which is dominated by the dechlorination of PVC.

The underlying mechanisms governing the co-pyrolysis of PVC with PET have been mechanistically described by Cao et al. [4]. According to the authors, the formation of hydrogen chloride during the initial decomposition of PVC promotes C–O bond cleavage in the polyester groups of the PET polymer backbone. In the complex TG Mix, several interaction effects occur simultaneously and overlap.

During the dechlorination phase of PVC at 300 °C, approximately twice the amount of volatiles is released compared with the value expected from the weighted sum of the individual polymer decompositions. By the end of this stage, 15.7 ± 0.0 wt.% of volatiles are formed, whereas only 7.0 ± 0.0 wt.% would be expected based on pure polymer behavior. This deviation highlights the significant interaction effects, particularly between PVC, PET, and PA6.

Products formed during the second decomposition stage are also increased by approximately 8 wt.% and reach 45.0 wt.% compared to the weighted average obtained from TG tests of the individual polymers. The mass release during the third stage appears generally consistent with the mixture composition, considering roughly 40 wt.% PE, 10 wt.% PP, and approximately 5 wt.% polyene residues originating from PVC. However, this represents a simplified approximation, as numerous interaction effects may occur throughout all stages of decomposition and remain difficult to quantify.
A limitation of TG analysis is the lack of detailed information regarding the composition of the evolved volatiles. To address this limitation, larger-scale experiments were conducted in a stirred tank reactor (STR), and the resulting pyrolysis oil was subsequently characterized.

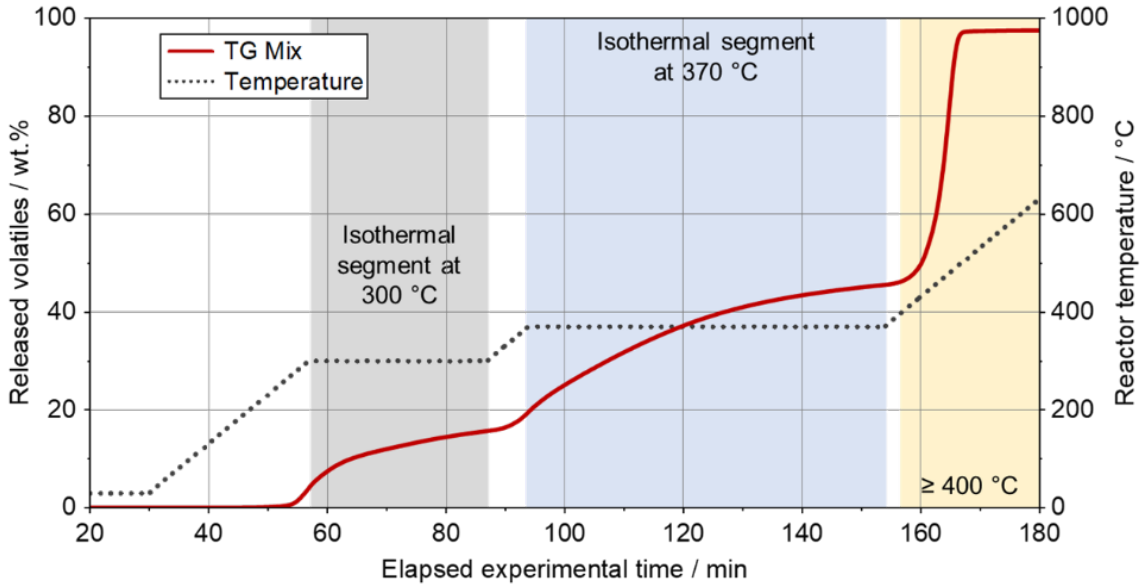


Figure 2 Staged TG experiments with isothermal segments at 300 ◦C for 0.5 h (grey) and 370 ◦C for 1 h (blue) performed the TG Mix, containing 20 wt.% each of LDPE and HDPE, and 10 wt.% each of PP, PS, ABS, PET, PA6, and PVC (adopted von [3]).

Stirred Tank Reactor (STR) Experiments

In contrast to TG experiments, these experiments enable mass balancing and in-depth chemical product analyses. Since an aliphatic-rich pyrolysis oil is the targeted product, only a two-staged pyrolysis is performed in contrast to the TG experiments. The first stage should ensure complete dichlorination and the removal of heteroatoms and aromatic compounds in one step. From the second stage, the aliphatic-rich product fractions are obtained.
Pyrolysis gas and solid residue are calculated for the entire experiment. Furthermore, an experiment with an isothermal segment at 370 °C for 90 min was performed, which is not listed in Table 1. This experiment showed no relevant condensate formation during the first stage. Only slight PVC dehalogenation was observed in this test run, and low amounts of gases were detected. Therefore, this experiment was neglected for evaluating the mass balance and product compositions.
The elemental composition reveals the mitigation of heteroatom-containing hydrocarbons into the condensable product fraction. Therefore, it allows for evaluating the potential enrichment of these oil species in the product obtained during the first isothermal pyrolysis stage. The elemental analysis proves the enrichment of oxygen, nitrogen, and chlorine-containing hydrocarbons in the pyrolysis oil of the first pyrolysis stage. These chemical elements exceed the content of the pyrolysis oil in the isothermal reference test significantly. A comparison of the pyrolysis oil obtained in the first stage at the 400 °C and 430 °C experiments show a higher carbon and hydrogen content than in the 430 °C condensate. This result supports the conclusion from the mass balance that relevant polyolefin decomposition occurs at the second pyrolysis stage. For the condensate fraction produced after the temperature increase, the heteroatom content is correspondingly lower.

Table 1 The condensate yields obtained in the STR Mix two-stage pyrolysis experiments compared to an experiment at a constant temperature of 500 °C and simultaneously lists the elemental analysis of the organic condensate obtained at each stage (adopted von [3]).

	Product fraction yield in mass %		Elemental composistion in mass %					
Experiment	**Acc. Condensate**	**Stages**	**C**	**H**	**N**	**Cl**	**H_2O**	**O***
Isotherm 500 °C	55.1		84.4	12.5	0.6	0.5	0	2.0
Staged Pyrolysis 400 °C -> 500 °C	57.0	1st stage 2.9	60.7	11.7	1.3	7.0	15.0	4.8
		2nd stage 54.1	85.6	13.7	0.2	0.2	0.0	0.3
Staged Pyrolysis 430 °C -> 500°C	57.6	1st stage 22.3	82.8	11.7	1.0	1.7	1.7	1.0
		2nd stage 35.3	86.8	12.6	0.3	0.2	0.0	0.0

*calculated by difference, corrected by calorific value

References

[1] Bockhorn, H., Hornung, A., Hornung, U., Schawaller, D.: *Kinetic study on the thermal degradation of polypropylene and polyethylene*, Journal of Analytical and Applied Pyrolysis, 48(2), 93-109, 1999. https://doi.org/10.1016/S0165-2370(98)00131-4

[2] Bockhorn, H., Hornung, A., Hornung, U., Weichmann, J.: *Kinetic study on the non-catalysed and catalysed degradation of polyamide 6 with isothermal and dynamic methods*, Thermochimica Acta, 337, 97–110, 1999. https://doi.org/10.1016/S0040-6031(99) 00151-3

[3] Netsch, N., Tauber, A., Merz, D., Bergfeldt, B., Tavakkol, S., Stapf, D.: *Optimizing product yield and composition in chemical recycling of mixed plastics through temperature-staged pyrolysis*, Chemical Engineering Science, 327, 123622, 2026. https://doi.org/10.1016/j.ces.2026.123622

[4] Cao, Y., Gao, R., Lei, J., Hou, Y., Xu, M., Cao, S., Chen, Z., Duan, Y., Du, H.: *Mechanistic insights into Cl transformation and calcium-based dechlorination during pyrolysis of waste plastics: Kinetics, product analysis and process optimization*, Journal of Environmental Chemical Engineering, 13, 119459, 2025. https://doi.org/10.1016/j.jece.2025.119459

Gasification characteristics of residues from container and packaging plastic recycling in a Bubbling Fluidized-bed Gasifier

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Background and Objective

Fluidized-bed gasification has a potential for feedstock recycling technology capable of converting heterogeneous waste plastics currently treated by incineration or landfilling into synthesis gas. Although significant progress has been made in mechanical recycling and chemical recycling routes such as pyrolysis, substantial amounts of recycling residues remain unavoidable. In previous studies using refuse paper and plastic fuel (RPF), optimization focused on the overall equivalence ratio and gasification temperature, while the distribution of the equivalence ratio between the Fluidized-bed and freeboard was not addressed [1]. For syngas utilization, maximizing CO and H_2 yields is essential. In this study, residues from container and packaging plastic recycling, which are generated in large quantities, were used as feedstock to investigate gasification characteristics in a Bubbling Fluidized-bed Gasifier.

Methodology

Gasification experiments were carried out using a Bubbling Fluidized-bed Gasifier with an inner diameter of 200 mm and a total height of approximately 3 m. Silica sand with an average particle size of 500 μm was used as the bed material, and the superficial gas velocity was controlled to maintain stable bubbling fluidization. The feedstock consisted of residues from container and packaging plastic recycling (Table. 1), which were pelletized to an outer diameter of 10 mm and a length of 20–50 mm to ensure stable feeding. The feed rate was fixed at 14 kg/h for all operations.

Table 1. Characteristics of residues from container and packaging plastic recycling

Items		Value
Moisture	[wt%-$_{wet}$]	1.2
Ash	[wt%-$_{dry}$]	3.9
Volatile	[wt%-$_{dry}$]	92.1
Fixed carbon	[wt%-$_{dry}$]	4.0

Items		Value
Carbon	[wt%-$_{dry}$]	74.84
Hydrogen	[wt%-$_{dry}$]	8.33
Nitrogen	[wt%-$_{dry}$]	0.21
Oxygen	[wt%-$_{dry}$]	10.94
Sulfer	[wt%-$_{dry}$]	0.04
Chrorine	[wt%-$_{dry}$]	1.75
LHV*	[kJ/kg]	34,000

*LHV: Lower Heating Value

Oxygen and steam were employed as gasifying agents instead of air. This configuration was adopted to minimize the size of downstream equipment and to avoid nitrogen dilution of the produced syngas, which is essential for subsequent chemical recycling applications. Oxygen was supplied independently to the Fluidized-bed and the freeboard, and the respective flow rates were adjusted to achieve the equivalence ratios specified in Table 2. Steam flow rates were controlled to maintain the target temperatures in the Fluidized-bed and the freeboard, as summarized in Table 2.

For gas composition analysis, a portion of the product gas was extracted from the gasifier and passed through a gas cleaning system before being continuously monitored using a gas analyzer (ETG 6500; ETG Risorse e Tecnologia) for CO, H_2, CH_4, and CO_2. In addition, gas samples were collected in gas bags and analyzed by a thermal conductivity detection (TCD) gas chromatograph (490 Micro GC;

Agilent Technologies Japan), with Molsieve 5A (Ar carrier; Agilent Technologies Japan) and PoraPLOT Q (He carrier; Agilent Technologies Japan) columns.
Helium was introduced as a tracer gas, and the product gas flow rate (Dry basis) was determined from the helium concentration measured by gas chromatography. Gasification performance was evaluated by gas compositions and carbon conversion ratio defined as the fraction of feedstock carbon converted into gaseous products, to identify suitable operating conditions for syngas utilization (Figure 1).

Table 2. Operational conditions

Parameters			Case1	Case2	Case3	Case4	Case5
ER*	Fluidized-bed	[-]	0.16	0.14	0.12	0.12	0.12
	Freeboard	[-]	0.24	0.26	0.27	0.27	0.28
	Total	[-]	0.40	0.40	0.39	0.39	0.40
Steam	Fluidized-bed	[kg/h]	5.4	5.4	5.4	8.7	8.7
	Freeboard	[kg/h]	13.0	14.0	15.5	9.5	8.5
Temperature	Fluidized-bed	[℃]	770	767	740	636	619
	Freeboard	[℃]	895	904	895	966	1,014

*ER: Equivalence Ratio

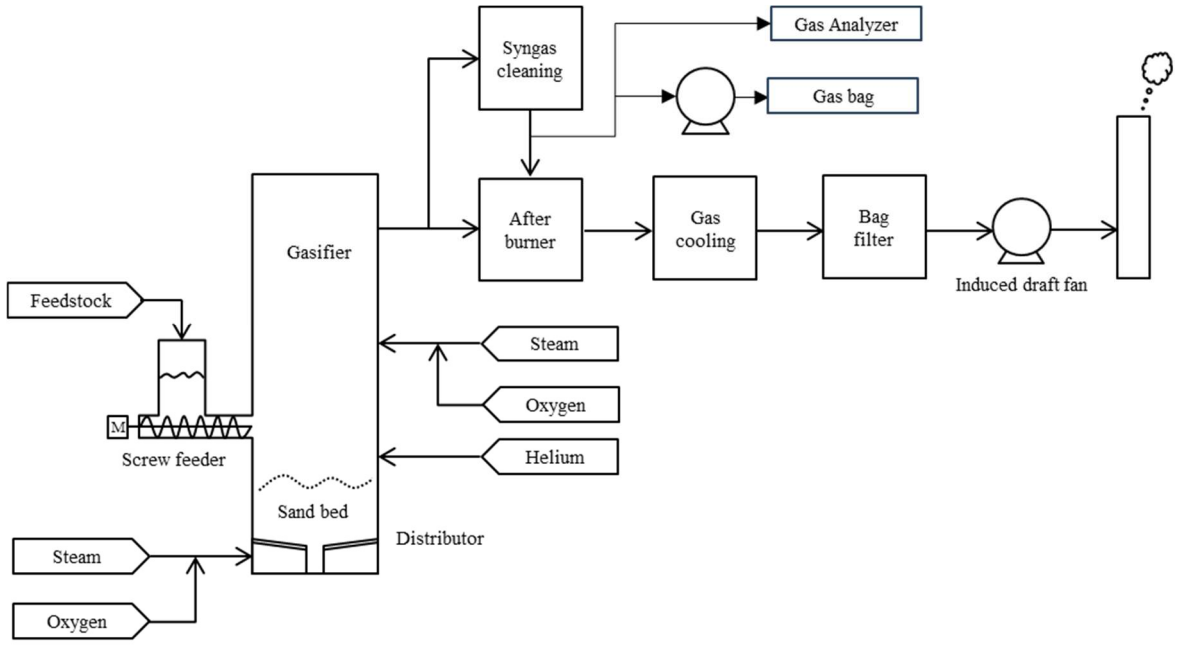


Figure 1. Process diagram of this study

Results and discussion

The results indicate that product gas compositions and the carbon conversion ratio are strongly influenced by the equivalence ratio between the fluidized-bed and freeboard, as well as by freeboard temperature. In Case1–Case3, decreasing the Fluidized-bed equivalence ratio (ER) from 0.16 to 0.12 resulted in a systematic increase in CO/CO_2 from 1.8 to 2.0, indicating an improvement in the product gas yield in terms of carbon retained as CO rather than oxidized to CO_2. This trend is consistent with the dry gas composition, where CO concentration increased from 42.7 to 44.7 vol% while CO_2 concentration decreased from 24.2 to 22.1 vol%. These results suggest that lowering the fluidized-bed ER suppresses over-oxidation reactions in the fluidized-bed and enhances selectivity toward synthesis-relevant gas components. The carbon conversion analysis supports this interpretation, showing an increase in the carbon conversion ratio to CO from 40.0% in Case1 to 43.9% in Case3.
In contrast, Case3–Case5 indicates a strong effect of freeboard temperature under nearly identical Fluidized-bed ER conditions. As freeboard temperature increased from approximately 900°C to over 1000°C, CO/CO_2 decreased significantly from 2.0 to 1.1 despite similar oxidant input to the Fluidized-

bed. This decrease is reflected by a decrease in CO concentration (44.7 → 32.7 vol%) and a marked increase in CO_2 (22.1 → 28.5 vol%). At the same time, CO/H_2 decreased from 2.7 to 1.3 while H_2 increased to 24.7 vol%. The breakdown of the carbon conversion ratio shows that the fraction classified as "Others" including gaseous tar component, tar, char, and soot, increased from about 15% in Case3 to over 25% in Case5. These trends suggest that elevated freeboard temperatures promote carbon diversion into soot-related formation pathways [2], thereby reducing effective syngas yield.

Table 3. Produced gas compositions

Parameters			Case1	Case2	Case3	Case4	Case5
Composition	H_2	[vol%-$_{dry}$]	15.1	15.4	16.4	18.2	24.7
	CO	[vol%-$_{dry}$]	42.7	43.7	44.7	40.8	32.6
	CH_4	[vol%-$_{dry}$]	9.9	9.8	9.5	8.0	7.7
	C_2H_n	[vol%-$_{dry}$]	5.5	5.2	5.1	2.6	2.0
	CO_2	[vol%-$_{dry}$]	24.2	23.1	22.1	21.4	28.5
	CO/H_2	[-]	2.8	2.8	2.7	2.2	1.3
	CO/CO_2	[-]	1.8	1.9	2.0	1.9	1.1

Table 4. Carbon conversion ratio

Parameters			Case1	Case2	Case3	Case4	Case5
CCR*	CO	[%]	40.0	42.7	43.9	42.5	33.3
	CH_4	[%]	9.2	9.5	9.3	8.3	7.8
	C_2H_n	[%]	10.3	10.2	10.0	5.4	4.1
	CO_2	[%]	22.6	22.6	21.7	22.3	29.1
	Others**	[%]	17.8	15.0	15.1	21.5	25.6

*CCR: Carbon Conversion Ratio

**Others: Includes gaseous tar such as Benzene, tar, char and soot

Overall, the results indicate that maximizing syngas yield requires careful balancing of ER between the Fluidized-bed and freeboard, together with strict control of freeboard temperature. Future work will focus on optimizing gasification conditions according to polymer resin composition. In addition, when syngas is targeted as the final product, downstream removal of tar and soot is essential; therefore, further analysis will extend beyond gas composition to include detailed characterization of by-products.

References

[1] Win, M. M., Asari, M., Hayakawa, R., Hosoda, H., Yano, J., Sakai, S.,: *Characteristics of gas from the fluidized bed gasification of refuse paper and plastic fuel (RPF) and wood biomass*, Waste Management, 87, 173-182, 2019

[2] Nedjalkov, I., Yoshiie, R., Ueki, Y., Naruse, I.,: *Tar and Soot generation behaviors from ABS, PC and PE pyrolysis*, Journal of Material Cycles and Waste Management, 19, 682-693, 2017

Steam Crackers of the Future

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Introduction

Steam crackers are a cornerstone of the chemical industry, supplying key intermediate molecules, including light olefins (such as ethylene, propylene, and butenes) and aromatic hydrocarbons (benzene, toluene, and xylenes) [1]. Despite their central role, several steam crackers in Europe, primarily those using naphtha as the feedstock, have been permanently shut down in recent years. These closures are driven by a global oversupply of ethylene and propylene [2]. The oversupply has largely resulted from the rapid expansion of lower-cost, higher-yield production routes, including ethane- and LPG-based steam cracking, as well as dedicated olefin technologies such as propane dehydrogenation (PDH) and methanol-to-olefins (MTO). Sustainability also poses a fundamental challenge for naphtha crackers. These units have been optimized for specific naphtha compositions. As a result, they have strict feedstock requirements and depend entirely on fossil resources [3]. Feedstock flexibility is crucial for sustainability. In this context, integrating plastic waste with steam crackers has recently attracted significant industrial attention [4].

Plastic waste integration is primarily pursued via pyrolysis, where plastic waste is converted into an oil with a naphtha-like hydrocarbon composition. After upgrading, this pyrolysis oil can be introduced into steam crackers, and several steam cracker operators have already begun doing so. However, the approach faces important limitations. Producing steam-cracker-grade pyrolysis oil requires extensive sorting of plastic waste followed by energy-intensive upgrading steps [4]. At each stage, substantial fractions of the feedstock are rejected, reducing the overall recycling rate. These losses are now explicitly exposed by the European Commission's mass balance rules, which require accounting for all rejected streams and reveal lower effective recycling rates than often assumed [5]. Pyrolysis offers a resilient way for converting diverse plastic waste streams into chemical feedstocks; however, the bottleneck lies in the stringent feedstock requirements of existing steam crackers. Securing the future of steam cracking will depend on reimagining this decades-old technology and transforming it from a fossil-optimized process into a cornerstone of a circular and feedstock-flexible chemical industry.

A promising solution is the reconfiguration of steam crackers into a dual fluidized bed (DFB) reactor concept. DFB reactors enhance feedstock flexibility by allowing the handling of heterogeneous feedstocks such as plastic waste while maintaining temperature and residence time regimes comparable to those of conventional steam crackers. Several semi-industrial DFB demonstrations over the last decade further support the potential for implementing such a reactor system at an industrial scale [6,7]. This work summarizes experimental results from a semi-industrial DFB steam cracker using virgin polyethylene (PE), mixed packaging waste (MPW), and untreated polyolefin pyrolysis oil (PyOil) as feedstocks. Results are evaluated with a carbon-based mass balance to determine recycling rates in compliance with the European Commission's mass balance rules for thermochemical recycling. The study also introduces a common mass balance framework for processes using plastic waste as feedstock, allowing comparisons between conventional and DFB steam cracking.

Method

The experiments were conducted in a semi-industrial DFB reactor at Chalmers University of Technology. The system comprises two interconnected units: a circulating fluidized bed (CFB) and a bubbling fluidized bed (BFB). The BFB operates in steam cracking mode, utilizing steam as the fluidization medium, while the CFB serves as a biomass combustor that supplies the endothermic heat required for steam cracking to the BFB. The BFB has a feedstock processing capacity equivalent to 150 kg/h of PE and can be operated within a temperature range of 700–825°C. For a detailed description of

the DFB reactor system at Chalmers University of Technology, readers are referred to the authors' earlier work. Table 1 details the experimental conditions and properties of the feedstocks used in this work [7].

Table 1. Description of the feedstocks and the experimental conditions used in this work.

Feedstock	Polyolefin content (%carbon)	Plastic content (%carbon)	Feeding rate	Steam cracking temperature
PE	100%	100%	90 kg/h	760°C
MPW	60%	80%	40 kg/h	
PyOil	100%	100%	50 kg/h	

Each experimental point reported in Table 1 corresponds to at least one hour of stable operation under the specified conditions. This period of stable operation provides sufficient time for collecting representative product gas samples, which are required to derive a mass balance over the steam cracker. A detailed description of the sampling procedures and analytical techniques used for product gas analysis is available in earlier work performed by the authors [7].

Mass balance approach and assumptions

In a steam cracker, multiple by-products are generated alongside the main products. To ensure a comprehensive accounting of all material flows, a mass balance approach is applied that considers all streams produced by the steam cracker. The process flow diagrams shown in Figure 2 illustrate the main products, along with the associated by-products, obtained from a DFB steam cracker.

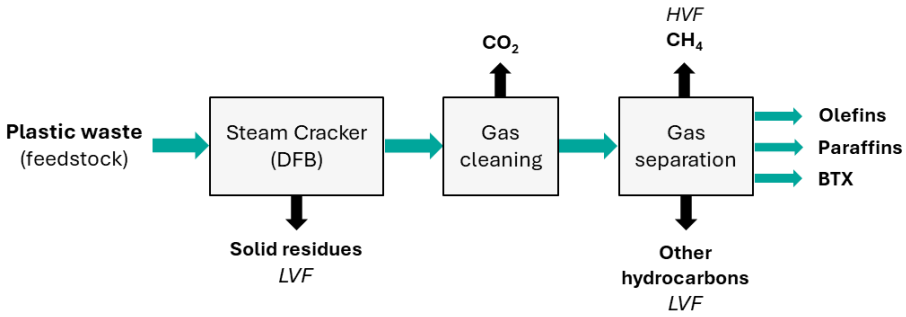


Figure 1. Process flow diagram for a DFB steam cracker highlighting the product streams.

The product streams from a steam cracker for plastic waste are divided into four categories based on their downstream use. The main products comprise olefins, paraffins, and BTX, which serve as key building blocks for polymer production; although paraffins are not monomers, they can be converted to olefins with near-quantitative efficiency. High-value fuels (HVF) include hydrocarbons that can be used directly as transportation fuels, primarily methane. Low-value fuels (LVF) consist of lower-quality hydrocarbons that are typically incinerated for energy recovery, with fuel oil (C8+ fraction) being a representative example. In addition, a separate CO_2 stream is produced, which can be utilized as a feedstock for synthesis processes.

A carbon-based mass balance directly reflects the role of carbon as the fundamental element in plastic waste and its transformation during recycling. Tracking carbon flows provides a consistent basis for quantifying how much of the input carbon is recycled into new polymer precursors versus lost as emissions or low-value residues. This approach is essential for evaluating plastic waste recycling routes, where the objective is to minimize fossil carbon losses and decouple plastic production from fossil resource extraction. The recycling rate is defined in Equation 1. The recycling rate can be generalized to any recycling process for fossil-based carbon materials by expressing the numerator as the total amount of fossil carbon displaced through recycling.

$$\textit{Rate of recycling}\ (\%) = \frac{\textit{Total carbon obtianed as olefins, paraffins, and BTX}}{\textit{Total fossil carbon in the feedstock}} \qquad (1)$$

Results and discussion

The carbon distribution among the products obtained from the Chalmers DFB steam cracker is presented in Figure 2. The figure illustrates how the carbon contained in PE and MPW is distributed among the defined product categories. Figure 2 also reports the recycling rate calculated according to Equation 1.

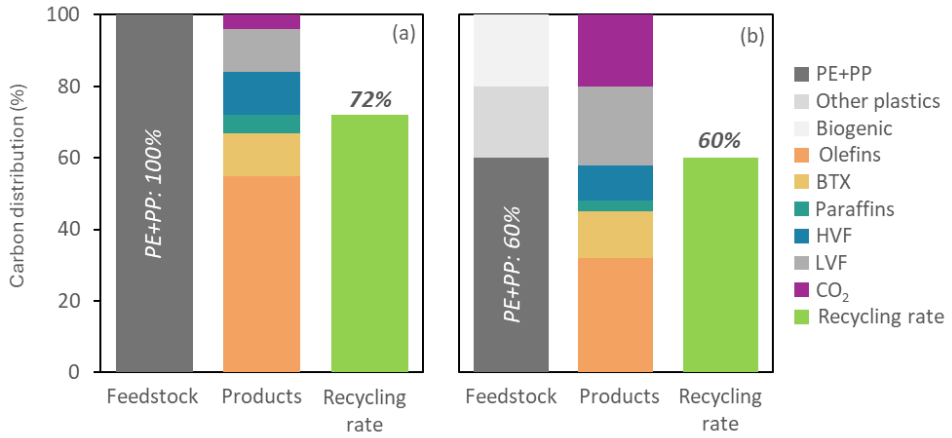


Figure 2. Carbon-based mass balance over the Chalmers dual fluidized bed steam cracker and the corresponding recycling rates for the feedstocks (a) PE and (b) MPW.

For PE, olefins, BTX, and paraffins account for 55%, 12%, and 5% of the total carbon in the products, corresponding to a recycling rate of 72%. With MPW, the recycling rate decreases to 60%. This reduction is primarily attributed to the presence of non-polyolefin plastics (~ 20%) in the feedstock, which contribute less to the formation of olefins and paraffins. In addition, oxygen originating from PET and cellulose leads to a significant CO_2 fraction, representing about 20% of the carbon in the product distribution. For MPW, the 60% recycling rate is determined with respect to the fossil carbon (plastic) fraction of the feedstock (see Table 1), in accordance with the definition provided in Equation 1.

A similar carbon balance can be applied to conventional steam crackers operating with pyrolysis oil as feedstock. In this case, the carbon balance must account for two sequential conversion steps: the pyrolysis process and the subsequent steam cracking process. All products and byproducts formed in both stages must therefore be included in the carbon distribution. Figure 3 illustrates the resulting carbon distribution for conventional steam cracking of pyrolysis oil, based on relevant literature sources [4,8], and compares it with the distribution obtained from the Chalmers DFB steam cracker using PyOil as feedstock. For a fair comparison, a common initial feedstock and pyrolysis process is assumed for both the DFB and the conventional steam cracker.

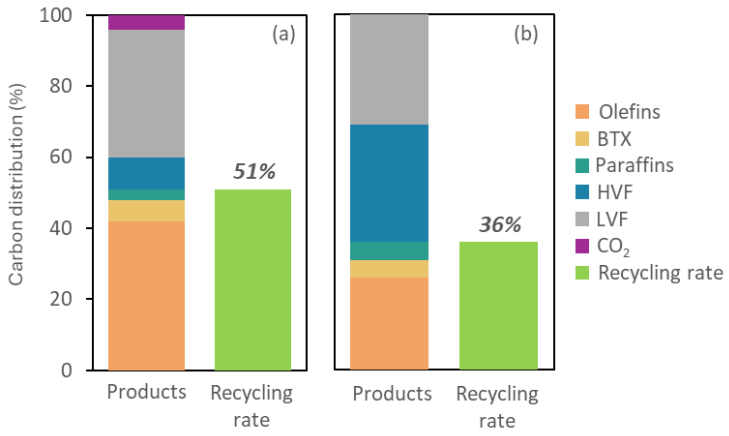


Figure 3. Carbon-based mass balance and corresponding recycling rate for steam cracking of PyOil in (a) a DFB steam cracker (this work) and (b) a conventional steam cracker (estimated).

The recycling rate for conventional steam crackers using pyrolysis oil as feedstock is estimated at 36%, which is significantly lower than the rate obtained with the DFB steam cracker. Despite assuming the same pyrolysis oil composition, the lower recycling rate in conventional steam cracking is primarily due to carbon losses during the upgrading stage required to meet strict feedstock specifications. Most of these losses occur during distillation and hydrotreatment, where hydrocarbons outside the naphtha range (C5–C12) are removed. These rejected fractions are reflected as HVF in the carbon balance. In contrast, the DFB steam cracker does not require feedstock upgrading to a defined naphtha range. Consequently, no upgrading of the pyrolysis oil was performed in this work, resulting in a lower HVF fraction and a higher recycling rate, as shown in Figure 3.

The results presented in this work demonstrate the potential of a DFB steam cracker to process heterogeneous feedstocks. By eliminating the need for upgrading pyrolysis oils, a DFB steam cracker reduces the share of fuel products that do not contribute to the recycling rate under the European Commission's mass balance framework. Nevertheless, further research is required prior to industrial implementation, particularly regarding the decontamination of cracker effluents to ensure compatibility with existing downstream gas separation systems. In addition, this study considered pyrolysis oil derived from a pure polyolefin stream; future work should evaluate pyrolysis oils obtained from real waste streams like MPW to fully assess the potential of the process.

References

[1] Z. Gholami, et al., A review on the production of light olefins using steam cracking of hydrocarbons, Energies (Basel). 14 (2021). https://doi.org/10.3390/en14238190.

[2] Y. Mujidah, A Perfect Storm? Europe's steam cracker closures highlight continent's struggles with competitiveness, S&P Global (2025).

[3] T. Ren, et al., Olefins from conventional and heavy feedstocks: Energy use in steam cracking and alternative processes, Energy 31 (2006). https://doi.org/10.1016/j.energy.2005.04.001.

[4] M. Kusenberg, et al., Assessing the feasibility of chemical recycling via steam cracking of untreated plastic waste pyrolysis oils: Feedstock impurities, product yields and coke formation, Waste Management 141 (2022). https://doi.org/10.1016/j.wasman.2022.01.033.

[5] M. Victory, EU Commission sets out chemical recycling mass-balance accounting approach, RECYCLING Magazine (2025).

[6] V. Wilk, H. Hofbauer, Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier, Fuel 107 (2013). https://doi.org/10.1016/j.fuel.2013.01.068.

[7] C. Mandviwala, et al., Steam cracking in a semi-industrial dual fluidized bed reactor: Tackling the challenges in thermochemical recycling of plastic waste, Chemical Engineering Journal 500 (2024). https://doi.org/10.1016/j.cej.2024.156892.

[8] C. Kim, et al., Catalytic hydrocracking of waste plastic pyrolysis oil for production of high-quality naphtha over NiMo/mesoporous HZSM-5 catalyst, Fuel 385 (2025). https://doi.org/10.1016/j.fuel.2024.134036.

Hydrotreating of plastic waste pyrolysis oil for the production of secondary raw materials

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Introduction

Heterogeneous plastic waste streams cannot be effectively recycled by conventional mechanical routes due to the incompatibility of constituent polymers and the presence of contaminants (both intrinsic additives and those acquired during use and waste management). Thermochemical conversion via pyrolysis offers a robust alternative for mixed and contaminated plastics, thermally decomposing the feedstock in the absence of oxygen to yield three main products: gases, liquids/waxes and solids (char). The liquid fraction (pyrolysis oil) is typically the most abundant and, owing to its hydrocarbon composition, has potential as a polymer precursor. However, in thermal pyrolysis processes, contaminants in the feedstock are largely transferred to the products. The liquid phase, in particular, accumulates trace metals, halogens and heteroatoms, which frequently exceed the stringent impurity limits of downstream petrochemical units when produced by thermal pyrolysis without vapour-phase upgrading [1]. Therefore, ex-situ upgrading of these liquids is required. Among available options, hydrotreating, an established catalytic process in petroleum refining that operates with hydrogen at elevated pressures and moderate temperatures, has been most extensively studied and has demonstrated effective desulphurisation and denitrogenation performance for plastic-derived pyrolysis oils [2-3].
This work reports the upgrading of halogen-containing pyrolysis oils derived from municipal solid waste (MSW) packaging plastics and waste electrical and electronic equipment (WEEE) plastics via a combined hydrotreating and distillation process.

Materials and methods

For the experiments, 15 L of plastic waste pyrolysis oil (PWPO) was prepared by blending 8 L of pyrolysis oil from MSW packaging plastics, 5 L of pyrolysis oil from WEEE plastics, and 2 L of styrene. The pyrolysis oils were real-world industrial products supplied by Nantek (Spain). Styrene was introduced both to approximate the composition of WEEE-derived oils and to lower the halogen content, thereby reducing the risk of catalyst poisoning.
The experimental programme was carried out in a continuous laboratory set-up employing two commercial hydrotreating catalysts, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$, at 10 MPa pressure. Each test spanned five days, with the reactor temperature raised by 30 °C every 24 h from 240 °C to 360 °C.
PWPO and the primary hydrotreated liquids were fractionated into naphtha (< 150 °C), kerosene (150-250 °C), atmospheric gas oil (AGO; 250-360 °C) and a > 360 °C residue using an automatic distillation apparatus (Fischer Technology) equipped with a Spaltrohr column.

Results

Feedstock characterisation

Table 1 summarises the elemental characterisation of the PWPO. The composition was dominated by carbon (86.5 wt.%) and hydrogen (9.6 wt.%), with oxygen present at 2.7 wt.%. The principal contaminants were nitrogen (7000 mg kg^{-1}), sulphur (337 mg kg^{-1}), chlorine (837 mg kg^{-1}) and bromine (346 mg kg^{-1}).

Table 1. Elemental analysis of the PWPO.

C (wt.%)	86.5
H (wt.%)	9.6
N (wt.%)	0.7
O (wt.%)	2.7
S (mg kg^{-1})	337
Cl (mg kg^{-1})	837
Br (mg kg^{-1})	346
Others (wt.%)	≈ 0.3 (balance)

Pollutant removal by hydrotreating

Figure 1 summarises the hydrodehalogenation (HDX) results observed in the hydrotreated liquid products. Both catalysts delivered very low halogen levels in the products, with the maximum chlorine observed at 76 mg kg^{-1} for CoMo at 300 °C. The temperature response was non-monotonic: activity was high at 240 °C, diminished at 270-300 °C, and increased again from 330 °C, with complete halogen removal at 360 °C for NiMo and at 330 °C for CoMo.

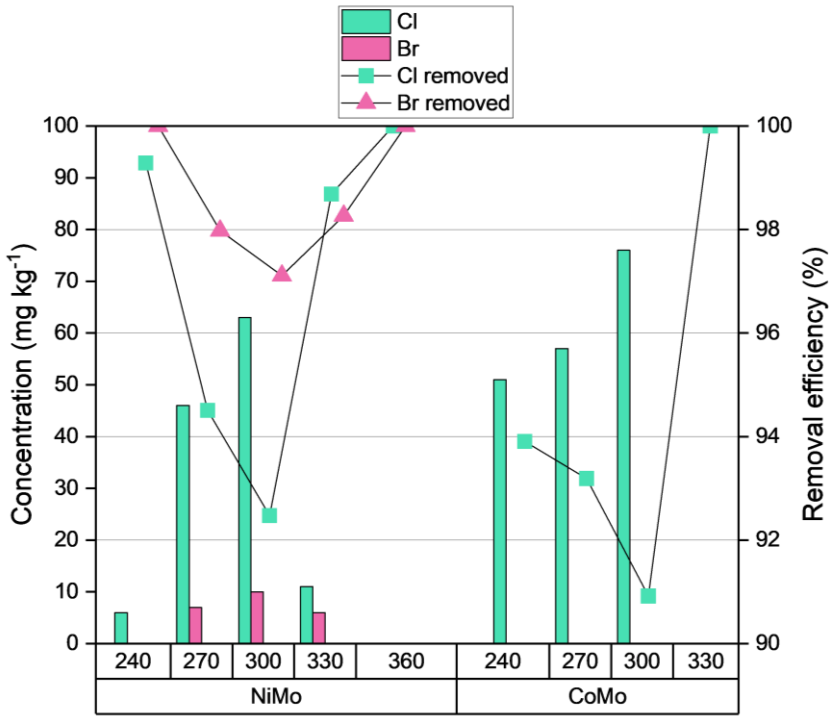


Figure 1. Halogens removal in hydrotreated liquids at different temperatures and catalysts.

Composition of hydrotreated distillation cuts

Figure 2 shows the distillation yields as a function of the catalyst used and temperature. In the case of the NiMo catalyst, the hydrotreatment at 240 °C caused a decrease in the light fractions (naphtha and kerosene) and the equivalent increase of the heavy fractions (AGO and residue) in comparison to the PWPO. However, as the temperature rose, there was an increase in the yield of light fractions to the detriment of heavy fractions, probably induced by hydrocracking reactions. The CoMo catalyst showed similar fraction yields, but with a notable difference: no increase in the naphtha fraction was observed with increasing temperature.

The two catalysts delivered broadly similar product compositions. In general, increasing temperature (from 240 to 360 °C) led to higher proportions of saturated hydrocarbons, lower olefin content, a slight decrease in aromatic hydrocarbons, and reduced non-hydrocarbon content for both catalysts.

The best naphtha outcome was obtained at 360 °C with the NiMo catalyst, yielding ≈ 20 wt.% saturates, 2 wt.% olefins, 78.5 wt.% aromatics, and 200 mg kg^{-1} non-hydrocarbons (down from 4.2 wt.% in the original naphtha cut). Complete hydrogenation of styrene to ethylbenzene was achieved even at the lowest temperatures.

Regarding kerosene, the NiMo catalyst at 360 °C produced also the most favourable kerosene cut, with very high hydrogenation efficiency: fewer olefins and more saturates than the corresponding naphtha under the same conditions, and a 19 % reduction in non-hydrocarbons.
Finally, the hydrotreatment generated an atmospheric gas oil (AGO) fraction that was virtually free of heteroatoms and enriched in polyaromatic hydrocarbons.

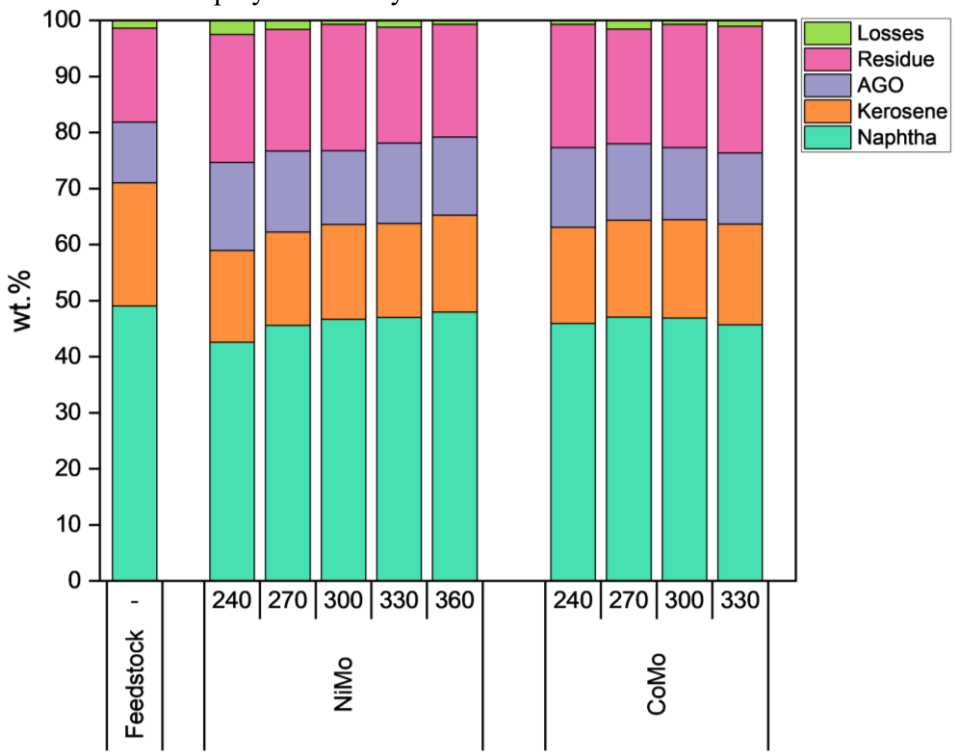


Figure 2. Distillation cuts of hydrotreated liquids obtained at different temperatures with NiMo catalyst and CoMo catalyst

Conclusions

Effective upgrading of halogen-contaminated pyrolysis oils was achieved by hydrotreating at 330-360 °C. While both catalysts performed well, NiMo surpassed CoMo in hydrogenation intensity and heteroatom/halogen removal. The distilled fractions permit BTEX recovery for subsequent re-polymerisation and can also be utilised as resin additives, bringing a step closer to closing the plastics loop.

References

[1] M. Kusenberg, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. De Meester, K. M. Van Geem: Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?', Waste Management, vol. 138, pp. 83–115, 2022.

[2] A. J. Abdulrahman, M. Kusenberg, M. Auersvald, C. Pernalete Piña, B. Parvizi; M. Havei, J. W. Thybaut, K. M. Van Geem: Advancing circular plastics: hydrotreatment of pyrolysis oils for high-yield ethylene production', Waste Management, vol. 211, p. 115287, Jan. 2026.

[3] P. Straka, M. Auersvald, D. Vrtiška, H. Kittel, P. Šimáček, and P. Vozka: Production of transportation fuels via hydrotreating of scrap tires pyrolysis oil', Chemical Engineering Journal, vol. 460, p. 141764, 2023.

CO_2 Biomass Gasification using a Two-stage Gasification Process to Produce CO-Rich and Low-Tar Syngas

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Introduction

This study investigates biomass gasification utilizing CO_2 as a gasifying agent to evaluate the possibility of producing CO-rich syngas with low tar concentrations. Biomass CO_2 gasification enables the conversion of renewable carbon resources into CO-rich syngas while incorporating CO_2 into the reaction environment, providing an alternative pathway for CO production that does not rely on fossil-fuel-derived carbon sources [1]. However, biomass gasification in bubbling fluidized bed reactors is commonly associated with two major operational challenges: tar formation and bed agglomeration. Tar formation can lead to condensation and deposition of heavy organic compounds, resulting in operational instability and potential process shutdowns [2]. Activated carbon (AC) has attracted attention as a tar removal material due to its high surface area [3] and low cost [4]. Bed agglomeration, another critical issue in fluidized bed gasification, occurs when alkali and alkaline earth metals (AAEMs) in biomass ash react with silica-based bed materials to form low-melting-point eutectic compounds (about 770 °C), such as potassium silicate (K_2O-nSiO_2). These compounds can lead to sintering, defluidization, and poor heat transfer [5]. Accordingly, the objective of this study is to evaluate the feasibility of producing CO-rich syngas from the CO_2 gasification of biomass (wood chips) while mitigating tar formation and preventing bed agglomeration under stable reactor operation. To achieve this objective, a two-stage gasification process developed at the University of Seoul (UOS) was applied (Fig. 1), providing insights into a potential pathway toward more sustainable and practically relevant gasification technologies.

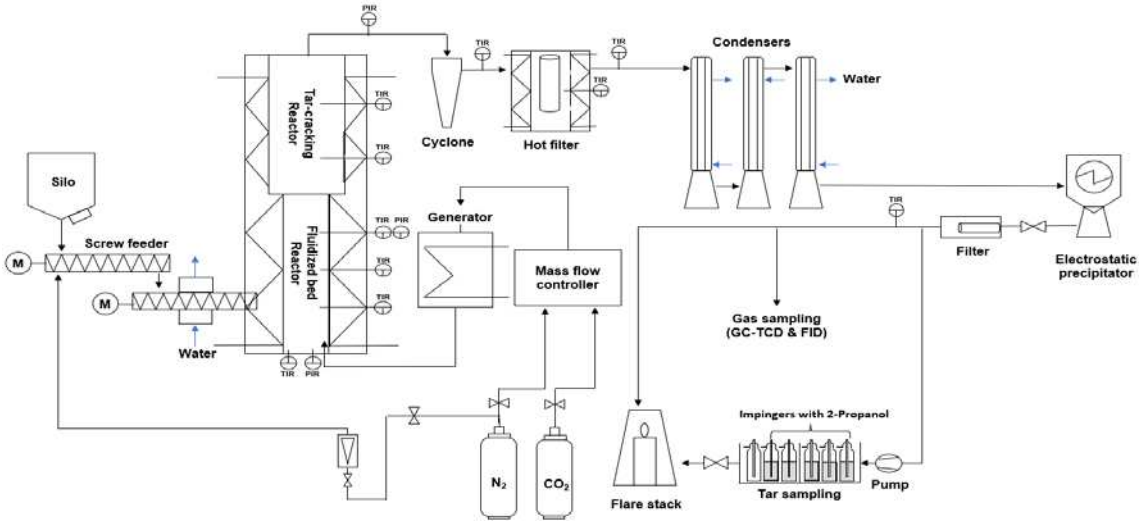


Figure 1. Diagrams of University of Seoul (UOS) two-stage gasification process.

The UOS two-stage gasification system consists of a bubbling fluidized bed gasifier (BFBG), in which silica sand is used as the bed material, followed by a tar-cracking reactor (TCR) packed with AC. Unlike conventional single-stage fluidized bed gasification, this configuration allows the primary gasification and secondary tar conversion steps to be controlled separately, thereby facilitating tar removal using AC without directly constraining the operating conditions of the gasifier.

Experimental conditions

The table below shows the reaction conditions of CO_2 gasification of biomass. The feed material was oak wood chips (OWC).

Table 1. Reaction conditions for CO_2 gasification of OWC in the UOS two-stage process.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
TCR temperature (°C)	806 ± 4	804 ± 5	805 ± 3	803 ± 3	802 ± 4	842 ± 2	839 ± 4	805 ± 2
BFBG temperature (°C)	799 ± 6	793 ± 9	703 ± 5	704 ± 12	704 ± 6	703 ± 4	711 ± 8	705 ± 9
Reaction medium (Vol.%)	N_2 (100)	CO_2 (100)	N_2 (100)	N_2:CO_2 (50:50)	CO_2 (100)	N_2 (100)	CO_2 (100)	CO_2 (100)
CO_2/C ratio	-	2.1	-	1.0	2.0	-	2.1	2.1
AC (g)	1500	1500	1500	1500	1500	1500	1500	0
Gasification time (min)	60	60	60	60	60	60	60	60

TCR: tar-cracking reactor; BFBG: bubbling fluidized bed gasifier. AC: activated carbon

In this study, the effects of BFBG temperature, TCR temperature, the CO_2 fraction in the reaction medium, and the use of AC were investigated.

In Runs 1, 3, and 6, N_2 was used as a reaction medium because the outlet CO_2 resulting from CO_2 gasification contained both unreacted injected CO_2 and CO_2 generated from the OWC, requiring a reference value to distinguish between them. The CO_2 detected under N_2 conditions was assumed to originate from the thermal decomposition (pyrolysis) of OWC and tar and was used to quantify the amount of OWC-derived CO_2 produced. This method allowed for estimating the proportion of injected CO_2 that participated in the gasification reaction. For the experiment on the BFBG temperature effects (Runs 2 at 793 °C and 5 at 704 °C), Runs 1 and 3 were performed under N_2 to determine the amount of CO_2 reacted in Runs 2 and 5, respectively. For the evaluation of TCR temperature effects (Runs 5 at 802 °C and 7 at 839 °C), Run 6 was conducted under N_2 to determine the amount of CO_2 reacted in Run 7. The effects of the CO_2 fraction in the reaction medium were assessed by comparing Runs 3, 4, and 5, whereas the role of AC was evaluated by comparing Runs 5 and 8.

All experiments were conducted at a constant feed rate of 8.3 g/min (500 g per run). The CO_2 feed rate ranged from 14 to 30 g/min (CO_2/C = 1.0–2.1), and the superficial gas velocity of the reaction medium was maintained at 2.4 times the minimum fluidization velocity (U_{mf}). The BFBG was packed with 2200 g of silica sand (150–425 μm).

Experimental results

Table 2 presents the CO_2 gasification results calculated excluding teh amount of unreacted CO_2.

Table 2. Gasification performance after excluding unreacted CO_2.

	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8
Reaction medium (vol.%)	N_2 (100)	CO_2 (100)	N_2 (100)	N_2:CO_2 (50:50)	CO_2 (100)	N_2 (100)	CO_2 (100)	CO_2 (100)
Product distribution (wt.%)								
Syngas (Nm^3/ $kg_{daf\ owc}$)	1.19	1.26	1.08	1.19	1.12	1.21	1.38	0.75
Syngas ($kg/kg_{daf\ owc}$)	0.83	1.23	0.78	1.06	1.09	0.81	1.29	0.72
Char ($g/kg_{daf\ owc}$)	114.09	80.86	149.17	135.63	148.99	137.64	99.12	101.40
Condensed tar ($g/kg_{daf\ owc}$)	19.24	0.90	0.43	1.44	3.08	0.98	3.07	24.18

Condensed liquid (g/kg_{daf_owc})	33.30	238.01	67.12	179.38	243.96	56.26	255.01	158.08
H_2 (g/kg_{daf_owc})	45.18	21.31	40.47	27.94	19.35	50.44	26.55	10.69
CO (g/kg_{daf_owc})	492.22	945.87	434.22	738.59	786.58	504.03	1038.64	466.65
Tar in syngas (mg/Nm^3)	163.49	17.61	56.54	189.91	120.62	88.73	90.01	7990.64
LHV(MJ/Nm^3)	11.24	11.30	10.68	11.36	11.25	10.55	11.05	18.06
Gasification efficiency (%)								
CGE	79.69	84.91	62.50	80.59	74.92	76.32	90.61	80.35
OCCE	-	85.45	-	78.98	77.34	-	85.65	-
CTRE	-	96.29	-	94.05	87.28	-	87.32	Base
CO_2 utilization indicator								
CO_2UE (%)	-	15	-	22	14	-	18	-
SCCR ($kg_{reacted\ CO2}/kg_{daf_owc}$)	-	0.55	-	0.38	0.49	-	0.65	-

CGE: Cold gas efficiency, OCCE: Overall carbon conversion efficiency, CTRE: Condensed tar removal efficiency, CO_2UE: CO_2 utilization efficiency, SCCR: specific CO_2 consumption rate

Compared to the experiment without AC (Run 8), the use of AC (Run 5) increased the syngas yield from 0.75 to 1.21 kg/kg_{daf_owc}, while decreasing the condensed tar yield from 24.2 to 3.1 g/kg_{daf_owc}, achieving a CTRE of 87 %. The tar concentration in syngas also decreased from 7,991 to 121 mg/Nm^3. Furthermore, the CO and H_2 yield increased significantly from 466.7 to 786.6 g/kg_{daf_owc} and from 10.7 to 19.4 g/kg_{daf_owc}, respectively. These improvements were attributed to effective tar adsorption on AC followed by thermal/catalytic cracking and reforming reactions, enabling continuous in situ regeneration of AC. The two-stage process extended the contact time and repeated contact between CO_2 and carbonaceous material, improving CO_2UE and SCCR compared to the single-stage fluidized bed gasifiers. Despite maintaining the BFBG temperature below the eutectic compound formation temperature (approximately 770 °C) to prevent bed agglomeration (Run 5), high CO yield (786.6 g/kg_{daf_owc}) and gasification performance were achieved. These results indicate that the proposed two-stage process enables stable operation together with substantial improvements in syngas quality and carbon utilization, offering a promising approach for efficient biomass-to-syngas conversion while minimizing the bed agglomeration.

References

[1] Islam, M.W., 2020. Effect of different gasifying agents (steam, H_2O_2, oxygen, CO_2, and air) on gasification parameters. International Journal of Hydrogen Energy. 45(56), 31760–31774. https://doi.org/10.1016/j.ijhydene.2020.09.002.

[2] Cortazar, M., Santamaria, L., Lopez, G., Alvarez, J., Zhang, L., Wang, R., Bi, X., Olazar, M., 2023. A comprehensive review of primary strategies for tar removal in biomass gasification. Energy Conversion and Management. 276, 116543. https://doi.org/10.1016/j.enconman.2022.116496.

[3] Curdts, B., Pflitsch, C., Pasel, C., Helmich, M., Bathen, D., Atakan, B., 2015. Novel silica-based adsorbents with activated carbon structure. Microporous and Mesoporous Materials. 210, 202–205. https://doi.org/10.1016/j.micromeso.2015.02.007.

[4] Shaheen, J., Fseha, Y.H., Sizirici, B., 2022. Performance, life cycle assessment, and economic comparison between date palm waste biochar and activated carbon derived from woody biomass. Heliyon. 8(12), e12388. https://doi.org/10.1016/j.heliyon.2022.e12388.

[5] Yao, X., Hu, Y., Ge, J., Ma, X., Mao, J., Sun, L., Xu, K., Xu, K., 2020. A comprehensive study on influence of operating parameters on agglomeration of ashes during biomass gasification in a laboratory-scale gasification system. Fuel. 276, 118062. https://doi.org/10.1016/j.fuel.2020.118083.

JFE's C-PhoeniX Process: Waste Gasification and Waste-to-Chemical Technology

~ A Missing Piece for Circular Economy ~

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C-PhoeniX Process: JFE's Waste Gasification Technology

JFE Engineering has developed a proprietary waste gasification technology using pure oxygen that produces refined synthesis gas (consisting of H_2, CO and CO_2) from various waste streams, including municipal, industrial, and plastic waste. The company's extensive expertise in facility operations and maintenance, accumulated through managing five commercial facilities in Japan since 2000, has been instrumental in perfecting this technology. This 25-year journey of hands-on operational experience, rigorous maintenance protocols, and continuous technological refinement has positioned JFE Engineering as a global leader in waste gasification technology.

Application of C-PhoeniX to Waste-to-Chemical Initiative

The refined synthesis gas can be used as a feedstock for chemical manufacturing processes to produce plastic raw materials and Sustainable Aviation Fuel (SAF) without relying on fossil-derived resources. Waste to Chemical Recycling (WtC) technology is emerging as a key solution to become carbon-neutral or even carbon-negative in the waste sector, with waste gasification serving as its cornerstone. Our proven gasification technology, underpinned by over two decades of practical operational knowledge and sophisticated maintenance expertise, has captured significant industry attention.

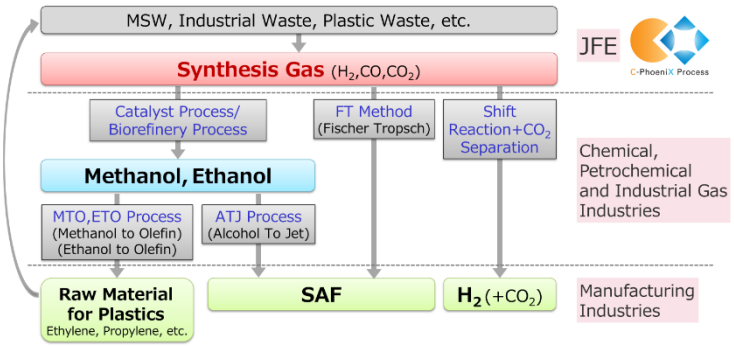


Figure 1. Whole view of chemical recycling scheme with C-PhoeniX process

Demonstration Test with Green Innovation National Fund

With support from the Japanese government's Green Innovation Fund, we are currently advancing two key technological developments, building upon our comprehensive operational experience:
(1) enhancing the production of high-quality, stable refined synthesis gas in our gasification facilities.
(2) optimizing the integrated system that combines waste gasification with chemical production processes
Demonstration tests started in December 2025, with commercial implementation targeted for around 2030. We will introduce the latest achievements and future perspectives in this conference.



Figure 2. View of demonstration test plant in Chiba, Japan

Basic Chemical Production and Circular Resource Business via Gasification-based Chemical Recycling of Post-Consumer Plastics

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Introduction

Mechanical recycling and chemical recycling are widely recognized as major approaches for plastic recycling. Chemical recycling, in particular, has attracted attention as a complementary option to mechanical recycling. However, within the range of chemical recycling, gasification remains less widely recognized than other options. As policy discussions on plastic recycling continue to progress in various regions, there is a possibility that gasification may not be sufficiently considered in comparison with other approaches. In this context, it is important to enhance understanding of plastic gasification that have already been successfully implemented in Japan and to clarify their potential for future global deployment. These perspectives are important in promoting the realization of a sustainable society through resource circulation and a circular economy.

Historical background

Resonac has produced ammonia in Japan since the commencement of operations at its Kawasaki site in 1931 for originally agricultural promotion purpose, utilizing feedstocks suited to each era. The source of hydrogen used as a feedstock for ammonia production has undergone multiple transitions, beginning with water electrolysis and subsequently shifting to naphtha, off-gases from petroleum refining, and city gas. At present, post-consumer plastics are used as the feedstock, and since 2003—over more than 20 years—we have continuously operated our business that produces and sells basic chemicals obtained through gasification-based chemical recycling (Kawasaki Plastic Recycle, hereafter abbreviated as "KPR", licensed by Ebara Corporation (now EBARA Environmental Plant Co., Ltd.) and Ube Industries, Ltd. (now UBE Corporation) as the EUP process. These products include hydrogen, ammonia, carbon dioxide, and their derivatives. To date, a cumulative total of more than 1.2 million tons of post-consumer plastics has been recycled through KPR business.

Overview of the Gasification Chemical Recycling Manufacturing Process

KPR comprises two steps; manufacturing densified feedstock called “molded plastic”, and gasification. A schematic overview of the process is shown in **Figure 1**, and pre-treatment process is shown in **Figure 2**.

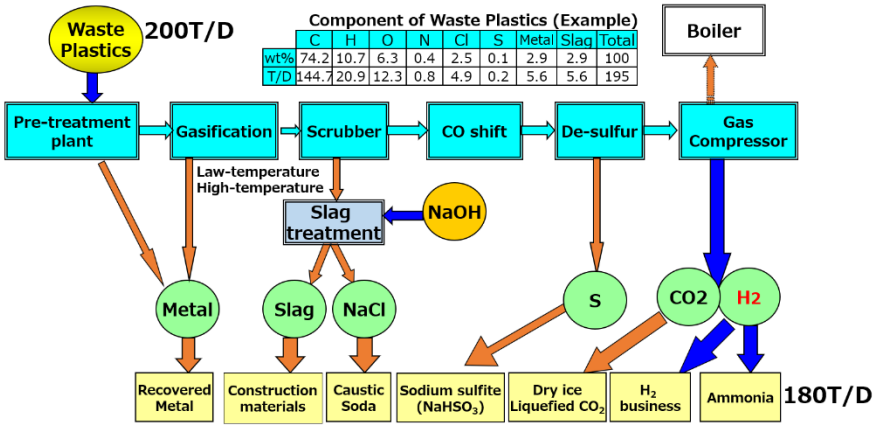


Figure 1. Overview Process flow in KPR

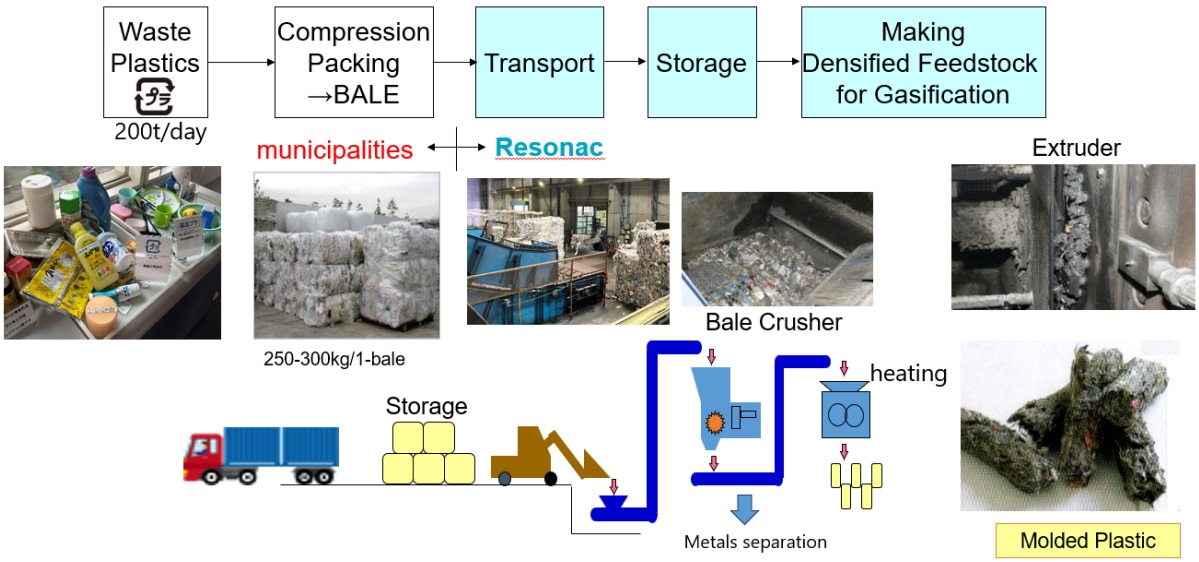


Figure 2. Process flow in KPR pre-treatment

Compressed bales (250–300 kg) of post-consumer plastic containers and packaging collected as waste plastics by local governments are shredded in a bale crusher. Metallic contaminants are then removed magnetically, and the plastics are extruded into cigar-shaped "molded plastic". Formed plastics are decomposed at the molecular level in a two-stage gasification process shown in **Fugure 3**, producing syngas which mainly consists of hydrogen and carbon monoxide. Non-combustible metals are recovered in an unoxidized state from the low-temperature gasification furnace, while ash from the high-temperature furnace is rapidly quenched and collected as granulated slag.

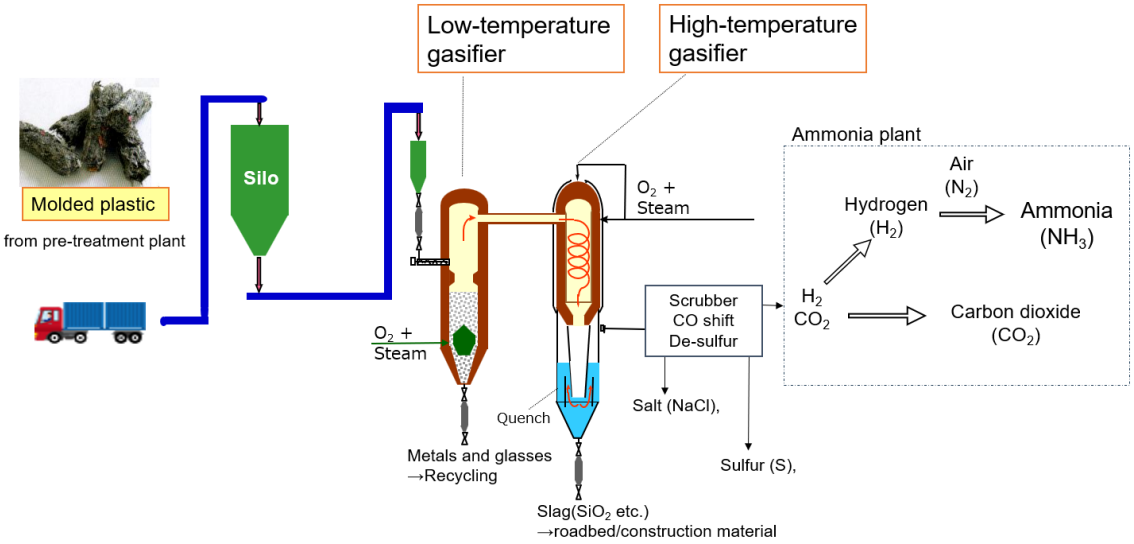


Figure 3. Process flow in KPR Gasification

This series of processes is characterized by three key features: (1) omnivorous feedstock acceptance, (2) zero emissions, and (3) energy self-sufficiency. The process can handle a wide variety of used plastics without prior separation, tolerating contaminants such as metals, food residues, and small amounts of chlorine-containing plastics. Composite materials and inorganic components are recovered as metals, glass, or slag, which is effectively reused as construction material. Nearly all syngas produced is utilized as products, and residues such as metals, slag, chlorine, and sulfur are also effectively recycled, resulting in an overall zero-emissions system. In addition, because plastic gasification is an exothermic reaction, the process operates using only the energy contained in the plastics themselves after startup, reducing fossil fuel consumption and associated CO_2 emissions.

GHG Reduction Effect of the Gasification Chemical Recycling

In 2022, Resonac obtained third-party verification from the Japan Life Cycle Assessment Foundation (LCAF) confirming that the life cycle assessment methodology complies with ISO 14040 and ISO 14044. The results demonstrate that ammonia produced from post-consumer plastics via the process achieves approximately 80% reduction in greenhouse gas (GHG) emissions compared with ammonia produced from city gas, a fossil-based feedstock as the conventional ammonia production process. The assessment was conducted using the avoided burden approach, which incorporates the environmental benefits associated with the effective utilization of post-consumer plastics [1-3].

Potential applications for hard-to-recycle industries

Beyond improving efficiency and reducing costs, gasification-based chemical recycling must adapt to societal needs by diversifying both feedstock inputs and product outputs. Feedstock diversification is essential not only for plastics but also for post-consumer products in general, from the perspectives of resource circulation and the circular economy. In cooperation with apparel brand owners, Resonac is developing a circular economy system that regenerates post-consumer textile products into acrylic fibers via hydrogen and ammonia, with acrylonitrile as an intermediate. Recycling of waste textiles remains limited, particularly for blended fibers, which are difficult to recycle. Mixing such materials with post-consumer household plastics including plastic containers and packaging at suitable ratios to form densified feedstock, followed by conversion into synthesis gas via gasification, is expected to support the broader advancement of recycling in society. Similarly, plastics generated from the agricultural industries are being examined. Moreover, as this approach is potentially applicable to plastics discharged from various industries, such as the automotive, electronics, and construction, further investigations are planned. At the conference, several concrete case studies will be presented.

Final Remarks

Furthermore, regarding the diversification of product outputs obtained from recycling, it is necessary to consider expanding beyond hydrogen, ammonia, and carbon dioxide. It is also possible to produce methanol from syngas obtained from gasification chemical recycling and utilize it as a low-carbon methanol to promote carbon recycling. Resonac is currently working to add environmental value to this expansion of resource recycling through the diversification of raw materials and products by branding it as "CirculaC". In this way, by broadening and diversifying the range of raw material inputs and product outputs, gasification has great potential to adapt to societal demands. We hope that the widespread adoption and development of these technologies, along with their early implementation in society, will contribute to the early realization of a sustainable society.

References

[1] Y, Shimazu, *Challenges and Measures for Development of Circular Use of Plastics – A Case of Gasification Process of Plastics –* , Journal of Life Cycle Assessment of Japan, 19, 136, 2023.
[2] T. Beppu, *Production of Hydrogen and Ammonia from Used Plastics*, Osaka Industrial Research Association, Kagaku To Kogyo (Osaka), 99, 65, 2025.
[3] T. Beppu, *Production of Basic Chemicals from Used Plastics*, The Catalyst review, 10, 2025.

Comparative Life Cycle Assessment of a Pre-Commercial Chemical Recycling Process for Post-Industrial Plastic Waste

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Whether in everyday products, technical applications, or medicine, plastics are an integral part of today's life. After use, most plastics end up in household waste and are either deposited in landfills, incinerated to generate energy, or mechanically recycled. The amount that goes into recycling is not just determined by the existence of recycling facilities, but also by the characteristics of the waste streams: pure and clean plastics are well suited for mechanical recycling processes, while contaminated fractions or materials that are difficult to separate, such as compound materials, are hard to recycle mechanically. To increase the circularity of these fractions and keep the carbon in loop, chemical recycling technologies are being developed that can convert those waste fractions into either monomers for repolymerization of new plastics, or into other valuable petrochemical products. One of the most investigated chemical recycling process type is pyrolysis. During pyrolysis, the polymer is cracked at temperatures ranging from 250 to 900 °C, in the absence of oxygen and with or without the use of catalysts [1]. The resulting products are mainly liquid and range from specific monomer fractions to general petrochemical fractions, such as naphtha and diesel, which are intended as substitutes for fossil fuels in the chemical industry.

From an environmental perspective, these processes pursue two main objectives: Firstly, reduce the environmental burden compared to the state-of-the-art end of life technologies, and secondly, provide products with a lower environmental footprint than those produced from fossil crude oil. Pyrolysis processes are energy-intensive and the resulting products require several upgrading steps before they can be reintegrated into the chemical industry, which makes these comparisons non-trivial. Previous studies have already shown the potential of chemical recycling, resulting in lower environmental burdens than end of life pathways, such as incineration, as well as resulting in lower emissions for petrochemical products. Still, these results are mostly based on results derived from literature, lab-scale experiments, or simulation data. This often leads to overestimations of product qualities (e.g., oil = 100% naphtha), literature-based process energy demands and neglect of essential and energy-intensive pre- and posttreatment steps. For this reason, review papers on life cycle assessments of pyrolysis processes recommend that such analyses should be carried out once better data is available [2]. Furthermore, comparisons of technologies and studies are limited due to the use of incomparable functional units. These units vary from the mass of a specific type of plastic, a petrochemical product or the energy content of a specific product. This submission presents a life cycle study that addresses these criticisms. The life cycle inventory is based on primary data of a preindustrial plant, missing data for posttreatment steps are supplemented with a process simulation to ensure a complete system, and a new functional unit of total obtained products is introduced to ensure a comparability for future studies.

The system boundaries applied for this study are shown in **Figure 1**. The process consists of several pretreatment steps, including a sieve, tray, ferrous and non-ferrous metal separator, and a dryer, where moisture is removed. Before the feedstock enters the reactor, catalyst is added. The reactor has a capacity of up to 200 kg/h [3] and is powered by electricity. Besides two liquid products, a waste residue and a waste gas fraction are generated during the process. To this point, the mass balance is conducted using weighing lists, electricity meters and flowmeters for two experimental trials based on 6–9 tons of polyethylene/polyamide feedstock. The liquid products are then post treated in a hydrogenation and distillation step to the final petrochemical products of naphtha, diesel, and the monomer caprolactam.

The mass and energy balances of these process steps are derived through process simulations in the ASPEN Plus software. The product feeds are implemented based on the compositions derived in two-dimensional gas chromatography.

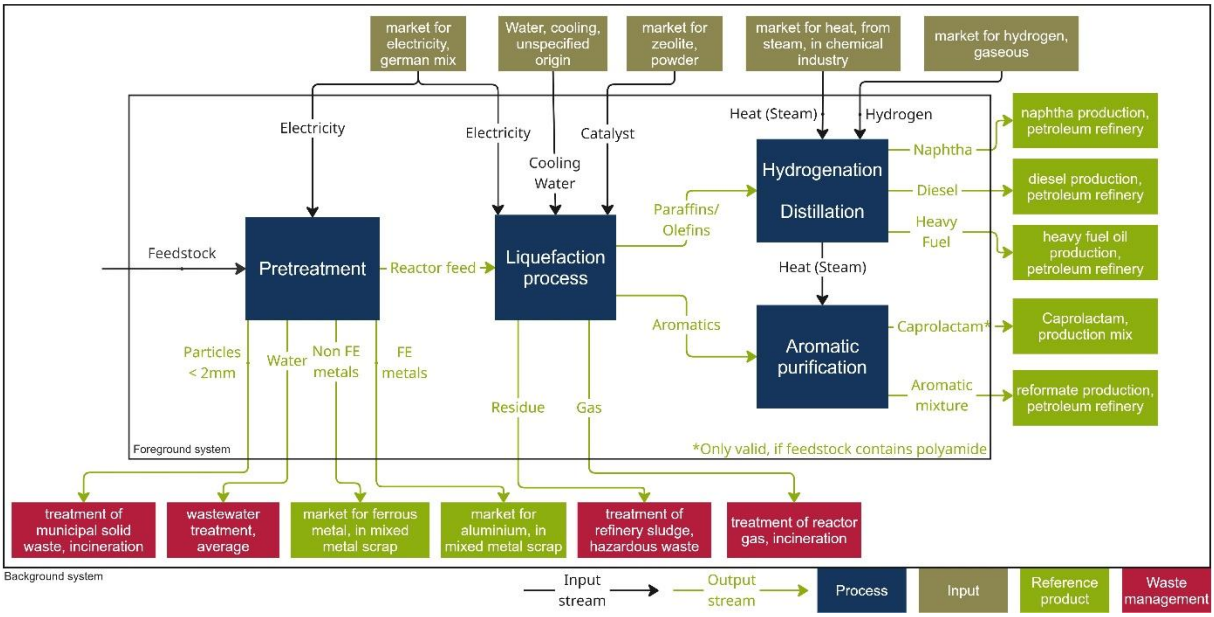


Figure 1. System boundary of the chemical recycling process including the process steps (foreground system) and data sources (background system).

The life cycle assessment is conducted based on DIN EN ISO 14040/44 standards, as well as on recent guidelines of Chemical Recycling Europe [4]. The impact assessment is performed using the ReCiPe Midpoint (H). This method provides impact categories for terrestrial and aquatic ecosystems, as well as on fossil and mineral resource consumption, in addition to the commonly used global warming potential. The functional unit (FU) for the comparison to the state-of-the-art waste treatment is defined as 1 kg of plastic waste input. For the comparison to the fossil production route, a new FU is introduced as 1 kg of total obtained products. This FU represents the production of 1 kg of products, incorporating the distribution of all the main and by-products generated in the process. It is then compared to the fossil production mix, with the same product distribution. Using this method, the life cycle assessment calculations are no longer dependent on allocation assumptions or on a substitution-credit system. This, in turn, enables a smoother comparison to other LCA studies, as this FU works independently of a specific product type, such as, e.g., naphtha, a specific monomer or polymer type.

The process's global warming potential emissions are divided into three main contributors. The majority of emissions result from electricity consumption and catalyst use in the process, accounting for up to 53% of the total emissions. Up to 36% of the process emissions are caused by treating waste gases and residues. Although these side streams are considered waste streams with significant emission contributions, they are often treated as products in other studies. This leads to the neglect of waste treatment emissions, and in addition to that, provides environmental credits, resulting in even lower process emissions. This underlines the importance of decision making when conducting a life cycle assessment, as it can completely shift the results. The third contributor, responsible for up to 20% of total emissions, is the post-treatment of liquid products. This emphasises the importance of including these processes within the system boundaries.

Comparing the results to state-of-the-art end of life processes, such as incineration, the chemical recycling process results in a 50% lower global warming potential. Compared to fossil production, the chemical recycling process provides petrochemical products with up to 40% lower emissions. More importantly, these results are sensitive to regional aspects, as well as to process efficiency, which is shown in **Figure 2**. In this figure, the deviations in the global warming potential compared to the initially

calculated base scenario are highlighted, in either resulting in a higher (+) or a lower (-) environmental burden compared to the base case.

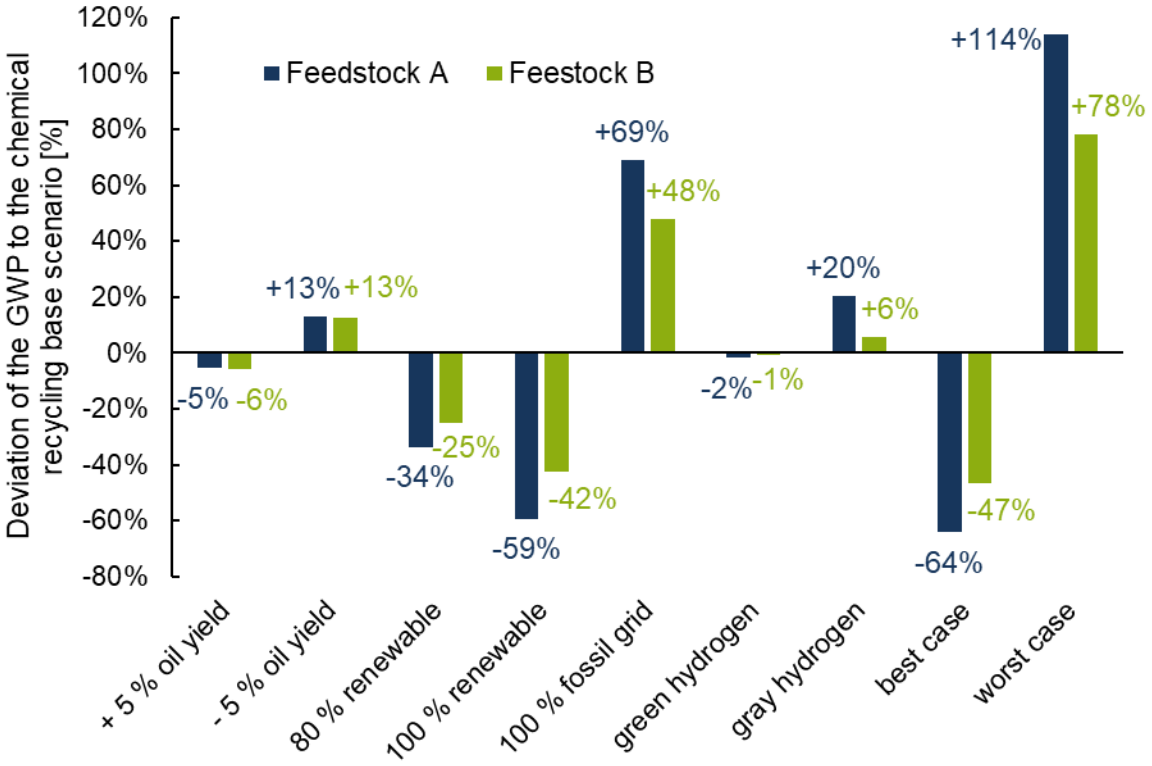


Figure 2. Sensitivity of the Global Warming Potential (GWP) to regional utility availability and process efficiency.

The sensitivity analysis shows that the results are significantly dependent on the liquid product yield of the process, the electricity grid used to power the process, as well as the source of hydrogen for product upgrading. Combining a fully fossil electricity grid, a use of grey hydrogen, with a 5% lower oil yield, the emissions caused by the process are more than doubled, with an increase of +114%. On the other hand, powering the process with a fully renewable grid, using green hydrogen, and increasing the process efficiency by 5% oil yield, the emissions can be reduced by 62%. However, this reduction means that chemical recycling as a standalone technology cannot provide a net-zero emission transition for the plastics sector.

References

[1] Laghezza M, Fiore S, Berruti F.: *A review on the pyrolytic conversion of plastic waste into fuels and chemicals*, Journal of Analytical and Applied Pyrolysis, 179, 106479, 2024.

[2] Pires Costa L, Vaz de Miranda DM, Pinto JC.: *Critical Evaluation of Life Cycle Assessment Analyses of Plastic Waste Pyrolysis*, ACS Sustainable Chemistry & Engineering, 10(12), 3799–807, 2022.

[3] Biessey P, Vogel J, Seitz M, Quicker P.: *Plastic Waste Utilization via Chemical Recycling: Approaches, Limitations, and the Challenges Ahead,* Chemie Ingenieur Techni, 95(8), 1199–214, *2023.*

[4] Levis, J., Martinez, A., Karg, J.: *Guidelines for Chemical Recycling LCAs*, Sphera Solutions, Report v1.0, 2025.

Process-consistent comparative assessment of hydrolysis- and pyrolysis-based PA6 recycling routes for ε-caprolactam

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Plastics play a key role in modern society. However, a significant proportion of plastic waste is still incinerated or landfilled at the end of its life cycle. In Europe, fossil-based plastics accounted for approximately 54.6 Mt in 2024, while only 8.4 Mt of produced plastics were reported as circular plastics, corresponding to a circular share of 15.4 % [1]. This illustrates the persistent gap between plastic production and effective material circularity, underlining the need for advanced recycling strategies that go beyond conventional approaches. Among engineering plastics, polyamides, and particularly polyamide-6 (PA6), are of high industrial relevance due to their widespread use in fibres, technical components and multilayer packaging materials [2]. Despite production volumes of approximately 6.5 Mt in 2023, only a limited fraction of PA6-containing waste streams is effectively recycled [3]. Mechanical recycling approaches are often constrained by material degradation, contamination and complex product structures, limiting their applicability to post-consumer and mixed waste streams [4]. Therefore, chemical recycling is a promising alternative to recover monomers, such as caprolactam, and enable circular material flows for PA6. A handful of concepts for chemical recycling of PA6 have been proposed in the literature, including depolymerization routes based on hydrolysis, as well as pyrolysis-based approaches combined with downstream processes. These routes differ fundamentally in terms of their process characteristics and feed requirements. Hydrolysis-based concepts typically yield relatively clean caprolactam streams but rely on specified, low-contaminated feeds, making them feed-sensitive technologies [5]. In contrast, pyrolysis-based routes are more robust and can, in principle, handle more heterogeneous waste streams at the expense of increased downstream separation and purification effort [6].

To date, however, a process-based comparison basis between these recycling routes is largely missing. Existing assessments often rely on idealized process representations or favourable feed assumptions such as pure or narrowly specified PA6 waste streams, negligible contaminant levels or simplified downstream separation requirements, limiting the reliability of evaluations regarding technical feasibility and environmental performance. Consequently, the impact of different PA6 waste compositions on the suitability of hydrolysis- and pyrolysis-based recycling concepts for circular caprolactam recovery remains unclear. Against this background, this contribution investigates the recovery of circular caprolactam from PA6 waste streams by comparing the technical and environmental performance of hydrolysis- and pyrolysis-based recycling routes. This is achieved using process representations that are consistent in terms of system boundaries, target product quality, and downstream processing scope, combined with a unified life cycle assessment framework. The focus lies on identifying the influence of feed composition and downstream processing on the technical feasibility and environmental performance of these respective routes, thereby enabling a realistic and knowledge-based evaluation of chemical PA6 recycling concepts.

To enable this comparison, a consistent framework is applied, building on the process representations defined above. This framework ensures that any observed differences between recycling routes can be attributed to intrinsic process characteristics and feedstock dependencies rather than to inconsistent assumptions or idealized system configurations. Both recycling routes are assessed using the same target product: caprolactam of a defined quality and consistent system boundaries, providing a common basis for technical and environmental evaluation.

For the present comparison, the hydrolysis-based recycling route is represented by the aqueous depolymerization of PA6 to caprolactam, as described by McNeeley et al. (2024), which mainly focuses on relatively pure PA6 waste streams such as carpet waste [5]. This conversion route is typically associated with clean product streams and well-defined separation tasks but relies on narrowly specified feed compositions with low levels of contamination. Within the present framework, it represents monomer recovery under favourable and controlled feedstock conditions. In contrast, the pyrolysis-based route considers the thermal conversion of PA6-containing waste streams into a complex product mixture, followed by downstream processing for caprolactam recovery. A model-based process representation is developed to reflect realistic separation and purification requirements arising from mixed and contaminated feeds. Relevant impurities, including nitrogen-containing compounds (such as lactams, amides, amines and nitriles), oxygenated compounds, phenolic species, carboxylic acids and esters, as well as aliphatic and aromatic hydrocarbons are explicitly considered, and downstream processing is structured to meet predefined, practice-oriented product quality specifications rather than assuming ideal separations.
Based on the consistent framework described above, qualitative process representations are derived for both recycling routes to illustrate key differences in feed sensitivity and downstream processing efforts.

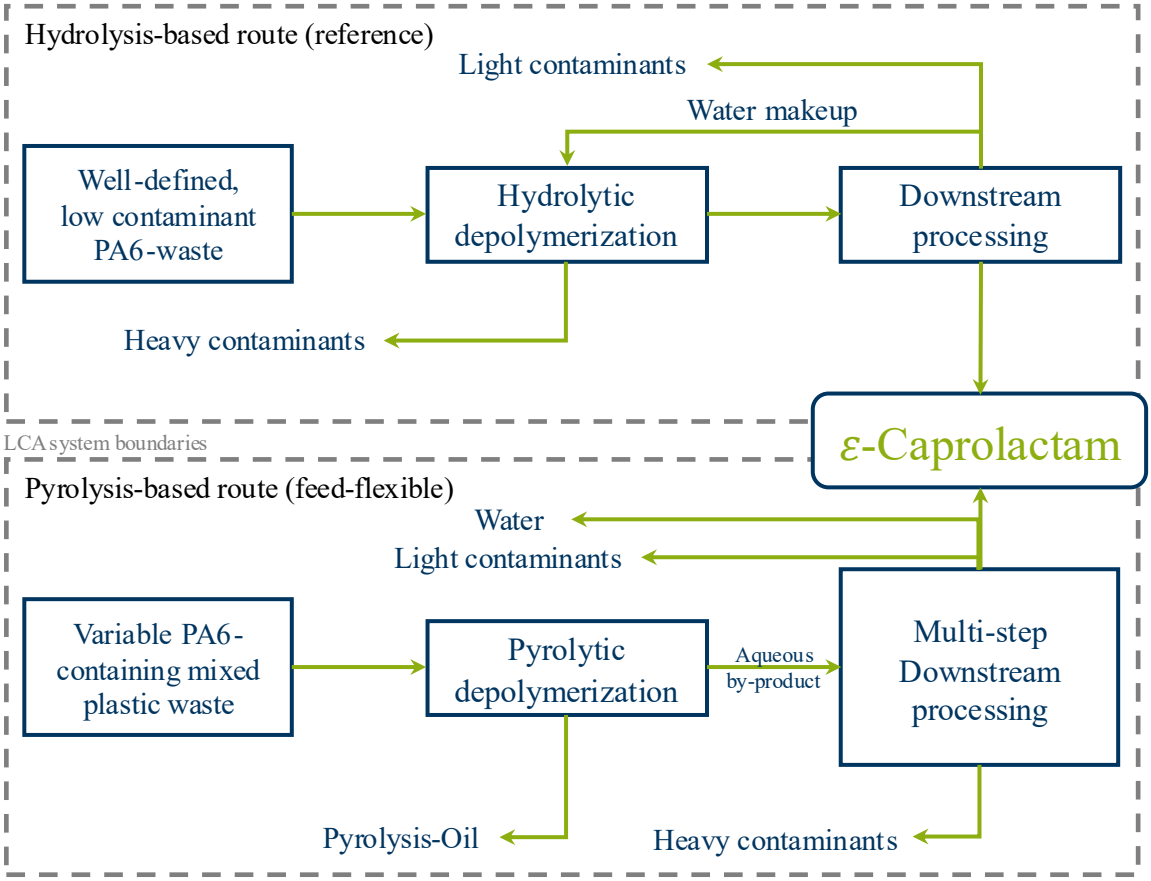


Figure 1. Qualitative process representation of hydrolysis- and pyrolysis-based routes for caprolactam-recovery from PA6-waste stream. The schematic highlights differences in feedstock requirements and downstream processing complexity.

As illustrated in **Figure 1**, the two recycling routes differ fundamentally in their process characteristics and in the role of feed composition: for the hydrolysis-based reference route, feed composition constitutes a fixed boundary condition, whereas it serves as a variable parameter for the pyrolysis-based route. Accordingly, feed composition is treated as a central influencing parameter within the comparison.

Variations in PA6 content and the presence of accompanying impurities are considered to reflect realistic waste stream conditions and to assess their influence on process requirements and downstream processing effort.

The preliminary comparative assessment indicates that the suitability of both PA6 recycling routes strongly depends on the composition of the processed waste streams. While the hydrolysis-based reference route enables efficient caprolactam recovery for almost pure PA6 waste streams obtained by carpets, its applicability remains limited to such conditions. In contrast, the pyrolysis-based route exhibits a higher tolerance to feed variability but requires increasingly complex downstream processing to achieve comparable product quality. Initial trends suggest that increasing feed complexity leads to higher separation effort and energy demand for the pyrolysis-based route, which directly affects its environmental impact. At the same time, the ability to process waste streams that are not accessible to hydrolysis-based recycling represents is a key advantage of the pyrolysis route. This trade-off between robustness and downstream processing effort emerges as a central aspect of the comparison. From an environmental perspective, the results obtained so far indicate that neither recycling route can be regarded as universally superior. Instead, the relative performance of both concepts shifts depending on the given feed composition and the configuration needed. These observations underline the importance of consistent process representations and a unified assessment framework when evaluating chemical recycling concepts under realistic conditions.

References

[1] Plastics Europe, Plastics the Fast Facts 2025: Global and European plastics production and economic indicators, 2025.

[2] G. Abts, Kunststoff-Wissen für Einsteiger: Grundlagen, Eigenschaften und Recycling polymerer Werkstoffe, fourth., aktualisierte und erweiterte Auflage, Hanser, München, 2020.

[3] MarketGrowthReports, PA6 and PA66 Market, 2023. https://www.marketgrowthreports.com/de/market-reports/pa6-and-pa66-market-113371 (accessed 8 January 2026).

[4] P.P.X. Yap, Z. Yen, T. Salim, H.C. Lim, C.K. Chung, Y.M. Lam, The impact of mechanical recycling on the degradation of polyamide, Polymer Degradation and Stability 225 (2024) 110773. https://doi.org/10.1016/j.polymdegradstab.2024.110773.

[5] A. McNeeley, Y.A. Liu, Assessment of Nylon-6 Depolymerization for Circular Economy: Kinetic Modeling, Purification, Sustainable Process Design, and Industrial Practice, Ind. Eng. Chem. Res. 63 (2024) 16953–16989. https://doi.org/10.1021/acs.iecr.4c01975.

[6] M. Holtkamp, M. Renner, K. Matthiesen, M. Wald, G.A. Luinstra, P. Biessey, Robust downstream technologies in polystyrene waste pyrolysis: Design and prospective life-cycle assessment of pyrolysis oil reintegration pathways, Resources, Conservation and Recycling 205 (2024) 107558. https://doi.org/10.1016/j.resconrec.2024.107558.

Supercritical water gasification of plastics.

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Purpose

Since the 1950s, global plastics production has grown steadily, reaching an annual output of 413 Mt in 2023. However, according to the OECD, only 9% of this production is recycled worldwide. The rest is landfilled, incinerated or released into the environment [1], [2]. Plastic waste therefore represents a significant resource that can be recovered. An interesting application recently reported in the literature is the use of hydrothermal processes to treat plastics waste and mixtures that are difficult to sort [3], [4]. The process studied here is supercritical water gasification (SCWG). The aim of this study is to understand the reaction mechanisms involved in the thermo-conversion of common plastics (PE, PP, PS) and their mixtures under supercritical water conditions. This work contributes to the pollution mitigation and promotes the circular economy of resources.

Materials and methods

The feedstocks used are pellets of low-density and high-density polyethylene (LDPE, HDPE), polypropylene (PP), polystyrene (PS) provided by Sigma Aldrich. These raw materials were characterized in depth from a (thermo)chemical (CHNS, FTIR, TGA, and SEC) and morphological perspective.

A determined mass of plastic (~15 g) is introduced into a batch autoclave reactor with 60 g of de-ionized water (i.e., dry matter ratio of 20%). The reactor is then heated to the operating temperature and the stirrer is set at 300 rpm. At the end of the reaction, the gas composition is analysed with a Micro-GC. The aqueous phase is analysed by TOC-L and ion chromatography. Both solid biochar and organic phase are characterized by TGA and GC-MS/FID. Elemental analyses are also performed. Organic phases are also analysed by Fourier Transform Infrared Spectroscopy (FTIR) while solid phases are characterized with XRD.

Results and discussion

Temperature is one of the most important parameters affecting the conversion of the feedstock in SCWG process. The influence of the temperature was studied at two different levels (450 °C and 600 °C) on the feedstocks described earlier. Figure 1 shows that total gas yield increases with temperature, in line with other results found in the literature [3]. For example, by increasing the temperature from 450 °C to 600°C in LDPE experiment, the gas yield (GE) is enhanced from 2.5 mol gas/kg dried matter to 20.5 mol gas/kg dried matter. This generates an increase in the carbon gasification efficiency (CGE) from 6.3 % at 450°C to 34.9 % at 600°C. The same upward trend in gas yield and CGE is observed as in the PET trials conducted by Sepini *et al*. [5].

Moreover, gas distribution differs with the increase of temperature. The major species present in the gas at 450°C are methane, C2 (ethane, ethylene) and C3 for LDPE, HDPE and PP, and methane, hydrogen and CO_2 for PS. On the other side, at 600 °C, the main gas present for all plastics is methane, exceeding 70% of the total composition, followed by C2 and hydrogen. Thus, conversion to methane is highly favoured at 600 °C in comparison with experiments at 450°C.

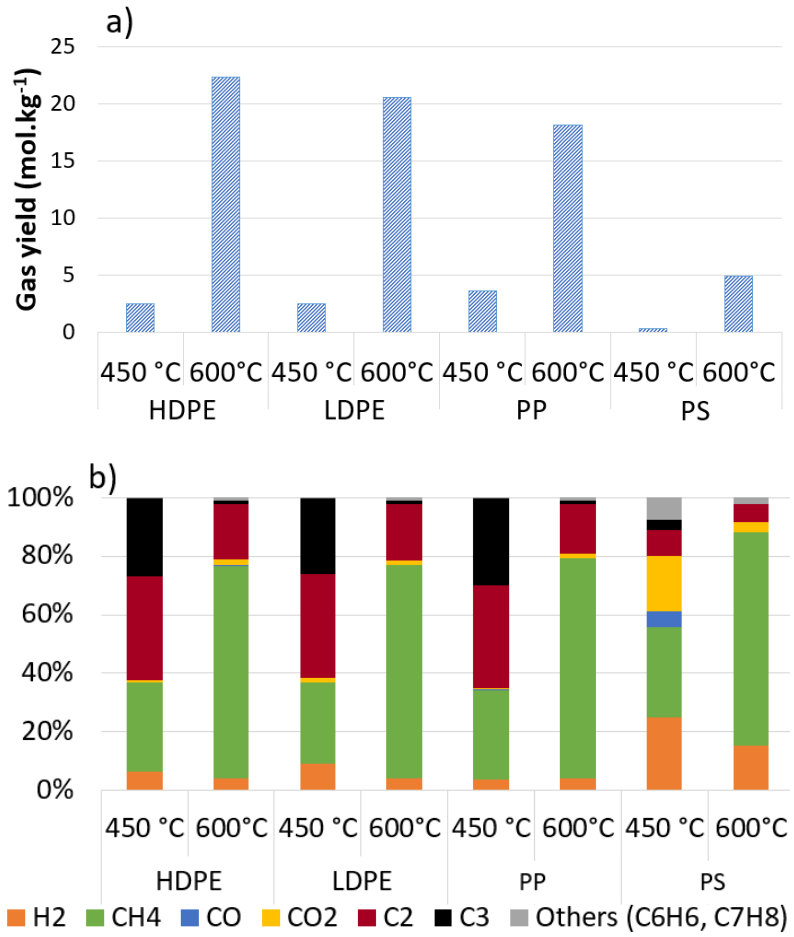


Figure 1. Gas analysis results of SCWG of HDPE, LDPE, PP and PS at 450°C and 600°C: a) Total gas yield; b) Gas distribution.

Another interesting finding is that, in terms of gas, LDPE and PP have similar conversion both on yield and composition. On the other side, SCWG of PS forms more carbon oxides and aromatics such as benzene and toluene, especially at 450°C. Despite these differences, the gases obtained are all highly calorific, regardless of temperature, with a higher heating value (HHV) exceeding 51 MJ/mol.

Analyses of the different products enable to determine the distribution of carbon at the end of the reaction. Carbon distribution in the different phases is presented in Table 1.

Table 1. Carbon distribution in the different phases

Feedstock	Temperature	Gas	Aqueous phase	Organic phase/char
HDPE	450 °C	6,3%	0,4%	70,1%
HDPE	600°C	38,0%	0,5%	35,4%
LDPE	450 °C	6,3%	0,5%	53,0%
LDPE	600°C	34,9%	0,1%	33,8%
PP	450 °C	9,7%	0,4%	65,5%
PP	600°C	30,5%	0,1%	34,7%
PS	450 °C	0,5%	0,2%	Under analysis
PS	600°C	6,5%	0,2%	50,0%

TOC-L analyses on aqueous phases reveal a very low carbon content, less than or equal to 1 g/L. This concentration represents less than 1% of the carbon introduced at the start of the experiment; this indicates a very limited formation of polar compounds.
At 450°C, most of the carbon contained in the products is present in the organic phase. FTIR and GC-MS analyses demonstrate that the products present in the oil depend on the polymer used. The oil obtained from the hydrothermal gasification of polyethylene is rich in alkanes and alkenes from C7 to C25. The oil obtained from polypropylene mainly contains short branched molecules (< C13) as well as cyclic and aromatic molecules. Finally, oil obtained from polystyrene mainly contains mono- and polycyclic aromatic molecules (C7 to C18).
At 600 °C, a carbon-rich solid phase is formed. Elemental analyses show a carbon content higher than 94% for all chars produced, regardless of the polymer used. XRD analyses reveal an amorphous carbon structure. The molecules analysed by GC-MS/FID after extraction with ethyl acetate are all polycyclic aromatic hydrocarbons from C10 to C22.

Conclusions and perspectives

These results show that SCWG of plastics can produce a high calorific gas with a PCS of about 51 MJ/kg. This gas is highly concentrated in methane, with a content exceeding 70% at 600°C. The maximum CH_4 yield was obtained at 600 °C with HDPE (16.3 mol/kg dry matter). The carbon-rich phases obtained depend on the temperature: oil is obtained at 450°C while a char is formed at 600°C. The results obtained in this study provide an initial understanding of the conversion of plastics under supercritical water conditions. Further trials will be conducted in order to understand reaction pathways involved in non-catalytic SCWG. Moreover, catalytic SCWG tests will be conducted in order to steer reactions towards chemical intermediates of interest for plastic synthesis.

References

[1] Organisation de Coopération et de Développement Economiques (OCDE), Plastics, OECD. [Online]. Retrieved from https://www.oecd.org/en/topics/plastics.html
[2] Plastics Europe, Plastics - the Facts 2025. [Online]. Retrieved from https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2025/
[3] Chen, J., Fu, L., Tian, M., Kang, S. *Comparison and synergistic effect analysis on supercritical water gasification of waste thermoplastic plastics based on orthogonal experiments*, Energy, 261, 2022.
[4] Shibasaki, Y., Kamimori, T., Jun-ichi, K., Hatano, B., Tagaya, H., *Decomposition reactions of plastic model compounds in sub- and supercritical water,* Polym. Degrad. Stab., 83 (3), 481-485, 2004.
[5] Sepini, L., Mochel, R., Petri, I., Chappaz, A., Demey, H., *Understanding the conversion mechanisms in supercritical water conditions of PET as a model compound of plastic wastes,* Chem. Eng. J., 488, 150567, 2024.

Plasma-Assisted Secondary Cracking of Plastic Pyrolysis Volatiles for Carbon Black and H_2-Rich Gas Production

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Chemical recycling of plastic waste using thermochemical conversion techniques into value-added products, particularly carbon black (CB) and hydrogen gas, represents a promising pathway to address two major environmental challenges simultaneously: mitigating CO_2 emissions from both plastic disposal and conventional CB production. In Europe, incineration remains the dominant plastic waste treatment method, while globally landfilling, as the predominant treatment path, accounts for approximately 178 million metric tons of plastic disposal annually. These practices highlight the urgent need for circular, low-emission alternatives that recover material and energy value from plastic waste streams.

CB is an essential industrial product with a global market value estimated at USD 23.5 billion in 2024 and a projected compound annual growth rate (CAGR) of 4.4% for the period of 2025-2033 [1]. Current annual demand has reached approximately 15 million metric tons [2]. CB is widely used in printing inks, coatings, electrodes, and as a UV stabilizer in plastics; however, nearly 90% of global production is consumed by the rubber industry, with tire manufacturing alone accounting for approximately 65% of total demand [3].

At present, approximately 95% of industrial CB is produced via the furnace process, which relies on the incomplete combustion of hydrocarbons, mainly using aromatic oils, crude oil or natural gas as a feedstock [3]. This process is inherently carbon-intensive, with estimated emissions of 3.5 kg of CO_2 per kilogram of CB produced [2]. As global demand for CB continues to rise, the environmental burden of this production route becomes increasingly significant, highlighting the necessity for alternative, low-carbon or preferably climate-neutral technologies capable of supplying this valuable material.

Polypropylene (PP), one of the most widely used materials in food packaging, polystyrene (PS) and mixed plastic packaging waste (MPPW) was selected as CB feedstocks in this study due to exceptionally low recycling rates of these polymers. For instance, only about 1% of post-consumer PP is recycled, leading to large volumes being disposed of in landfills and compounding the issue of plastic pollution [4]. Furthermore, mechanical recycling often decreases the mechanical and physical properties of PP, as elevated processing temperatures can partially break polymer chains, resulting not only in reduced tensile strength but also contamination by volatile organic compounds [5]. Consequently, mechanically recycled PP rarely meets food-grade safety requirements and is generally unsuitable for reuse in food packaging applications. In this context, the valorization of plastics with low recyclability rates through thermochemical conversion represents a promising treatment strategy advancing in mitigating plastic pollution.

Most studies on the conversion of plastics into solid carbon and hydrogen have focused on a two-step approach, consisting of an initial pyrolysis stage followed by catalytic pyrolysis using transition metals, with the solid product primarily being carbon nanotubes [6]. However, the synthesis of amorphous carbon, particularly CB, from hydrocarbons requires a catalyst-free, high-temperature environment of at least 1200 °C to cleave strong C–H bonds and initiate dehydrogenation [7]. Numerous studies on the slow pyrolysis of plastics have shown that this process mainly produces a diesel-like oil composed of light- to mid-range liquid hydrocarbons (C_6–C_{20}) [8]. Knowing that hydrocarbon oils are one of the main feedstocks for CB production, the hypothesis in the present research was raised: the hydrocarbons from slow pyrolysis of plastics are a suitable feedstock for CB production via a more sustainable plasma-assisted pyrolysis.

A combined slow pyrolysis–plasma-assisted pyrolysis approach was employed to convert plastic feedstocks into CB and hydrogen-enriched gas while investigating the effect of N_2 plasma working gas flow rate on product yield

and quality. Slow pyrolysis was conducted at 500 °C with a heating rate of 33 °C/min. TG-GC/MS and TG-FTIR analyses revealed that PP primarily generated branched olefins during the first stage, with 2,4-dimethyl-1-heptene and 7-methyl-1-undecene as the dominant intermediates, alongside minor oxygenated species. Slow pyrolysis of PS distinguished itself with the highest product selectivity, generating mostly styrene. While MPPW yielded a broad range of hydrocarbons, including aromatic and aliphatic compounds with the dominance of 2,4-dimethyl-1-heptene, a recognized characteristic marker for polypropylene [9], indicating a high PP content in the mixture. The intermediate hydrocarbons were continuously transferred via a heated line to a 3.5 kW plasma torch and injected downstream of the thermal plasma arc. A collected CB yield of up to 26.7 ± 4.7 wt.% was achieved from aliphatic precursors, with higher yields expected following optimization of the solid carbon collection system. Under these conditions, a carbon conversion efficiency of 31% was obtained at an N_2 flow rate of 6 L/min, with minimal differences between the two feedstocks. The gaseous products at the decomposition peak, determined by GC-TCD, consisted predominantly of hydrogen (up to 89 ± 1.13 vol.%), with acetylene accounting for up to 8 ± 3.14 vol.%. Transmission electron microscopy (TEM) imaging (Figure 1) confirmed the characteristic CB morphology of the plastic-derived carbon, consisting of quasi-spherical primary particles with diameters ranging from 16 to 100 nm, forming aggregates and agglomerates. CB-characteristic turbostratic carbon layering was observed within the primary particles.

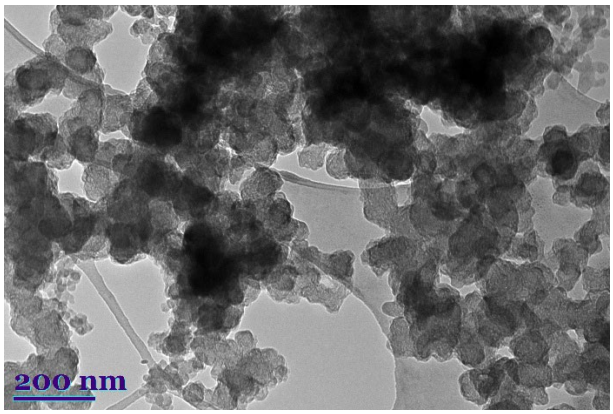


Figure 1. TEM image of carbon black produced from polypropylene

In conclusion, the results of this study demonstrate the potential of the proposed slow-pyrolysis – thermal plasma-assisted pyrolytic process for CB production, highlighting plastic waste as a promising secondary feedstock.

References

[1] Sharma A.: *Carbon Black Market Size & Outlook, 2025-2033*, Industry report, Straits Research, 2025. URL: https://straitsresearch.com/report/carbon-black-market

[2] Rosner, F., Bhagde, T., Slaughter, D. S., Zorba, V., Stokes-Draut, J.: *Techno-economic and carbon dioxide emission assessment of carbon black production*, Journal of Cleaner Production, 436, 140224, 2024.

[3] J.B. Donnet, R.C. Bansal MJW: *Carbon Black Science and Technology*, 2nd edition, Marcel Dekker, Inc., New York, 1997.

[4] Alsabri, A., Tahir, F., & Al-Ghamdi, S. G.: *Environmental impacts of polypropylene (PP) production and prospects of its recycling in the GCC region*, Materials Today: Proceedings, *56*, 2245-2251, 2022.

[5] Saldaña-Pierard, C., Nguyen, P. M., Debeaufort, F., Vitrac, O., & Auras, R.: *Impact of emerging packaging regulations on international trade and product safety with emphasis on plastic reuse and recycling in Europe and North America*, Journal of Industrial Ecology, 29(5), 1473-1504, 2025.

[6] Williams, P. T.: *Hydrogen and carbon nanotubes from pyrolysis-catalysis of waste plastics: a review*, Waste and Biomass Valorization, 12(1), 1-28, 2021.

[7] Ahmed, S., Aitani, A., Rahman, F., Al-Dawood, A., & Al-Muhaish, F.: *Decomposition of hydrocarbons to hydrogen and carbon*, Applied Catalysis, 359(1-2), 1-24, 2009.

[8] Das, P., Tiwari, P.: *Valorization of packaging plastic waste by slow pyrolysis*, Resources, Conservation and Recycling, 128, 69-77, 2018.

[9] Gnoffo, C., Frache, A.: *Identification of plastics in mixtures and blends through pyrolysis-gas chromatography/mass spectrometry*, Polymers, 16(1), 71, 2023.

Thermal plasma cracking of low-value hydrocarbon streams

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Introduction

Ethylene is one of the main petrochemical products from cracking plants [1]. The lion's share of its production is represented by steam crackers, where hydrocarbons undergo high temperature pyrolysis with water as diluting agent. Depending on the feedstock, non-negligible fractions of byproducts result from the process. For conventional ethane or naphtha crackers, methane and other byproducts comprising tars and pyrolysis oil can weigh from 20 to 45%(wt.) of the product stream [2,3]. They often end up as fuel either fed to the cracker or sold to refineries. These molecules still contain valuable carbon atoms for plastic production. The utilisation of low-value hydrocarbon byproducts will become of high importance under the perspective of circular plastic production, as cracking units will remain relevant in the future for treating feedstocks stemming from plastic waste.

Plasma-enabled technologies are a promising alternative for material recovery of carbon streams. They offer compact and modular assemblies with fast response times, facilitating the deployment to stranded, intermittent energy sources [4,5]. Plasma technologies can be divided into non-thermal (cold) and thermal (warm), depending on the thermodynamic condition of the excited gases. In the former, electrons have a much higher temperature compared to the surrounding ions and radicals, whereas in the latter the local thermodynamic equilibrium is reached, i.e. the temperature of the gas species is homogeneous [6]. Cold plasma platforms have gained increased interest in the past couple decades as a lower power demand alternative [5,8]. The Dielectric Barrier Discharge (DBD) is one of the most popular configurations, with temperatures of the discharges low enough to allow for co-catalysis [5]. The majority of literature on cold plasma assemblies is at lab-scale, and the commercialisation of cold plasmas is still far. In contrast, thermal plasma pyrolysers show already a sufficiently high TRL. In fact, first examples of industrial uses of thermal plasma date back to the '40s in Germany, where an 8 MW setup was in use to produce acetylene and the technology has also been demonstrated for methane cracking in USA and Germany [7,9]. Thermal configurations do not need the presence of a catalyst to provide the required activation energy for the reactions, thus avoiding problems with catalyst poisoning and deactivation. Considering the heterogeneous character of low-value hydrocarbons streams, direct current (DC) thermal plasma arc torches would be a robust preferable technological platform to further crack stable compounds to olefins or reforming to syngas for subsequent synthesis to feedstock molecules.

A variety of hydrocarbons for plasma-enhanced cracking have been considered in literature to simulate real streams; from single C_3-C_{12} n-alkanes, to blends such as naphtha, gasoline, diesel [5]. Main reaction pathways include steam or dry reforming to provide partial oxidation conditions, or pyrolysis. The main products targeted are small, unsaturated C_2-C_3 hydrocarbons, main commodities for polymerisation plants, and hydrogen, either pure or as synthesis gas with carbon monoxide [5]. However, for most of the plasma assemblies used, the selectivity to these molecules is not commercially relevant when heavier molecules are processed. At the same time the investigated feedstocks just represent a surrogate of real streams, which contain a more heterogeneous blend. The aim of this work is to provide a proof of concept to process waste hydrocarbons streams into synthesis gas, or ideally, to desired C_2 unsaturated hydrocarbons. Commercial-grade propane was preliminarily selected to reform for its ease of handling, as it is gaseous at room temperature, thus not requiring heated lines or spray injection equipment, while still being a C_{2+} hydrocarbon.

Methodology

Tests were performed in a 1.5 kW thermal plasma torch. Nitrogen was preliminarily chosen as plasma forming gas as a more inexpensive option compared to argon, while being relatively inert. N_2 was set at 2 Nlpm. The flowrate for propane was set at 0.25 Nlpm. Roughly 43 l h^{-1} of water from the mains was provided as coolant to the assembly. The cooling circuit cools first the hollowed-out cathode, and then it continues to the jacketed, copper anode. The reactor is not cooled. Injection was performed at different distances from the plasma source, by means of a small probe positioned counter flow to the plasma torch. The injection distance influences both the energy available for reforming the species, and their residence time inside the reactor. It was studied to assess the conversion of propane and its influence on the relative product gas composition. Samples were taken from the effluent at the end of the reactor into gas bags, after a 5 µm filter and a centrifugal pump to ensure a consistent volume of gas between samples. Each gas bag was sampled immediately afterwards both with a GC-TCD and GC-VUV chromatographer.

Preliminary results

In **Figure 1**, the volumetric fraction composition of the products can be observed as function of the injection distance, starting from the position closest to the plasma source, i.e. the downstream the anode end. Close to the plasma source, the conversion of propane is greatest, with maximisation of the hydrogen production, and after 5 cm the conversion does not decrease further. Acetylene and ethylene show opposite trends, with the former fraction decreasing as the injection distance increases, and the latter fraction increasing. The fraction of produced ethane was in all conditions below 1%. From the GC-VUV it was possible to determine qualitatively the presence of other species in the products. Specifically, some C_4 species such as isobutane, vinyl acetylene and 1,2-butadiene were detected. Further, traces of benzene and toluene were also present in the sampled product.

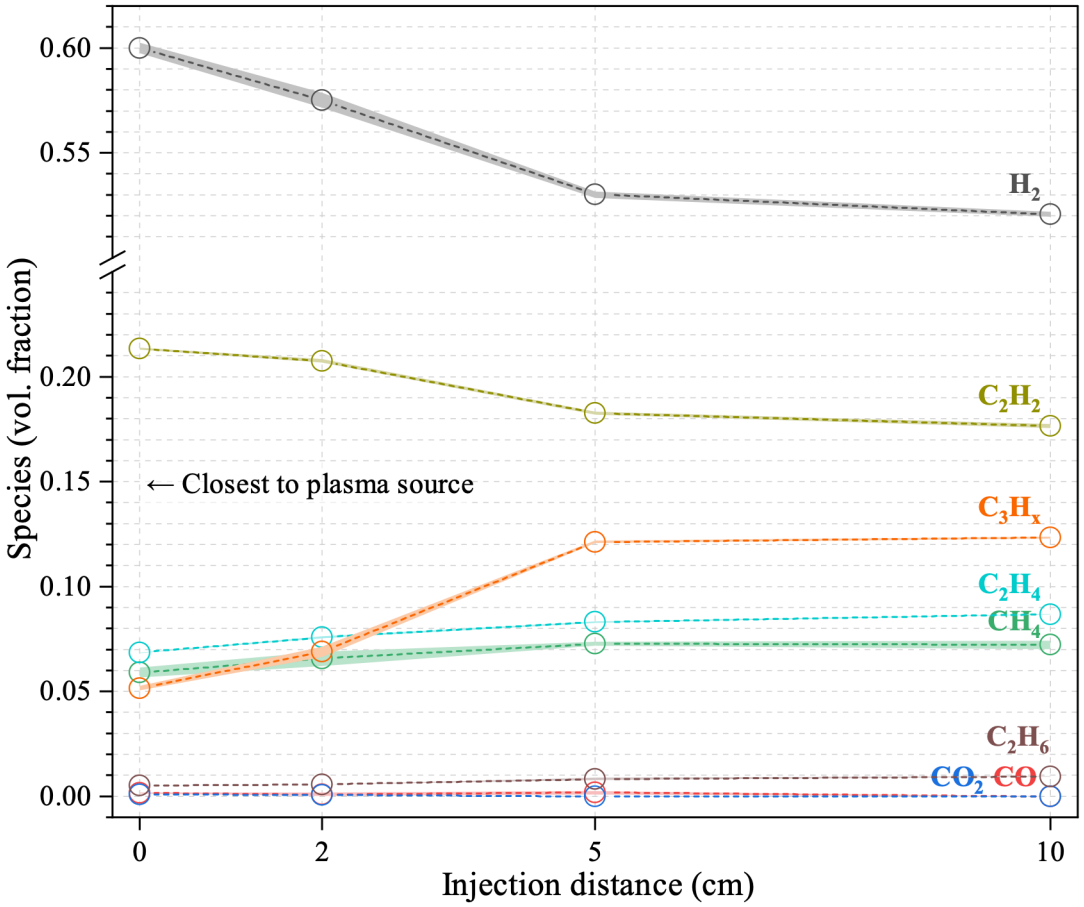


Figure 1. Volumetric fractions of the products as function of the injection distance. N_2 has been removed for convenience. Shaded areas represent the standard deviation in the measurement. Please note the ordinate break.

Conclusions

Preliminary results show a promising reforming potential of heavier hydrocarbon species via DC thermal arc plasma torches. The produced gas consisted mainly of hydrogen and acetylene. While full conversion was not achieved, the results at different injection distances indicate that injection closer to the plasma source is beneficial for enhanced conversion of C_3 chemicals and should be focus of further investigation.

Based on the results presented for propane, it is of interest to investigate more heterogeneous streams and heavier hydrocarbons behaviour in DC plasma, provided that the feedstock is appropriately introduced in the plasma reactor. For example, the hydrogen deficiency in feedstock mixes rich in aromatics needs to be compensated by excess hydrogen in the mixture, e.g. via a deployment of CH_4 as plasma forming gas. Further work will include investigating other relevant plasma forming gases too, such as CO_2, which can facilitate downstream separation and/or subsequent processing. The energy performance of such type of assembly will be assessed, and the feedstock selection will start considering molecules with unsaturated bonds (-CH-), moving towards more complex molecules, up to tars from real streams from steam crackers.

References

[1] Statista.: *Global Petrochemical Industry*, Statista, 2024.
[2] Zimmermann, H., Walzl, R.: Ethylene, *Ullmann's Encyclopedia of Industrial Chemistry*, 2009.
[3] IEA.: *The Future of Petrochemicals,* 2018.
[4] Gimžauskaitė, D., Tamošiūnas, A.: Plasma technology for reforming of hydrocarbons, *Energy From Plasma*, 2025.
[5] Cameli, F., Stefanidis, G. D.: *Valorization of C2 + Hydrocarbons Via Plasma Processes,* Plasma Chem. Plasma Process., 45(2), 639–658, 2025.
[6] *Handbook of Thermal Plasmas*, Springer International Publishing, Cham, 2023.
[7] Fincke, J. R., Anderson, R. P., Hyde, T., Detering, B. A., Wright, R., Bewley, R. L., Haggard, D. C., Swank, W. D.: *Plasma Thermal Conversion of Methane to Acetylene,* 2001.
[8] Bromberg, L., Cohn, D. R., Rabinovich, A., Alexeev, N.: *Hydrogen Manufacturing Using Low Current, Non-Thermal Plasma Boosted Fuel Converters,* American Chemical Society, Proceedings of the Symposium on "ENERGY FOR THE 21ST CENTURY: HYDROGEN ENERGY," San Diego, CA, 2000.
[9] ETP Clean Energy Technology Guide – Data Tools, *IEA*.

Conversion of plastic pyrolysis oil into sustainable aviation fuel via hydroprocessing

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Introduction

The global energy transition and European climate policy are driving the development of alternative non-fossil carbon cycles with a high degree of urgency. Today's fuels are mainly produced in petroleum-based refineries, while the chemical industry uses petroleum-based naphtha (a side-product in petro-refineries) as low-value carbon-stream for plastic production. In the EU, and especially in Germany, regulatory frameworks are emerging that require both the provision of sustainable aviation fuels (SAF) and the greatest possible circularity of plastic-carbon flows in the spirit of a modern circular economy [1, 2]. While synthetic fuels based on CO_2-based Fischer-Tropsch or methanol chemistry are increasingly becoming the focus of research and political interest, the short-term focus of legislation and research in terms of polymer recycling lies more on converting plastic residues via pyrolysis and cracking into naphtha-streams and back into polymers. The question remains if the production of a single product-stream (low-value naphtha) will lead to economical processes in the upgrading of plastic residues while keeping the cost of sustainable polymers at an appropriate level.

An alternative solution for the integration of fuel- and plastic-based carbon streams in the future is shown in Figure 1. In this scenario post-consumer plastic residues are converted thermochemically into pyrolysis oil which is furthermore converted into sustainable aviation fuel via hydroprocessing. Future refineries produce mainly sustainable fuels and sustainable naphtha as low value side-product for the chemical industry. This scenario has closed carbon cycles and advantages in energy demand for fuel production as plastic residues have already valuable hydrocarbon chains (See equation 1, where N_C is the carbon chain length).

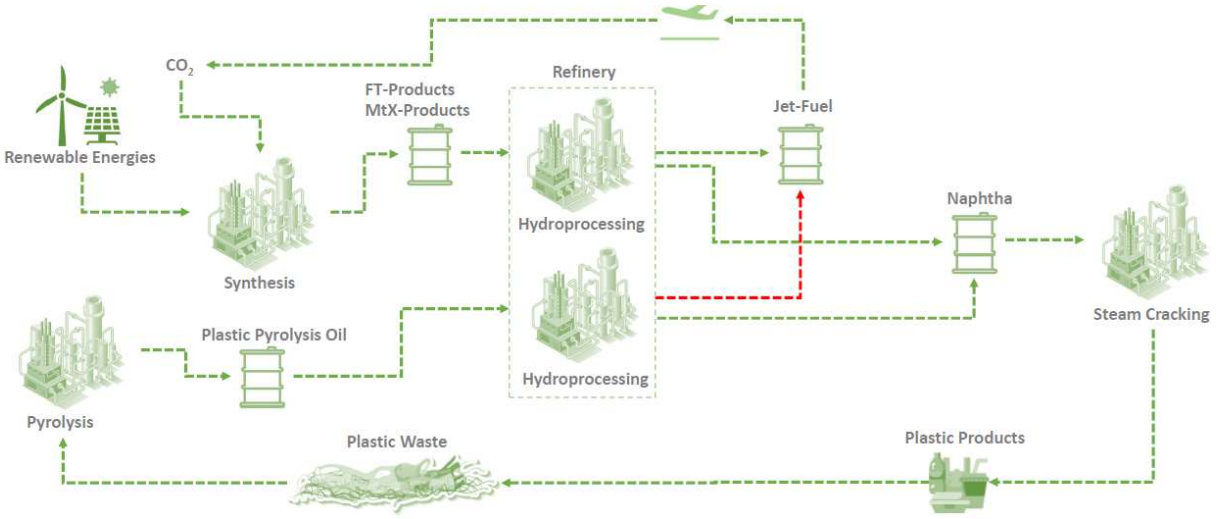


Figure 1: Integration of fuel and polymer production in future carbon cycles.

$$N_{C,Plastics} > N_{C,Pyrolysis\ Oil} > N_{C,Jet\ Fuel} > N_{C,Naphtha} \quad (1)$$

Under increasing regulatory pressure to comply with SAF quotas while closing material cycles, experimental validation of the jet fuel yields that can actually be achieved from plastic pyrolysis oil via catalytic hydrotreating and downstream hydrocracking appears to be highly relevant both technologically and politically.

Challenges

The conversion of plastic pyrolysis oil into jet fuel can be achieved by hydroprocessing. Pyrolysis oil itself has insufficient properties to meet strict specifications of sustainable aviation fuels (ASTM7566). Thermal stability, viscosity, gum formation, acidity and heating value can be improved by hydrotreating [3]. Unwanted heteroatoms like oxygen, nitrogen and chlorine are removed as well as olefins and aromatics. To meet important cold-flow properties of jet-fuels, heavier fractions need to be converted via hydrocracking at the same time n-paraffinic compounds are converted into isoparaffinic compounds with better cold-flow behaviour.

Experimental

The aim of this work is the experimental investigation of jet fuel and naphtha yields from plastic pyrolysis oil using a two-stage hydroprocessing process (hydrotreating and hydrocracking). The pyrolysis oil was produced by thermal conversion of a municipal waste model mixture and represents a typical plastic waste mixture from Germany. The pyrolysis feed contained the hydrocarbon polymers Low-density Polyethylen (LDPE), Polypropylen (PP), and Polystyrene (PS), the nitrogen-containing Polyamid-6 (PA6) and Acrylntrile-Butadien-Styrene-Copolymer (ABS), the oxygen containing Polyethyleneterephthlate (PET) and the chlorine containing Polyvinylchloride (PVC).

In the first hydroprocessing step of the pyrolysis oil, heteroatom-containing impurities as well as olefinic and aromatic structures are removed. In the second stage, heavy-end fractions will be selectively hydrocracked into lighter boiling products with a focus on the jet fuel range (C9–C16). Hydroprocessing experiments are performed in a fixed-bed reactor at 1 kg·d^{-1} at elevated temperatures and pressures. Figure 2 shows the experimental setup used for both hydroprocessing steps. While pyrolysis oil is the feedstock of the first step (hydrotreating), the collected hydrotreated liquid product is the feedstock for the second step (hydrocracking).Two different industrial catalyst are used for both hydroprocessing steps.

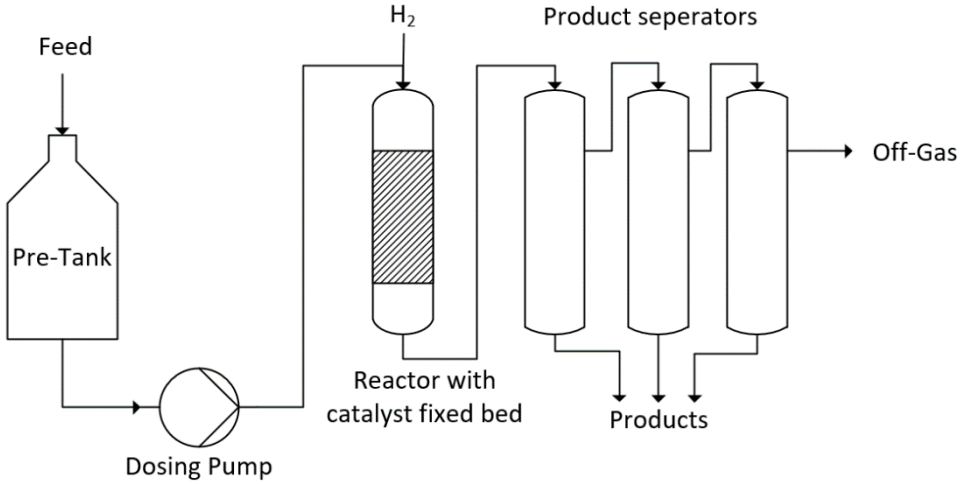


Figure 2: Schematic representation of experimental setup.

Liquid feeds and products for both hydroprocessing steps were analysed by two-dimensional gas-chromatography (GCxGC-FID/MS) and groupe-type-analysis were performed qualitatively and

quantitatively. Gas phase was analysed quantitatively via online-gaschromatography. Successful hydrotreating was verified via elemental analysis. Hydrocracking feed and products were additionally analysed for cold-flow behaviour.

References

[1] European Union: *Regulation (EU) 2023/2405 of the European Parliament and of the Council of 18 October 2023 on ensuring a level playing field for sustainable air transport (ReFuelEU Aviation), http://data.europa.eu/eli/reg/2023/2405/oj* last updated 23.12.2025.

[2] European Comission: *Accelerating Europe's transition to a circular economy: a pilot for boosting the circularity of plastics, https://environment.ec.europa.eu/document/download/60277c52-77f0-4860-b6cc-cdaf6665e336_en?filename=COM_2025_805_1_EN_ACT_part1_v3.pdf* last updated 31.10.2023.

[3] Faisal, F., Rasul, M. G., & Jahirul, M. I.: *Upgrading MSW pyrolysis oil through distillation and hydrotreatment for automobile engine applications: a short review*. Energy Reports, 9, 555-560, 2023.

Strategies to assess contaminants and impurities in steam cracking treatment of plastic waste towards high-value olefins production

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Abstract

Europe's annual olefines (building blocks of polymer manufacture) production capacity is ~20 million metric tons (PlasticsEurope; IEA; ICIS, CEH), primary from naphtha crackers. According to Wood Mackenzie Global Olefins Cost Curve US (2023-2024) naphtha-based crackers have a cost of 640–1100 EUR/ton of ethylene and produces 2.0-2.7 ton CO_2/ ton of ethylene (IEA). The high costs and CO_2 generation have led to high risk in closing these systems across Europe. *Diversifying feedstock*, such as the use of plastic waste, is a strategic solution to address this issue by reducing overall carbon emissions and costs. Commonly, crude-oil-derived naphtha is used for olefins production due to its hydrocarbon content, ranging from C5 to C12. However, impurities such as sulfur-, nitrogen-, and oxygen-containing compounds are also present [1,2], which must be removed to prevent poisoning of the catalyst used during the reforming process. The nitrogenated compounds found in straight-run naphtha are pyridines, quinolines, indoles, carbazole and derived pyrroles [1,3], which are easily absorbed in catalyst acidic sites blocking the active sites. Hydrotreatment, a cleaning step in steam cracking of naphtha, has been effective in removing these impurities, but some sub-ppm can remain [3]. A similar scenario is observed in the context of utilization of plastic waste, where with unsorted waste streams the increase of impurities generation can take place due to the wide variety of mixed materials. This is true for the production of plastic-waste-derived naphtha via pyrolysis [4] but also in new processes such like direct steam cracking of plastic waste in fluid bed reactors where the solid feedstock is directly converted into the cracker effluent. To counter the effects, it is fundamental to comprehend the formation and fate of contaminants to the design and operation of a full thermochemical recycling system, including the downstream cleaning and separation sections when plastic waste is used as feedstock.

The semi-industrial scale high-temperature (700-800^{o}C) steam cracker at Chalmers University of Technology effectively transforms plastic waste into valuable resources, and represents a proof of concept to replace current naphtha-based tubular steam cracking technologies in chemical refinery clusters [5-7]. Waste streams suitable for direct steam cracking comprise minor quantities of nitrogen containing polymers such as polyurethanes (PU) and polyamides (PA) which pose a contamination risk through accumulation of their products in the fractionation or contamination of the valuable product streams used for polymerization. Despite the expected presence of nitrogenated compounds in the products, derived from PU and PA present in the fuels, their identification remains challenging due to their low concentration.

In this work high-nitrogen materials have been used as sole polymers, such as nylon 6.6 and PU, to facilitate the development of a suitable sampling and analysis methodology for nitrogen containing species in the effluent of a fluidized bed steam cracker based on GC-VUV and GC-MS. Such method is essential to create a comprehensive understanding of the thermal decomposition of these materials and the formation of nitrogen-containing hydrocarbons in the product stream. Initial tests have been performed in a laboratory-scale bubbling fluidized bed (BFB) steam cracker using silica-sand as bed material employing the setup for polyethylene steam cracking carried out by Mandviwala et al. [8] at temperatures between 700 and 800^{o}C. Preliminary findings, based on the analytical approach outlined by Mandviwala et al. [5] using GC-VUV analyzer, indicate the formation of aliphatic-nitrogenated species from C2 to C6 in the gas phase, comprising between 5 and almost 7% of the total carbon content in Nylon 6.6. The carbon distribution of these nitrogenates and other compounds found in the gas phase are presented in Figure 1.

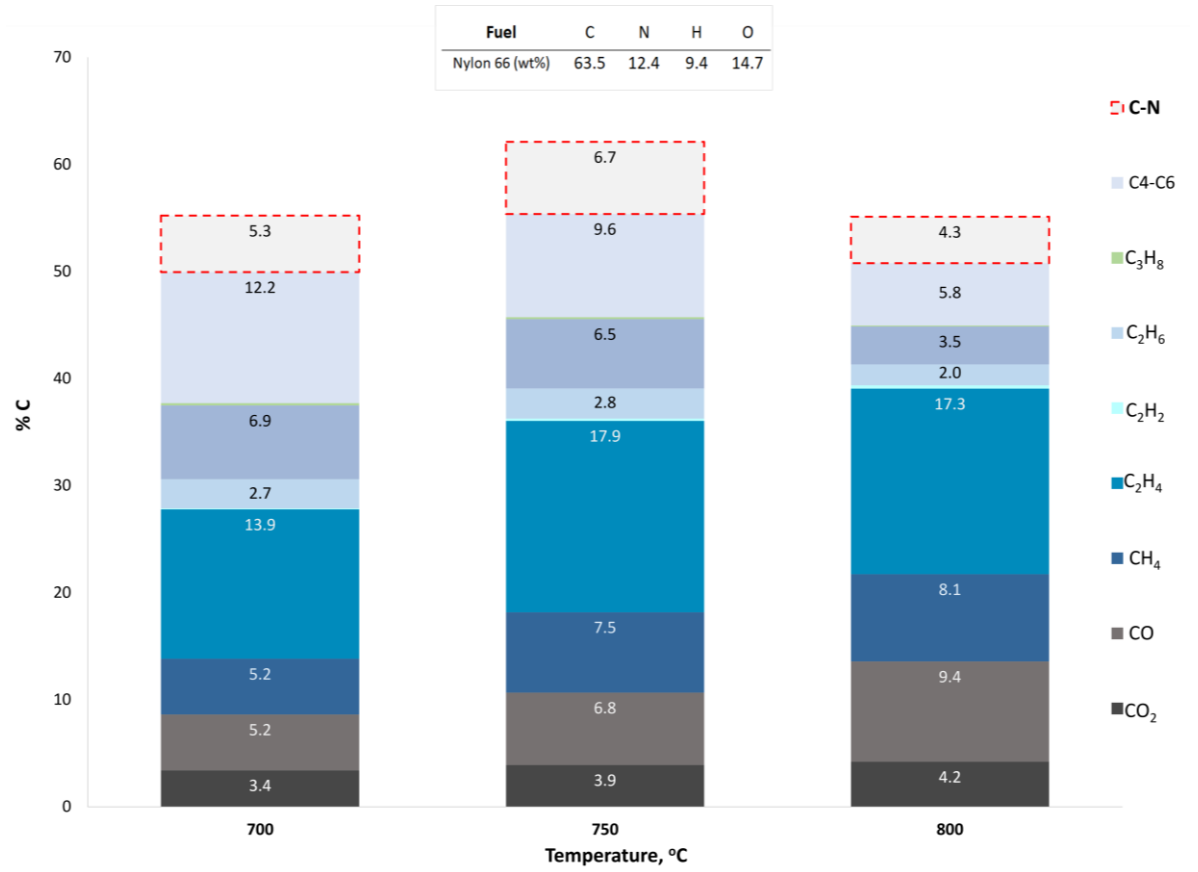


Figure 1. Product carbon distribution in gas phase of steam cracking of Nylon 6.6. Aliphatic-nitrogenated species (C-N) are highlighted in red. Aromatics are not considered.

These nitrogenated species fall into a boiling point range between 80 and 117°C, a temperature range that can potentially compromise the efficacy of ethylene (C_2H_4) separation and purification processes, particularly when these compounds remain unidentified. Furthermore, comprehensive chemical analyses of both phases (condensable and non-condensable gases) generated during the steam cracking of Nylon were conducted using GC–MS. Due to the high sensitivity of the technique, which facilitates the detection of compounds at trace levels, approximately 10–15 nitrogen-containing species were identified in the gaseous phase, which includes pyrrole and pyridine; and around 50 in the tar fraction, where quinolines and indoles were identified. The present investigation revealed the presence of a range of nitrogen species that might be relevant to be investigated further in real feedstocks for direct steam cracking as they have the potential to interfere with the commercially relevant product streams.

Abbreviations: Independent commodity intelligence services (ICIS); S&P Global Commodity Insights Chemical Economics Handbook (CEH); International Energy Agency (IEA)

References

[1] Antos, G.J. and A.M. Aitani, *Catalytic naphtha reforming*. 2nd , rev. and expanded / edited by George J. Antos, Abdullah M. Aitani. ed. Chemical industries ; 100. 2004, New York: Marcel Dekker.

[2] Speight, J.G., *Hydrocarbons from crude oil*, in *Handbook of Industrial Hydrocarbon Processes*. 2020. p. 95-142.

[3] Speight, J.G., *The Chemistry and Technology of Petroleum*. 2014, CRC Press.

[4] Kusenberg, M., et al., *Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?* Waste Management, 2022. 138: p. 83-115.

[5] Mandviwala, C., et al., *Method development and evaluation of product gas mixture from a semi-industrial scale fluidized bed steam cracker with GC-VUV.* Fuel Processing Technology, 2024. 253.

[6] Forero-Franco, R., et al., *Developing a parametric system model to describe the product distribution of steam pyrolysis in a Dual Fluidized bed.* Fuel, 2023. 348.

[7] Thunman, H., et al., *Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery.* Sustainable Materials and Technologies, 2019. 22.

[8] Mandviwala, C., et al., *Comparing bed materials for fluidized bed steam cracking of high-density polyethylene: Olivine, bauxite, silica-sand, and feldspar.* Journal of Analytical and Applied Pyrolysis, 2023. 173.

Integrated Mechanical-Chemical Recycling: Investigation of Extrusion-Induced Effects on Polyethylene Pyrolysis Products

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Abstract

Polyethylene (PE) has a large fraction of plastic production and utilization in daily life. It can be used in various applications such as shopping bag, pipeline, packaging and so on. On the other hand, high amount of single-used waste PE in landfill has been challenging points on environmental problems. Circular economy becomes high impact for the future sustainability of plastics. Among them, recycling is a main approach for converting waste plastics to other valuable products. However, each approaches have a limitation which affects on less ratio of plastic recycling. This study, a post-consumer high-density polyethylene (PCR-HDPE) is recycled via an integrated mechanical-chemical recycling. PCR-HDPE is firstly extruded with a novel twin-screw extruder (TSE) with various extrusion conditions. As a result, the mechanical properties were varied based on the differences of TSE types and conditions. After the evaluation of mechanical properties, the mechanically recycled PCR-HDPE was subjected to continuous chemical recycling via pyrolysis using a tubular reactor. The results showed that the reduction of mechanical properties enhanced the oil and wax composition around 85% and 13% compared to the PCR-HDPE original material (Org), respectively. In other way, the regeneration of mechanical properties affected the increasing of wax composition around 10% compared to Org. This integrated mechanical-chemical recycling expected to be a new guideline for development of plastic circular economy of our future sustainable world.

Introduction

High amount of waste plastics is one of the main environmental problems. Recycling is a key factor for the completion of plastic circular economy and prolonging the lifetime used. Mechanical Recycling (MR) and Chemical recycling (CR) are two main plastic recycling approaches which have different advantages and drawbacks [1]. MR converts waste plastics to the recycled products via mechanical processes: extrusion and injection moulding. It is the best method based on the study of life cycle assessment due to low energy demand and less CO_2 emissions. On the other hand, shear and heat in mechanical process affected the degradation of physical properties resulted in the downgraded applications of mechanical-recycled products. CR converts waste plastic to variable products: oil, gas, wax, char, and valuable chemicals. The chemical-recycled plastic products are clean and be able to produce as a virgin material. However, processing cost, high energy demands, and waste treatment are the challenging issues. Based on this motivation, the synergistic approaches of plastic recycling are attractive for enhancing plastic recycling quality. Siqueira et al. [2] studied the use of mechanical recycling extrusion as a pretreatment for pyrolysis of PE. Extrusion process was performed at 220 and 450 ºC for 1 and 2 min of residence time, respectively. The results shown that molecular weight was notable reduced resulted in the increasing of conversion and yield of liquid and gas products. In this study, PCR-HDPE was recycled via an integrated mechanical-chemical recycling. The novel MR was focused and compared between the general TSE and TSE with additional molten resin reservoir (MRR) unit. MRR was a blank space connected between the end of screw zone and the die zone. The using of TSE with MRR regenerated the mechanical properties, lamellar structure, and morphology of waste polyolefin [3-4]. With this difference of mechanical properties of PCR-HDPE caused by different TSE types and extrusion conditions, the relationship between mechanical properties and pyrolysis product composition was evaluated.

Materials and Methods

PCR-HDPE pellet derived from waste dialysis bottle was obtained from Kansai Chemicals Group, Japan. It was in a milky white pellet shape with 120-140 ºC of melting point and 0.93-0.97 g/cm^3 of specific gravity. Mechanical recycling was performed by using a TSE (Labo Plastomill®, Toyoseiki Seisaku-sho Ltd., 2D15W) with 15 mm of screw diameter and L/D = 17. The extrusion condition was controlled at 200 ºC, 10 g/min of feed rate, and 30 rpm of take-up speed. Screw speed (45 and 135 rpm) and the presence of MRR were the variable extrusion condition factors. All re-extrusion products were fabricated as thin film with 100 µm of thickness by hot compression moulding prior to characterize the mechanical properties, degree of crystallinity, molecular weight, and lamellar structures. The mechanical-recycled pellet products were performed a chemical recycling via pyrolysis using a tubular reactor. 100 mg of pellets were tested at 600 ºC for 15 min under 50 mL/min of He atmosphere. All pyrolysis products were collected and clarified as char, wax, oil, and gas. The weight composition and product distribution of each phase were compared between PCR-HDPE original material (Org) and the mechanical-recycled products. **Figure 1**. showed the schematic diagram of an integrated mechanical-chemical recycling in this study.

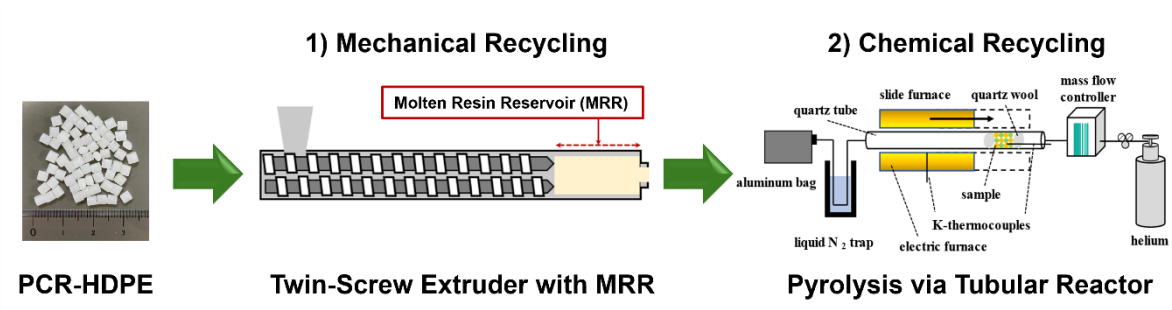


***Figure 1**. Schematic diagram of an integrated mechanical-chemical recycling in this study.*

Results and Discussion

To evaluate the difference of properties of mechanical-recycled PCR-HDPE, the tensile test was performed. **Figure 2.** showed the elongation at break of PCR-HDPE Org and mechanical-recycled products. Re-extrusion via TSE without MRR affected the reduction of elongation at break compared to its PCR-HDPE Org. Especially at high screw speed (135 rpm_No-MRR), the elongation at break was decreased around 36.6% from Org. Interestingly, the addition of MRR at TSE significantly enhanced the elongation at break. It was not only improved than one without MRR (No-MRR), the elongation at break of mechanical-recycled PCR-HDPE using TSE with MRR were increased than its Org around 32.6% even at high screw speed (135 rpm_MRR). From these results, the additional MRR unit greatly affected the changes of mechanical properties of PCR-HDPE. This is because the blank space of MRR led to the relaxation of shear memory in polymer melts resulted in the rearrangement of structures and entanglement [3-4]. As a result, the mechanical properties of PCR-HDPE were extensively regenerated.

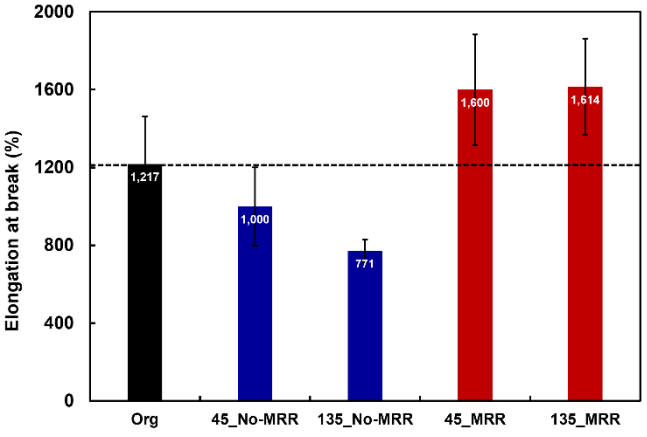


***Figure 2**. Elongation at break of PCR-HDPE original sample (Org) and mechanical-recycled products with different screw speed and types of TSE.*

PCR-HDPE Org and the mechanical-recycled products were continuously performed the chemical recycling via pyrolysis using a tubular reactor. The weight composition of pyrolysis products was showed in **Figure 3**. Compared with PCR-HDPE Org without any re-extrusion, 135_No-MRR was increased in the amount of oil and wax around 85% and 13%, respectively. On the other hand, the amount of char and gas was reduced around 81% and 25% compared to Org, respectively. This can be implied that the degradation of mechanical properties in 135_No-MRR affected the enhancement of wax and oil composition. On the other hand, 135_MRR which was regenerated the mechanical properties via TSE with additional MRR showed the similar product composition with PCR-HDPE Org. Wax composition was also increased around 10%; however, char, oil, and gas were decreased around 34%, 42%, and 8%, respectively. From these results, the difference of mechanical properties of PCR-HDPE greatly affected the pyrolysis product composition. The degradation of mechanical properties enhanced the amount of wax and oil. However, the significant regeneration of mechanical properties via TSE with MRR promoted the increasing of wax while char, oil, and gas amount was decreased compared to Org. The relationship between the changes of structure and properties of PCR-HDPE from mechanical recycling and the obtained products from chemical recycling will be further evaluated and discussed.

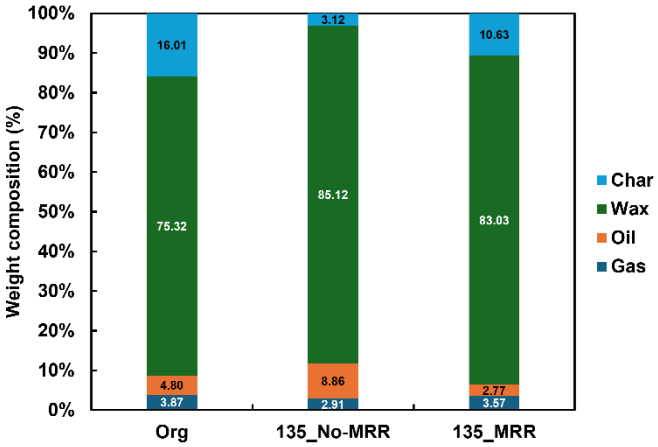


***Figure 3**. Weight composition of pyrolysis products: PCR-HDPE Org and mechanical-recycled products with different extrusion conditions.*

Conclusion

PCR-HDPE was recycled via an integrated mechanical-chemical recycling approach.

1) MR: The general TSE affected the decreasing of mechanical properties of PCR-HDPE. Interestingly, the mechanical properties were regenerated via extrusion with novel TSE with additional MRR unit.

2) CR: Pyrolysis product composition was different with the mechanical properties of PCR-HDPE. The degradation of mechanical properties affected the increasing of oil and wax amount compared to its Org. However, the regenerated mechanical properties increased in the amount of wax while char, oil, gas were decreased than Org.

The relationship between the mechanical properties and the changes of lamellar structures caused by mechanical recycling affected the pyrolysis product composition of PCR-HDPE. This integrated mechanical-chemical recycling with the optimized extrusion conditions has a potential to adjust and enhance the number of valuable products from waste plastics.

References

[1] Plastic Waste Management Institute: *An introduction to plastic recycling*, Japan, 2022.

[2] Siqueira, Y.F., Miranda, D.M.V., Carvalho, L.L.A., Sitton, N.K., Azeredo, A.P., Nonemacher, R.F., Mauler, R.S., Borges, L.E.P., Pinto, J.C.: *Impact of extrusion pre-treatment on polyethylene waste pyrolysis*, Polymer Engineering & Science, 65, 4020-4034, 2025.

[3] Okubo, H., Kaneyasu, H., Kimura, T., Phanthong, P., Yao, S., *Effects of a twin-screw extruder equipped with a molten resin reservoir on the mechanical properties and microstructure of recycled waste plastic polyethylene pellet moldings*, Polymers, 13(7), 1058, 2021.

[4] Phanthong. P., Miyoshi, Y., Yao, S., *Development of tensile properties and crystalline conformation of recycled polypropylene by re-extrusion using a twin-screw extruder with an additional molten resin reservoir unit*, Applied Sciences, 11(4), 1707, 2021.

Acknowledgement

This study was supported by the Environment Research and Technology Development Fund of the ERCA (JPMEERF20253G02) funded by the Ministry of the Environment, Japan. Part of this work was based on results obtained from a project no. JPNP20012 commissioned by the New Energy and Industrial Technology Development Organization (NEDO), Japan.

A Study on the Resource Circulation of Used Portable Lithium-ion Batteries in Japan

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Introduction

Lithium-ion batteries (LIBs) are indispensable to modern society. They are widely used in automobiles, industrial applications, and portable devices. The circulation of these resources is particularly important as LIBs contain critical metals such as Ni, Co, and Li. However, it is challenging to collect portable LIBs after they are distributed to consumers. Since 1991 (amended in 2006), the EU has comprehensively regulated batteries through the Battery Directive, which was replaced in 2023 by the Battery Regulation. This regulation requires producers to establish a system for collecting used portable batteries and to meet collection rate targets [1][2]. Since Japan faces similar challenges to those in Europe, the resource potential of portable LIBs in Japan was evaluated [3].

The current situation of used portable LIBs in Japan

Oguchi *et al*. [4] estimated that approximately 8,000 tons of portable LIBs were discarded in Japan in fiscal year 2020. However, this estimate differs significantly from that of the Japanese Ministry of the Environment (MoE). It is estimated that only 14% of discarded 8,000 tons LIBs are collected by certified recyclers. Meanwhile, 19–23% are mixed into household waste, and the remaining 60–70% cannot be accounted for.

The Japan Portable Rechargeable Battery Recycling Center (JBRC) is the producer responsibility organization that is responsible for collecting and recycling portable rechargeable batteries in Japan. However, the JBRC does not collect products manufactured by non-member companies, damaged products, or laminate-type batteries without casings. The increasing number of LIBs built into small appliances has also complicated the recycling process because they are collected with their devices rather than as individual batteries.

In recent years, fire accidents attributed to used LIBs have frequently occurred during household waste collection and treatment processes. According to the MoE, the number of such incidents reached 8,543 in fiscal year 2023. Some of these accidents caused damages of up to several ten million US dollars. In 2025, the MoE notified municipalities to include lithium-ion batteries in separate collection systems. Additionally, in 2025, the Ministry of Economy, Trade and Industry (METI) amended the Resource Efficiency Promotion Act to require manufacturers and importers of mobile phones, power banks, and e-cigarettes to implement collection and recycling systems.

Battery collection system in Sendai City

In Sendai City, home of Tohoku University, waste dry-cell, Ni-Cd and Ni-MH batteries are regularly collected at garbage collection sites. Since 2022, LIBs have been added to the regular collection. Citizens can dispose of all household batteries , including LIBs, by placing them in a transparent plastic bag and taking them to the collection site, just like cans, glass, and PET bottles. The collection also covers batteries that remain integrated within devices, such as those in smartphones, power banks, e-cigarettes, shavers, and electric toothbrushes. Batteries used in electric-assisted bicycles and vacuum cleaners are

collected after being detached from the devices. All collected batteries are sorted at the city's sorting center. This is an example for other municipalities to follow in implementing a collection system for portable LIBs.

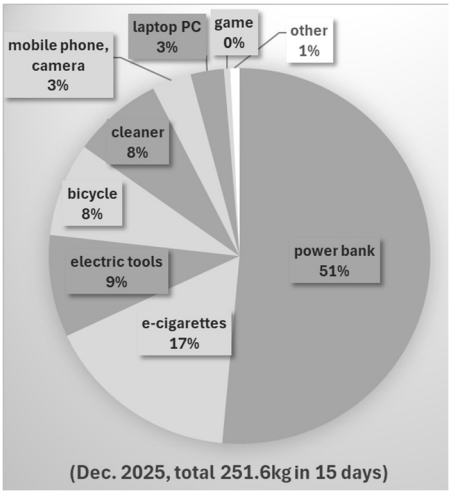


Figure 1. Classification result of used LIBs collected in Sendai City.

Analysis of collected LIBs in Sendai City

A survey of the collected LIBs was conducted at Sendai City's sorting center over four periods from 2024 to 2025. First, the LIBs collected within each period were classified by type. **Figure 1** shows the most recent results from December 2025. A particularly high proportion of power banks is notable. Compared to past surveys, the collection volume of power banks and e-cigarettes has significantly increased. Furthermore, heat treatment was performed to separate metals and organic content (polymer and solvent). The metal content of the LIBs was analyzed based on their classification to confirm their resource potential.

There are various types of lithium-ion batteries, and sorting them by type enhances the resource value of used LIBs. In Japan, the Battery Association of Japan released a guideline of labeling to indicate the composition of LIBs materials. In addition, batteries have labels corresponding to technical and safety standards in different countries. An attempt was made to verify the labels on the collected batteries; however, in many cases, the labels were extremely small, making it difficult to locate the necessary sorting information.

Conclusion

The collection and recycling system for used LIBs in Japan is still under development and faces various challenges. First, national legislation is strengthening collection efforts by businesses and local governments, which is expected to improve implementation and safety. Used LIBs are collected as either individual batteries or embedded within devices, each of which requires different handling methods. Reports on the EU WEEE Directive also indicate that items such as power banks and e-cigarettes may be missing from statistics because they are not properly classified by law [5]. Furthermore, although LIBs contain critical raw materials such as Ni, Co, and Li, it remains unclear where these materials are gone and recycled. Therefore, clarifying the resource potential and its circulation of portable LIBs is important.

Acknowledgement

This research was conducted with the support of the Environment Research and Technology Development Fund (JPMEERF20243002) from the Environmental Restoration and Conservation Agency, overseen by the Japanese Ministry of the Environment. We thank the Environmental Bureau of Sendai City for collecting the samples.

References

[1] Saito, Y. and Shiratori, T.: *A Study on International Trends in the Statutory Regulation of Batteries: A Focus on Lithium-ion Batteries in the EU*, J. Jpn. Soc. Mater. Cycles Waste Manag.33, 204-213, 2022

[2] Saito, Y., Shiratori, T., Saito, A., Nishiyama, T., Yoshioka, T.: *Study on Material Labelling of Portable LIBs in Japan*, EcoDesign2025 Conference Proceedings, Tokyo, Japan, 2025.

[3] Morita, Y., Saito, Y., Yoshioka, T., Shiratori, T.: *Estimation of recoverable resources used in lithium-ion batteries from portable electronic devices in Japan*, Resources Conservation & Recycling, 175, 105884, 2021

[4] Oguchi M., Terazono A., Hasunuma K.: *Estimation of discarded amount of portable LIBs and analysis of flow,* 35th Annual conference of Japan Society of Material Cycles and Waste Management, 2024

[5] European Commission: *Study supporting the evaluation of Directive 2012/19/EU on waste electrical and electronic equipment (WEEE)*, 2024

Waste-derived amides for reversible CO_2 capture

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1. Introduction

Plastic waste accumulation [1] and rising atmospheric CO_2 concentration [2] represent two of the most urgent global environmental challenges. Condensation polymers, as polyethylene terephthalate (PET) and polyamide 6,6 (or nylon 66, PA66), widely employed for beverage bottles, textile fibers and food packaging, constitutes a major fraction of post-consumer plastic waste. Conventional mechanical recycling is often limited by polymer degradation and quality loss,[3] whereas most chemical recycling efforts focus on depolymerization to monomers [4] without generating new functional materials. In parallel, liquid CO_2 sorbents — especially those based on aqueous amines — suffer from high regeneration energy penalties, corrosivity, and degradation issues.[5]

In this context, approaches that integrate waste valorisation and carbon capture are highly desirable. While previous studies have upcycled PET into porous carbons or metal–organic frameworks for gas adsorption, [6,7] these strategies mostly target physisorption and require high-temperature pyrolysis or complex processing steps.

This work proposes a chemical upcycling strategy that converts waste condensation polymers (polyesters and polyamides) into amides, from which a liquid can be obtained (in the form of a Deep Eutectic Solvent, DES, or a Low Transition Temperature Mixture, LTTM) and act as stable and reusable liquid CO_2 sorbent.

Recently, we upcycled PET into N,N′-bis(2-aminopropyl)terephthalamide (BAPTA), which, in the presence of propylene glycol (PG) already demonstrated to be capable of reversible CO_2 absorption, [8] but the same concept can be applied also to polyamide waste (as nylon in its various forms).

The approach aligns with circular economy principles, relying on mild reaction conditions, minimized waste generation, and solvent recovery.

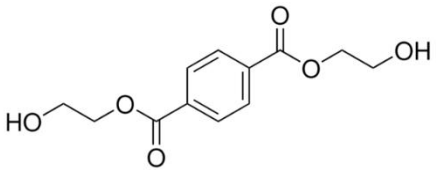
2. Materials and Methods

Waste PET was first converted into bis(hydroxyethyl) terephthalate (BHET, see Figure 1) via ammonium-bicarbonate-catalyzed glycolysis, a low-impact process previously optimized for scalability and compatibility with various PET waste streams.

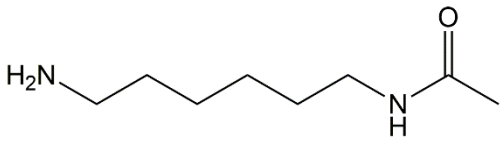
Subsequently, BHET underwent aminolysis with 1,2-diaminopropane, giving BAPTA, which is capable of forming a homogeneous liquid phase when mixed with PG under mild heating (≈120 °C).

The resulting BAPTA/PG mixtures were characterized through DSC, viscosity and conductivity measurements, NMR spectroscopy (including carbonation–decarbonation monitoring), and CO_2 absorption kinetics at 1 atm and temperatures ranging from 23 to 60 °C.[8]

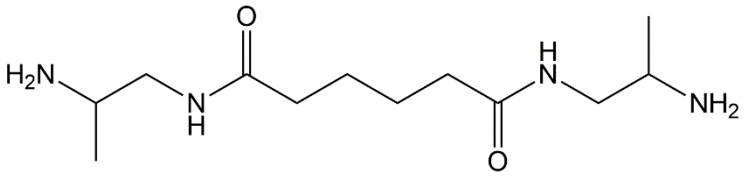
Waste PA66 was converted into a mixture of adipic acid and 1,6-hexamethylenediammonium dichloride via an acidic hydrolysis, using either $HCl_{(aq)}$ 12M [9] or a DES composed by $FeCl_3 \cdot 6H_2O$ and acetic acid [10]. The two products have been separated by selective dissolution in ethyl acetate and both of them underwent amidation processes, forming bis(2-aminopropyl)adipamide (BAPA) and the N-(6-aminohexyl)acetamide. The characterization of the liquid formed by BAPA and NAHA with ethylene glycol is currently in progress.



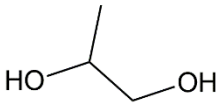
bis(hydroxyethyl) terephthalate (BHET)



N-(6-aminohexyl)acetamide (NAHA)



bis(2-aminopropyl)adipamide



propylene glycole

Figure 1. Main chemical structures discussed in this abstract.

3. Results and Discussion

3.1 Formation of the liquid sorbent

PET-derived BAPTA yielded a stable low-transition-temperature mixture (LTTM) when combined with 3–6 equivalents of PG. The liquid remained homogeneous for weeks at room temperature without crystallization. DSC analysis revealed a glass transition at 87 °C, consistent with LTTM behavior.

3.2 CO_2 absorption mechanism

Upon exposure to CO_2, the liquid mixture became more viscous and displayed a new ^{13}C NMR resonance at 164 ppm, consistent with the formation of a propylene-glycol carbonate species rather than a carbamate bound to the diamide. DFT calculations support carbonate formation as the thermodynamically preferred pathway ($\Delta G = 1.5$ kcal/mol).

The carbonation was fully reversible upon mild heating (≈90 °C), restoring the initial NMR profile and viscosity.

3.3 Sorption performance

At 30 °C, the BAPTA/PG (1:6) system reached a maximum CO_2 uptake of 52.4 g CO_2 kg^{-1} sorbent after 6 h under 1 atm. At room temperature (23 °C), the system approached saturation (≈50 g kg^{-1}) over ~8 h. The viscosity increased upon carbonation but remained within manageable limits for mass transfer. Temperature had a favourable effect on kinetics due to decreased viscosity, without compromising reversibility.

3.4 Robustness and recyclability

The sorbent maintained its performance for ≥10 consecutive absorption–desorption cycles, showing no signs of degradation (Figure 2). Minor losses of PG during desorption could be compensated by simple replenishment; alternatively, glycol could be condensed and recovered.

Comparative experiments with 1,2-diaminopropane (the amine precursor of BAPTA) revealed higher initial CO_2 uptake but no regenerability and issues of volatility/toxicity, reinforcing the role of PET-derived functionalization in stabilizing the sorbent.

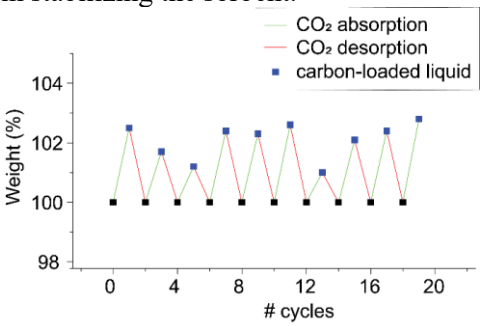


Figure 2. Weight variation of the BAPTA/PG liquid mixture during 10 absorption/desorption cycles.

3.5 Circular economy and upcycling significance

This process transforms plastic waste into a functional CO_2-capture medium, representing both:
Chemical recycling (PET → BHET → BAPTA)
Upcycling (waste-derived molecule with new CO_2-capture functionality)

The methodology avoids harsh conditions and converts 1 kg of PET into roughly 2.6 kg of sorbent, improving material productivity.

4. Conclusions

This work demonstrates a new paradigm in feedstock recycling, showing that PET waste can be converted into an efficient, stable and reversible liquid CO_2 sorbent via the formation of BAPTA-based LTTMs. The BAPTA/PG mixture exhibits:
Efficient CO_2 uptake (≈50 g kg^{-1} at 1 atm)
Fully reversible absorption/desorption cycles
Mild regeneration conditions
Non-ionic behavior and moderate viscosity
Scalability and low environmental impact

To our knowledge, this is the first liquid sorbent directly derived from PET waste, providing a promising route for integrated plastic waste valorisation and carbon capture, consistent with circular economy principles.

For polyamides waste, the work is currently underway, as the conversion from nylon waste to amides (BAPA and NAHA in this case) already proved to be possible. In the next weeks, the formation of liquids (DES or LTTM) and their performances in carbon capture will be investigated.

References

[1] Pilapitiya, P. G. C. N. T., Ratnayake, A. S.: *The world of plastic waste: A review*, Cleaner Materials, 11, 100220, 2024.
[2] Bardi, U., Bierwirth, P., Huang, K.-W., McIntyre, J.: *Carbon dioxide as a pollutant: the risks on human health and the stability of the biosphere*, Environmental Science: Advances, 2025(4), 1364, 2025.
[3] Schyns, Z. O. G., Shaver, M. G.: *Mechanical Recycling of Packaging Plastics: A Review*. *Macromolecular Rapid Communications* 42(3), 2000415, 2020.
[4] Peti, D., Dobránsky, J., Michalik, P.: *Recent Advances in Polymer Recycling: A Review of Chemical and Biological Processes for Sustainable Solutions*, Polymers, 17(5), 603, 2025.
[5] Meng, F., Meng, Y., Ju, T., Han, S., Lin, L., Jiang, J.: *Research progress of aqueous amine solution for CO_2 capture: A review*, Renewable and Sustainable Energy Reviews, 168, 112902, 2022.
[6] Teo, J.Y.Q, Ong, A., Tan, T.T.Y., Li, X., Loh, X.J., Lim, J.Y.C.: *Materials from waste plastics for CO_2 capture and utilisation*, Green Chemistry 24, 6086–6099, 2022.
[7] Poderyte, M., Lima, R., Golbækdal, P. I., Juhl, D. W., Olesen, K. L., Nielsen, N. C., Lanza, A., Lee, J.-W.: *Repurposing polyethylene terephthalate plastic waste to capture carbon dioxide*, Science Advances, 11(36), eadv5906, 2025.
[8] Rossi, E., Volpe, A., Rollo, M., Giuliotti, G., Botteselle, G., Bernazzani, L. Ciancaleoni, G.: *Valorisation of polyethylene terephthalate waste: An upcycling approach into a reusable CO_2 liquid sorbent*, Chemical Engineering Journal, 514, 163155, 2025.
[9] Češarek, U., Pahovnik, D., Žagar, E.: *Chemical Recycling of Aliphatic Polyamides by Microwave-Assisted Hydrolysis for Efficient Monomer Recovery*, ACS Sustainable Chemistry & Engineering, 8(43), 16274-16282, 2020.
[10] Rollo, M., Rastelli, F., Ximenis, M., Martinelli, E., Ciancaleoni, G., Sardon, H.: *Iron-based Lewis/Brønsted Deep Eutectic Solvents for the hydrolysis of nylon-6,6*, ChemRxiv, 10.26434/chemrxiv-2025-jcgmq, 2025.

The confusing terminology of "upcycling"

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Introduction

In recent years, the term "upcycling" has become increasingly common. Searching for the keyword "upcycling" in both general and academic search engines yields numerous results. But what exactly does upcycling mean? How does it differ from recycling? Isn't there a confusion of terminology?

This study analyses the usage of upcycling in academic fields and attempts to find a definition. The analysis of academic usage revealed that the term is particularly prevalent in the fields of "chemical/plastics/polymers" and "food/agriculture/bio." Focusing on usage examples from these fields, the study examined whether a common understanding of the term could be established.

"Upcycling" in society

Search engines such as Google™ were first used to investigate how upcycling is used in general and to find examples of its common usage on Japanese and English websites. Since many websites provide similar definitions, one representative example is provided below.

"Upcycling involves adding new value, such as design or ideas, to waste that would otherwise be discarded, thereby upgrading it into a new product. It is also called creative reuse. Unlike traditional recycling, which returns materials to raw form for reuse as resources, upcycling utilizes the original product's materials as-is [1]."

Numerous examples exist, such as repurposing discarded fabric into fashion items or converting food processing byproducts or unutilized parts into commercial products. While the above definition states that upcycling does not "return materials to raw form," many examples labelled as such involve using waste or underutilized resources as new materials or products. Examples include using marine plastic litter or thinned timber as raw materials.

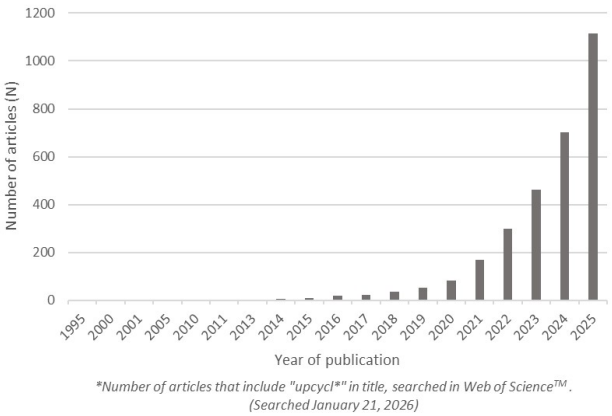


Figure 1. Number of academic articles that include "upcycling" in title.

"Upcycling" in academic articles

Web of Science™ was used to investigate the usage of the term "upcycling" in academic articles. It first appeared in a title in 1995. Until 2013, there were less than five occurrences per year. However, usage gradually increased from 2014 onward, surpassing 1,000 occurrences in a single year by 2025 **(Figure 1)**. Analyzing the keywords included in the 704 articles published in 2024 revealed that "chemical/plastics/polymers" appeared most frequently, followed by "food/agriculture/bio," "metals/battery," "construction," "consumer/education," "textiles," and others (**Figure 2**).

To examine how upcycling is used and defined, 79 review articles identified in the Web of Science search that were published in 2024 and had the phrase "upcycl*" in the title were analyzed. These articles were categorized by field and investigated to determine whether upcycling was defined within the text. The most common field was "chemical/plastics/polymers." Of these 40 articles, more than half (28) mentioned a definition of upcycling. Next was the "food/agriculture/bio" field, in which only four of 18 articles provided a definition. Therefore, the analysis primarily focused on papers from the "chemical/plastics/polymers" field to explore the common understanding of upcycling.

Of the 28 review articles addressing the definition of upcycling in the "chemical/plastics/polymer" field, 23 stated that upcycling involves "creating materials of higher value." Several articles provided more detailed definitions, distinguished upcycling as "producing a different material from the original in an open-loop process," which contrasts with closed-loop recycling. The inclusion of monomerization, and chemical recycling such as pyrolysis, varied among these articles. The discussed technologies often involve photochemical, electrochemical, catalytic, or biotechnological processes (19 out of 28 articles).

In the "food/agriculture/bio" field, for example, there is a definition as "Upcycled foods use ingredients that otherwise would not have gone to human consumption, are procured and produced using verifiable supply chains, and have a positive impact on the environment [2]." One notable description stated that if the technology "becomes a common and familiar process and is not innovative anymore, the food can also not be called 'upcycled' anymore [3]." This suggests that upcycling is a concept that inherently includes the innovative character of the process.

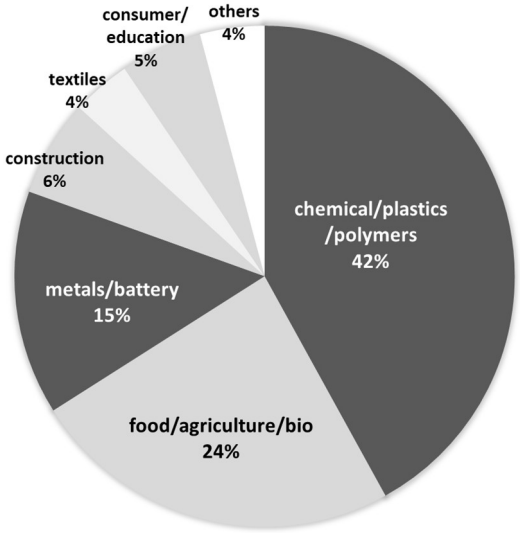


Figure 2. Research field analysis of academic articles that include "upcycling" in title, published in 2024. (N=704)

Research fields are classified by the keywords below included in the topic (title, abstract and keywords).
***Chemical/plastics/polymers**: *chemical*, *plastic*, *polymer*, *cataly*, *monomer**
***Food/agriculture/bio**: bio*, food*, agricultur*, *wood*, cosmetic*, microbio**
***Metals/battery**: *metal*, *batter*, e-waste*
***Construction**: building, construction, architect*, brick*
***Textiles**: textile, apparel, cloth**
***Consumer/education**: consumer*, education*
(Searched in Web of Science™. January 21, 2026)

Provisional definition of "upcycling"

Based on the above review, the following definition of upcycling is proposed: "Upcycling is a process that uses waste, byproducts, or similar materials to create high-value materials that are distinct from the original substances through innovative methods." This definition implies that the process must satisfy all four elements: (1) use of waste, byproducts, or similar materials (2) creation of high-value materials, (3) materials that are distinct from the original substances, and (4) use of innovative methods.

Discussion

Defining upcycling in this way shows that some applications do not fit this definition. For example, some processes that are commonly referred to as recycling or thermal recovery appear to fall under this category, which could cause confusion. Additionally, improving the quality of recycled metals has been termed upcycling. This may be influenced by the definition of downcycling as the phenomenon of metal quality degradation during recycling [4].

Acknowledgement

Part of this research was discussed at a workshop in the JST CREST project "[Degradation and Stability] Precise Material Science for Degradation and Stability."

References

[1] IDEAS FOR GOOD https://ideasforgood.jp/glossary/upcycle/ (Browsed January 21, 2026)
[2] THE UPCYCLED FOODS DEFINITION TASK FORCE: *Defining Upcycled Foods*, 2020
[3] Aschemann-Witzel, J., Asioli, D., Banovic, M., Perito, M. A., Peschel, A. O., Stancu, V.: *Defining upcycled food: The dual role of upcycling in reducing food loss and waste*. Trends in Food Science & Technology, 132, 132-137, 2023
[4] Helbig, C., Huether, J., Joachimsthaler, C., Lehmann, C., Raatz, S., Thorenz, A., Faulstich, M., Tuma, A.: *A terminology for downcycling*. Journal of Industrial Ecology, 26, 1164–1174, 2022

Policy Strategies for Industrial Deployment of Waste Plastic Pyrolysis in Korea

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Introduction

Plastic waste continues to rise due to structural shifts in consumption patterns, including rapid growth in e-commerce packaging and delivery-based consumption. At the same time, petroleum-based plastics generate substantial greenhouse gas (GHG) emissions across their life cycle, from production to use and disposal. These trends increase policy pressure to achieve both waste reduction and industrial decarbonization. In this context, chemical recycling, particularly waste plastic pyrolysis, is gaining attention as a complementary pathway to mechanical recycling. Pyrolysis is a thermochemical process that decomposes plastics in an oxygen-free environment, typically at temperatures of 600°C or below, producing pyrolysis oil and other by-products. It is frequently highlighted for its potential to (i) treat mixed or contaminated plastic streams that are difficult to mechanically recycle and (ii) generate hydrocarbon outputs that may substitute for petroleum-derived feedstocks in industrial applications [1]. However, whether pyrolysis delivers circularity and climate benefits depends on policy design across the value chain, including feedstock quality management, facility standards and emissions control, product certification, and credible GHG accounting. Korea has recently accelerated policy discussions on plastic reduction and circular economy competitiveness. In particular, the government announced a draft comprehensive plastics policy package at a national public forum in December 2025, aiming to reduce plastic waste from households and businesses by at least 30% from projected levels by 2030 [2]. This reinforces the need for updated policy tasks that position pyrolysis not merely as waste treatment, but as a regulated circular feedstock pathway within an integrated policy framework.

Purpose and Scope

This study proposes updated policy tasks for promoting waste plastic pyrolysis in Korea, focusing on the transition from fuel use toward feedstock substitution and circular material use. The scope centers on pyrolysis of waste plastics and the governance conditions required for scalable industrial deployment.

Updated Policy and Market Context

Korea's policy framework increasingly links pyrolysis to circular economy and carbon neutrality objectives. The government's plastic circularity agenda has emphasized higher-value recycling pathways, including chemical recycling, along with measures to expand recycled content and strengthen market formation. Recycling categories were further refined by amending [Annex 4-2] of the Enforcement Rule of the Waste Management Act, so that pyrolysis oil can be recognized and used as a recyclable feedstock[3]**.** In addition, the Enforcement Decree of the Act on the Promotion of Installation of Waste Disposal Facilities and Assistance to Adjacent Areas was amended to permit the installation of pyrolysis facilities on up to 50% of landfill sites located in industrial complexes subject to mandatory landfill facility installation requirements.

A major development is the draft comprehensive plastics policy package announced at the end of 2025 [2]. The plan frames plastic policy as a cross-cutting transition, covering virgin plastic reduction, sustainable design and production, expanded collection and recycling, and industrial competitiveness in circular economy sectors. This trend implies that pyrolysis policies should be designed to support not only facility expansion but also quality control, traceability, and stable market demand. Industrial investment trends also suggest rising demand for reliable pyrolysis oil supply chains and credible sustainability standards.

Policy Tasks for Scaling Waste Plastic Pyrolysis

1. Secure High-Quality Feedstock Through Sorting System Upgrades and Upstream Design Measures
Pyrolysis yield and product quality depend heavily on feedstock composition and contamination levels. To scale pyrolysis sustainably, policy must strengthen feedstock systems by:

- improving separation and collection of plastic films and mixed plastics
- introducing contamination control standards for moisture and foreign substances
- expanding dedicated sorting infrastructure that supports both mechanical recycling and chemical recycling
- linking upstream eco-design measures to downstream recycling feasibility (e.g., reducing multi-material structures and problematic additives)

2. Establish Facility Standards for Input Specifications, Safety Requirements, and Emissions Controls
Pyrolysis facilities require robust standards to ensure environmental performance and safety. A modern regulatory framework should include:

- detailed input specifications (e.g., moisture limits, thresholds for chlorine/PVC content, inert materials)
- safety criteria for managing flammable gases and carbonaceous residues
- mandatory monitoring and reporting protocols, including continuous measurement requirements where appropriate
- strengthened inspection procedures for both installation approval and periodic compliance audits

3. Develop Siting Strategies Linked to Industrial Demand and Regional Circular Economy Zones
To scale pyrolysis as a circular feedstock pathway, facility siting should be integrated with industrial demand and logistics systems. Policy directions include:

- promoting siting linkages with petrochemical and manufacturing clusters
- establishing circular economy demonstration zones that support shared quality control and logistics infrastructure
- introducing structured coordination mechanisms among central ministries and local governments to streamline permitting while ensuring environmental safeguards

4. Build Certification and Traceability Systems for Market Formation of Circular Feedstock
Market expansion requires institutional recognition of pyrolysis oil as a recycled input under transparent conditions. Policy tasks include:

- establishing certification criteria for pyrolysis oil as circular feedstock, including quality thresholds
- implementing chain-of-custody and traceability mechanisms, using appropriate accounting approaches where relevant
- developing national statistics and monitoring systems covering waste plastic supply, pyrolysis conversion, distribution, and end-use
- strengthening stockpiling and logistics infrastructure to stabilize supply and reduce volatility

5. Standardize GHG Accounting Rules and Expand LCI Databases for Credible Climate Claims
The credibility of pyrolysis as a climate mitigation pathway depends on consistent GHG accounting. Policy priorities include:

- standardizing life-cycle boundaries and assumptions for comparisons with incineration and alternative waste treatment routes
- accounting for avoided virgin feedstock production where applicable

- ensuring transparency on facility energy sources, process efficiency, and by-product management
- supporting standardized Life Cycle Inventory (LCI) datasets for waste plastics and pyrolysis pathways to enable consistent MRV (Measurement, Reporting, and Verification)

6. Institutionalize Stakeholder Governance for Integrated Implementation
Pyrolysis policy intersects multiple domains including waste management, petrochemicals, safety regulation, climate accounting, and community acceptance. To prevent fragmentation, it is necessary to institutionalize governance systems that enable:

- inter-ministerial policy coordination
- transparent public communication and dispute resolution mechanisms
- regular consultative platforms for industry stakeholders to address feedstock quality, certification, facility standards, and market development

Conclusion and Implications

Korea's recent policy evolution, including the December 2025 draft comprehensive plastics policy package, signals a transition from fragmented recycling measures toward a system-wide circular economy agenda. Under this shift, waste plastic pyrolysis may contribute to carbon neutrality and circular resource use if it is governed as a credible circular feedstock pathway. To scale pyrolysis while maintaining environmental integrity, Korea should prioritize: (i) feedstock quality systems, (ii) facility safety and emissions standards, (iii) industrial linkage siting strategies, (iv) certification and traceability for market creation, (v) standardized GHG accounting supported by robust LCI infrastructure, and (vi) institutionalized stakeholder governance. These integrated policy tasks will be essential for aligning pyrolysis deployment with Korea's 2030 plastic reduction goals and longer-term industrial decarbonization strategy.

References

[1] Ji Hye Jo et al.: *Pyrolysis of Plastic Waste: Current Status and Policy Tasks*, Korea Environment Institute, 2022.
[2] Ministry of Climate, Energy and Environment: *Draft Comprehensive Plastics Reduction Strategy, National Public Forum at the National Assembly*, December 23, 2025.
[3] Press Release from the Ministry of Environment: *Activating Waste Plstic Pyrolysis as a Crude Oil Substitute – Establishment of Recycling Standards*, March 3, 2022.

Acknowledgement

This research was supported by the Korea Environment Institute (KEI) under project No. WO2022-01.

Process modelling of polyethylene rich multilayer packaging waste conversion

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Introduction

Multilayer packaging, such as Tetra Pak®, are challenging to recycle due to their multicomponent composition. Hydro-pulping allows to recover paper fibers from multilayer packaging. Fibers are mostly recovered from these packaging waste due to their high recycling value, for example in paper industry, whereas the remaining solid residues, consisting of polyethylene, aluminium, and residual fibers, are mostly either landfilled or incinerated. Polyethylene, the main component of the solid residue, is a valuable polymer. Alternative treatments, such as pyrolysis and dissolution-precipitation, are promising conversion techniques for this waste, capable of producing valuable products [1,2]. In this work, we explore the potential of these treatments to establish a benchmark against combustion using Aspen Plus process modelling.

Experimentation and preliminary results

The experimental part was carried out using solid residues produced by hydro-pulping of Tetra Pak®. Tetra Pak® composes of cardboard (70 wt.%), polyethylene (25 wt.%) and aluminium (5 wt.%) [3]. For the pyrolysis study, hydro-pulped solid residue was used. These samples contain 7 wt.% of initial Tetra Pak® cardboard fibers, and aluminium and plastic part of Tetra Pak®. Slow pyrolysis of the solid residues was carried out in a semi-batch fixed bed reactor with trays assembly. Dissolution and precipitation experiments were carried out with short-term hydro-pulped Tetra Pak® in batch and semi batch reactors respectively, using xylene as solvent and isopropanol as antisolvent. Preliminary results include the experimental recovery of products from pyrolysis and dissolution-precipitation processes. Pyrolysis of raw Tetra Pak® and hydro-pulped Tetra Pak® yielded close amounts of solid pyrolyzates (**Table 1**). However, hydro-pulped Tetra Pak® produced lesser char-contaminated solids and more waxy liquids compared to raw Tetra Pak® on visual basis.

Table 1. Mass balance for pyrolysis based on lumped products

Material	Solid	Condensates	Gas
	wt.%		
Raw Tetra Pak®	24.8	43.0	16.4
Hydro-pulped Tetra Pak®	22.4	66.5	11.6

Note: Preliminary results (data treatment in progress)

Recovery rate of recycled polyethylene varied greatly between different dissolution-precipitation experiments due to more pronounced effect of heterogeneity of the material with coarser particles at lab scale (**Table 2**).

Table 2. Mass balance for dissolution precipitation based on recovered solids

Material	Aluminium-Fibers-Residual PE	Recycled polyethylene
	wt.%	
Hydro-pulped Tetra Pak®	54.8 – 73.5	13.4 – 35.4

Note: Preliminary results (data treatment in progress)

Dissolution-precipitation recycled polyethylene from Tetra Pak® was obtained with characteristics very close to different types of commercial polyethylene (**Table 3**). However, color contaminations and other micro contaminants were observed.

Table 3. Products physicochemical characteristics (wt.%, dry basis)

	Recycled polyethylene	Polyethylene	Linear low-density polyethylene
Source	Dissolution-precipitation	Sigma Aldrich	Sigma Aldrich
Proximate analysis			
Highly volatile	-	-	-
Medium volatile matter	99.8 ± 0.4	99.8 ± 0.1	99.8 ± 0.6
Fixed carbon	0.2 ± 0.1	0.2 ± 0.0	0.2 ± 0.0
Ash	-	-	-
Ultimate analysis			
C	83.2 ± 1.8	85.7 ± 0.2	84.5 ± 0.3
H	14.3 ± 0.6	14.3 ± 0.3	15.5 ± 0.5
O[a]	2.4 ± 1.9	-	-

a. Determined by 100 – C – H

Process modelling

The simulation framework was specifically designed to reproduce industrial-scale conditions. Process parameters (operational conditions, component database and properties, and process flow details) were obtained from experiments for pyrolysis and dissolution/precipitation. The thermodynamic modelling approach of Gibbs free energy minimization was used for the complete combustion. The three main process stages comprise of hydro-pulping, drying, and treatment process (**Figure 1**).

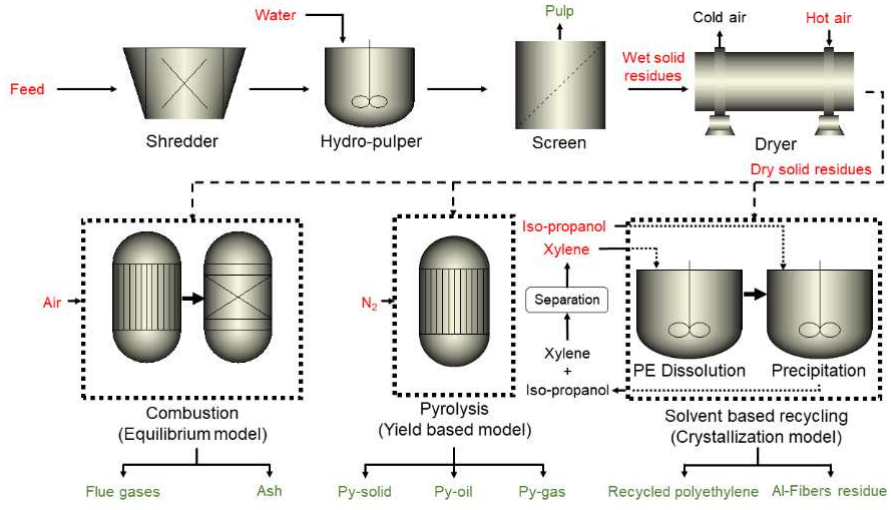


Figure 1. Process flow diagrams of the processes

The feedstock, imitating Tetra Pak®, was introduced as unconventional solids into the process model. It was defined based on its physicochemical properties such as ultimate and proximate analyses. After hydro-pulping, pulp containing fibers and majority of water was removed from the stream and the solid residues with the composition of hydro-pulped Tetra Pak® were subjected to conversion process after drying. Initial results confirmed the feasibility of the selected methodologies for the benchmark establishment. Thermodynamic modelling provided a good overview of the complete combustion of the material, which can be used as reference process. The process models for pyrolysis and dissolution precipitation will be further refined to establish a dynamic and rigorous comparison.

References

[1] Xu, Z., Sanchez-Rivera, K., Granger, C., Zhou, P., Munguia-Lopez, A.D.C., Ikegwu, U.M., Avraamidou, S., Zavala, V.M., Van Lehn, R.C., Bar-Ziv, E., De Meester, S., Huber, G.W.: *Solvent-based plastic recycling technologies*, Nature Chemical Engineering, 2(7), 407-23, 2025.

[2] Dogu, O., Pelucchi, M., Van de Vijver, R., Van Steenberge, P.H.M., D'hooge, D.R., Cuoci, A., Mehl, M., Frassoldati, A., Faravelli, T., Van Geem, K.M.: *The chemistry of chemical recycling of solid plastic waste via pyrolysis and gasification: State-of-the-art, challenges, and future directions*, Progress in Energy and Combustion Science, 84, 100901, 2021.

[3] Muñoz-Batista, M.J., Blázquez, G., Franco, J.F., Calero, M., Martín-Lara, M.A.: *Recovery, separation and production of fuel, plastic and aluminum from the Tetra PAK waste to hydrothermal and pyrolysis processes*, Waste Management, 137, 179–189, 2022.

Acknowledgements

The authors acknowledge the financial support by the French state managed by the National Research Agency in the name of France 2030 to conduct the French scientific program PAC-3R (ANR-22-PERE-0004). This work has also benefited from State aid managed by the Agence Nationale de la Recherche under the Programme d'Investissements d'Avenir with the reference ANR-18-EURE-0021.

Physics-Informed Carbon Bond Group Modelling for Steam Cracking of Highly Heterogenous Polymer Feedstocks

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Abstract

Plastic waste production continues to grow worldwide, while real-world waste streams increasingly contain mixed polymers, additives, and contaminants that challenge traditional recycling routes [1,2]. Mechanical recycling remains essential, but its performance and product quality can degrade sharply as feed heterogeneity increases. In this context, thermochemical conversion offers a complementary pathway capable of processing mixed or contaminated plastic fractions at scale, converting polymeric carbon into valuable chemicals and hydrocarbon feedstocks. Among thermochemical routes, steam cracking in dual fluidized bed (DFB) reactors is particularly relevant because of its industrial role in monomer production and its potential to integrate waste-derived feeds into petrochemical value chains [3–6]. However, predicting product selectivity for heterogeneous feeds remains difficult: detailed kinetic mechanisms become impractical as feed complexity grows, while purely data-driven models may extrapolate poorly and violate basic conservation constraints. These challenges motivate reduced, structure-aware models that preserve chemical meaning while remaining usable for process modelling and feedstock evaluation.

This work builds on the Carbon Bond Group (CBG) framework, previously introduced as a chemical-structure abstraction for analyzing feedstock–product correlations in heterogeneous polymer cracking [7,8]. Instead of representing a waste stream by polymer identities, CBG classifies carbon atoms by their local bonding environment, projecting heterogeneous feedstocks into three structural carbon groups: C–xE (heteroatom-bound carbon), C–AL (aliphatic carbon), and C–AR (aromatic-ring carbon).

Here, the framework is advanced into a physics-informed predictive model by formulating steam cracking as a constrained mapping between feed and product compositional spaces. Feed and products are represented as vectors in a ternary simplex space, and the reactor is modelled as a conversion operator that maps feed CBG fractions to aggregated product families (COx, aliphatics, aromatics) while enforcing conservation laws and physical admissibility by construction. Model parameters are estimated using through constrained optimization, yielding an interpretable surrogate whose coefficients quantify net carbon routing between structural groups and product families under given operating reactor conditions.

The model was trained on a comprehensive dataset from multiyear experimental campaigns in a semi-industrial dual fluidized bed (DFB) steam cracking reactor at Chalmers University. The dataset spans different reactor operative conditions with temperatures between 720–835 °C in silica sand and covers a wide range of heterogeneous waste-derived feedstocks (sorting rejects and complex polymer mixtures). Despite the diversity of feedstocks and conditions, the resulting condition-dependent CBG model achieves high predictive accuracy for aggregated product-family carbon distributions, with R^2 above 0.97 for COx and aliphatics, and ~0.9 for aromatics across the full training/validation dataset.

To extend the model assessment to an extreme real-world waste stream, we apply the CBG-based predictive mapping to automotive shredder residue (ASR), a highly heterogeneous polymeric mixture containing combinations of polyolefins (PP), cellulose-rich fractions, polyurethane, elastomers (tires)

and minor plastics, alongside very high ash contents (~32–47 wt%). ASR provides a stringent test case because its heterogeneity and contamination degree exceed that of typical mixed-plastic streams, and because oxygenated and elastomer-derived structures can shift carbon allocation toward COx and aromatics [9].

Figure 1 compares measured and predicted carbon distribution among aggregated product families (COx, aliphatics, aromatics) for two automotive shredder residue blends (ASR1–ASR2) evaluated at ~790 °C under steam-cracking conditions in the same semi-industrial DFB reactor described above.

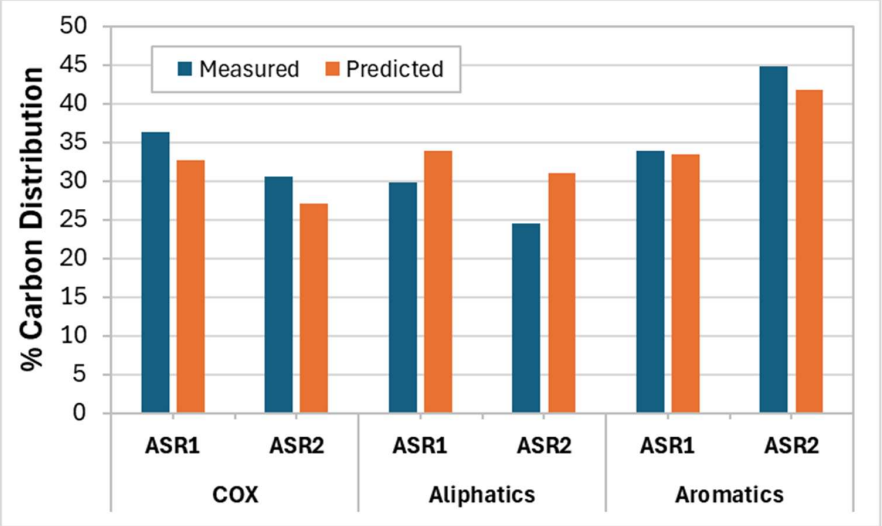


Figure 1. Measured versus CBG-model-predicted carbon allocation among aggregated product groups for two automotive shredder residue blends (ASR1–ASR2) evaluated at 790 °C in a semi-industrial scale DFB under steam cracking conditions. Values represent the fraction of total converted carbon distributed to each group.

Across both ASR blends, the model reproduces the overall allocation trends at the level of product families, with particularly close agreement for aromatics (~1.5–6.8% relative error) and moderate deviations for COx (~9.9–11.4%), while the largest discrepancies occur for aliphatics (~14–27%). The deviation pattern suggests that, for highly heterogeneous and ash-rich ASR, aliphatic allocation is more sensitive to factors not explicitly represented in the model's compact group description (e.g., ash-related effects in the bed and condition-dependent secondary reactions), whereas net routing to aromatics remains comparatively robust at the evaluated severity.

The ASR evaluation indicates that a compact, physics-constrained CBG mapping can remain informative even for highly heterogeneous, ash-rich waste streams, providing rapid estimates of how converted carbon partitions among COx, aliphatics, and aromatics at a given cracking severity. This supports the use of the model as a process-modelling surrogate and as a feedstock screening tool for complex recycling streams where full mechanistic modelling may become impractical and experimental coverage limited. At the same time, the larger deviations observed for the aliphatic family highlight aspects where the reduced representation can be strengthened for real highly complex residues such as ASR. Priority extensions include (i) introducing explicit descriptors for contamination and inert dilution (e.g., ash/mineral fraction) and (ii) refining the structural basis to better capture functionalized carbon environments and secondary reaction propensity under heterogeneous matrices. These steps are expected to improve robustness while potentially enhancing the interpretability of the current physics-informed formulation. Overall, these results demonstrate the potential of the developed structure-based, physics-informed framework as a basis for predictive feedstock assessment and digital-twin development aimed at monitoring and optimization of thermochemical recycling under feedstock variability.

References

[1] A. Alassali, C. Picuno, Z.K. Chong, J. Guo, R. Maletz, K. Kuchta, Towards Higher Quality of Recycled Plastics: Limitations from the Material's Perspective, Sustainability 13 (2021) 13266. https://doi.org/10.3390/su132313266.
[2] PLASTICS EUROPE, Plastics the Facts, 2022.
[3] H. Thunman, T. Berdugo Vilches, M. Seemann, J. Maric, I.C. Vela, S. Pissot, H.N.T. Nguyen, Circular use of plastics-transformation of existing petrochemical clusters into thermochemical recycling plants with 100% plastics recovery, Sustainable Materials and Technologies 22 (2019) e00124. https://doi.org/10.1016/j.susmat.2019.e00124.
[4] C. Mandviwala, Steam Cracking of Polyolefins in Fluidized Bed Systems: Influences of the Bed Materials on the Hydrogen Transfer Reactions, n.d.
[5] W. Kaminsky, M. Predel, A. Sadiki, Feedstock recycling of polymers by pyrolysis in a fluidised bed, Polym. Degrad. Stab. 85 (2004) 1045–1050. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2003.05.002.
[6] W. Kaminsky, The Hamburg Fluidized-bed Pyrolysis Process to Recycle Polymer Wastes and Tires, in: Feedstock Recycling and Pyrolysis of Waste Plastics, John Wiley & Sons, Ltd, 2006: pp. 475–491. https://doi.org/https://doi.org/10.1002/0470021543.ch17.
[7] R. Forero-Franco, I. Cañete-Vela, T. Berdugo-Vilches, J. González-Arias, J. Maric, H. Thunman, M. Seemann, Correlations between product distribution and feedstock composition in thermal cracking processes for mixed plastic waste, Fuel 341 (2023) 127660. https://doi.org/10.1016/j.fuel.2023.127660.
[8] R. Forero-Franco, I. Cañete-Vela, T. Berdugo-Vilches, C. Mandviwala, N.D. Perez, I. Gogolev, H. Thunman, M. Seemann, Towards sustainable textile waste management: Exploring valuable chemicals production through steam cracking in a dual fluidized bed, Fuel 397 (2025) 135731. https://doi.org/10.1016/j.fuel.2025.135731.
[9] S. Pissot, T. Berdugo Vilches, J. Maric, I. Cañete Vela, H. Thunman, M. Seemann, Thermochemical Recycling of Automotive Shredder Residue by Chemical-Looping Gasification Using the Generated Ash as Oxygen Carrier, Energy & Fuels 33 (2019) 11552–11566. https://doi.org/10.1021/acs.energyfuels.9b02607.

Integrated Design and Modelling of Polystyrene Hydrothermal Upcycling to Styrene and Low-Carbon Hydrogen via Steam Reforming and Syngas Chemical Looping

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Introduction

Plastics are deeply integrated into daily life, and global production continues to grow across a wide range of sectors, particularly packaging and other short-lived applications such as disposable containers. Their low cost, low density, and high chemical and mechanical stability offer clear advantages over many alternative materials. However, these same attributes also limit degradation after disposal, contributing to the long-term persistence and accumulation of plastic waste in landfills and the broader environment [1].

Polystyrene (PS) is the fourth most manufactured plastic globally [2]. PS is considered well-suited to chemical recycling because it undergoes comparatively simple thermal decomposition, enabling high liquid yields under appropriate operating conditions [3]. Hydrothermal processing (HTP) has emerged as a promising route for recovering energy from plastic waste. Compared with pyrolysis, HTP can deliver higher oil yields, plausibly because the hydrothermal medium improves mass transfer and diffusivity within the reacting phase. This transport advantage may also allow operation at comparatively milder conditions, depending on the feedstock and process configuration [4]. Several studies have identified hydrothermal processing (HTP) as a promising route for converting polystyrene (PS) into a diverse portfolio of chemical products. Gentilcore *et al*. reported a low-pressure HTP strategy that, under their experimental conditions, delivered 96–99% oil yield while limiting char formation to 1–2% at operating pressures of 2–3 MPa [5].

Methodology

The experimentally measured oil composition from the hydrothermal processing (HTP) setup published by Gentilcore *et al*. [5] was adopted as the basis for the present modelling. The oil is dominated by monomeric aromatics (C_7–C_9), dimeric species (C_{10}–C_{17}), and heavier aromatics (C_{16}–C_{20+}). Based on the generated oil, this work proposes a conceptual process design that upgrades the oil to styrene, with marketable co-products such as toluene and benzene. In this vein, lighter hydrocarbons such as styrene and toluene can be recovered through conventional distillation.

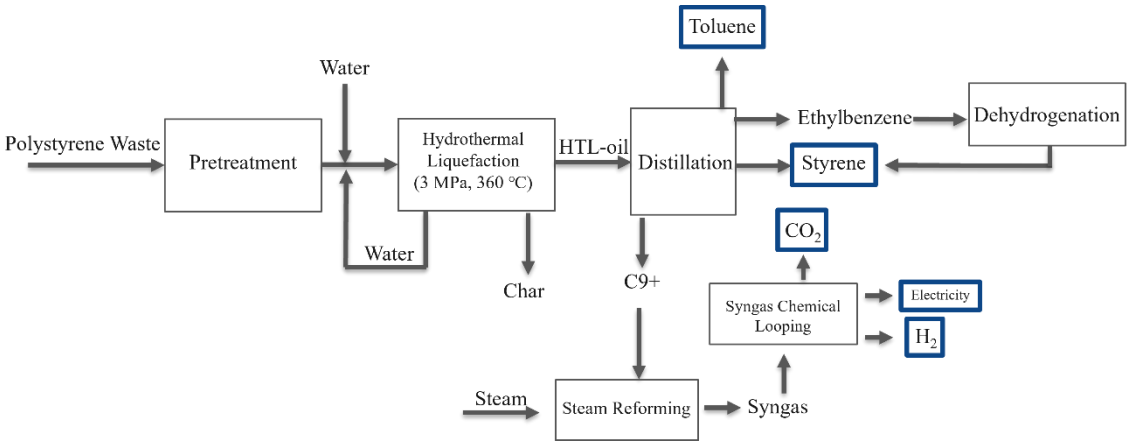


Figure 1. Block Flow Diagram of Polystyrene Waste Upcycling.

Ethylbenzene, which typically accounts for 15–20 wt% of the oil, is converted to styrene via dehydrogenation, thereby increasing the overall styrene yield. The remaining heavy fraction is routed to steam reforming for syngas production. The resulting syngas is subsequently utilized in a syngas chemical looping scheme to generate electricity and high-purity hydrogen while enabling in-process CO_2 capture. Figure 1 shows the block flow diagram of the proposed design for upcycling of polystyrene waste into value-added chemicals.

In the iron-based syngas chemical looping (SCL) concept, syngas is converted through cyclic redox reactions of an oxygen-carrier, while maintaining inherent separation of CO_2 and H_2 streams. Cleaned syngas is fed to the reducer, where the oxygen carrier is reduced, and the fuel is fully oxidized to a CO_2/H_2O-rich gas based on the following reactions [6]:

$$Fe_2O_3 + CO \rightarrow CO_2 + 2FeO \quad (1)$$
$$FeO + CO \rightarrow CO_2 + Fe \quad (2)$$
$$Fe_2O_3 + H_2 \rightarrow H_2O + 2FeO \quad (3)$$
$$FeO + H_2 \rightarrow H_2O + Fe \quad (4)$$
$$4Fe_2O_3 + 3CH_4 \rightarrow 3CO_2 + 6H_2O + 8Fe \quad (5)$$

The reduced solids are then contacted with steam in the oxidizer to produce a concentrated hydrogen stream via the steam–iron reaction:

$$Fe + H_2O \rightarrow FeO + H_2 \quad (6)$$
$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2 \quad (7)$$

Finally, the partially oxidized carrier is regenerated in the combustor with air, releasing heat for power generation:

$$4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3 + Heat \quad (8)$$

Figure 2 represents the block flow diagram of the syngas chemical looping process.

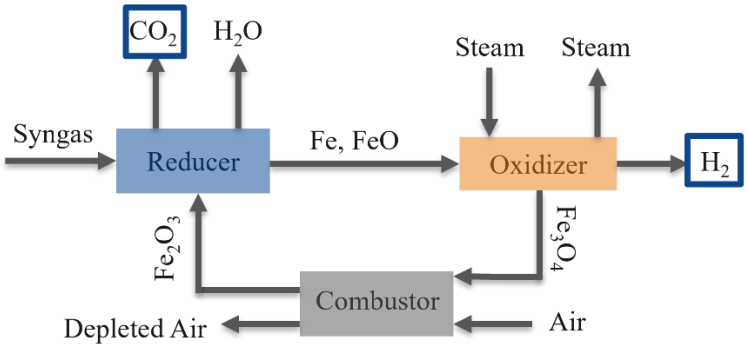


Figure 2. Overview of the chemical looping reactor system

Results and Discussion

An integrated process for upgrading polystyrene waste via low-pressure hydrothermal processing was modelled in Aspen Plus and linked to downstream separation, ethylbenzene dehydrogenation, steam reforming, and syngas chemical looping. Table 1 summarizes the principal mass flows at the inlet and outlet of the proposed process flow diagram and indicates that the concept warrants further assessment through techno-economic analysis, energy evaluation, and life cycle assessment.

Table 1. Input and output for the proposed design.

Variable	Final Value	Variable	Final Value
Input		**Output**	
Polystyrene Waste	12,000 kg/hr	Toluene	1603 kg/hr
Total Water	93,266 kg/hr	Benzene	10 kg/hr
Required Heat	196 MW	Styrene	1909 kg/hr
Required Cooling	105 MW	H_2	2057 kg/hr

It is revealed that at steady state, 12,000 kg/hr PS could yield about 1,603 kg/hr toluene, 1,909 kg/h styrene, and 2057 kg/hr H_2, with minor benzene, but the gross energy demand is still 196 MW and 105 MW for the required heating and cooling. The concept looks technically sound; the next step is heat integration and a full enviro-techno-economic assessment.

References

[1] Ryou H, Byun J, Bae J, Kim DK, Han J. Energy-efficient and environmentally friendly upcycling of waste plastic into fuels, chemicals, and polymer. Chemical Engineering Journal 2025;511:162256. https://doi.org/10.1016/j.cej.2025.162256.

[2] Zhang X, Qu X, Xie B, Gu S, Jiao T, Zhou H, et al. The influence of intrinsic minerals on volatiles releasing from coal pyrolysis in the presence of polystyrene. Journal of Analytical and Applied Pyrolysis 2026:107690. https://doi.org/10.1016/j.jaap.2026.107690.

[3] Monroy-Alonso A, Saldívar-Guerra E, Ramirez-Contreras JC, Cárdenas-Galindo MG, Díaz-Elizondo JA, Villarreal-Cárdenas LA, et al. Comparative study of thermal and catalytic pyrolysis of polystyrene at moderate temperatures. Effects of vacuum and the molecular weight of polystyrene on the selectivities of styrene and other aromatic products. Journal of Analytical and Applied Pyrolysis 2026;193:107469. https://doi.org/10.1016/j.jaap.2025.107469.

[4] Anonyuo S, Karunarathne S, Williams CL, Wheeler MC, Gunukula S. Co-depolymerization of lignin and plastic waste using hydrothermal liquefaction process. Journal of Analytical and Applied Pyrolysis 2026;193:107422. https://doi.org/10.1016/j.jaap.2025.107422.

[5] Gentilcore C, Jin K, Barzallo G, Vozka P, Wang N-HL. Low-pressure hydrothermal processing for conversion of polystyrene into oils. Journal of Environmental Chemical Engineering 2024;12:113836. https://doi.org/10.1016/j.jece.2024.113836.

[6] Tong A, Bayham S, Kathe MV, Zeng L, Luo S, Fan L-S. Iron-based syngas chemical looping process and coal-direct chemical looping process development at Ohio State University. Applied Energy 2014;113:1836–45. https://doi.org/10.1016/j.apenergy.2013.05.024.

Assessment of the Thermochemical Behavior of Paper Rejects

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Introduction

In Europe, 52.1 Mio. Mg of recovered paper are collected annually, of which approximately 46.1 Mio. Mg are reused in paper production. This corresponds to around 50 % of the total raw material input of the paper industry. The largest single stream is old corrugated cardboard (OCC), with about 30.7 Mio. Mg of recovered paper per year. [1]
In waste paper processing, OCC rejects are systematically generated as side streams from pulping, screening and sorting. In Germany, approximately 3 Mio. Mg of paper rejects per year are generated (EWC 03 03, 2021), of which more than 80 % are treated by thermal processes for energy recovery. [2].
Material utilization of these reject streams is challenging due to their heterogeneous composition. Paper-based packaging often consists of several functional material layers and contains fibers, plastics, polymer-based composite and barrier layers (e. g. paper/PE or paper/PE/Al laminations) as well as coatings. While the fibrous constituents can largely be recovered in the processing steps, polymeric and mineral components remain in the reject stream. This mixture of paper and plastics limits the mechanical recycling routes and makes thermochemical processes increasingly relevant as an alternative utilization option. Polyolefins in particular are a suitable feedstock for chemical recycling due to the absence of functional groups and heteroatoms and their favorable pyrolysis behavior. [3, 4, 5]

Materials and Methodology

For the investigations, 40 Mg of OCC paper reject were fractionated by Tomra Feedstock GmbH (together with the ANTS-Institute of RWTH Aachen University) using near-infrared (NIR)-sorting. From the unsorted feed material, polymer-rich target fractions were obtained. These fractions, as well as the feed material, were subjected to proximate and ultimate analysis and to thermogravimetric analysis (TGA) with Fourier-transform infrared (FTIR)-spectroscopy of the product gas.
The NIR sorting resulted in two polymer-rich fractions: a polyolefin (PO) fraction and a mixed polyolefin-polystyrene fraction. Polystyrene (PS) was intentionally captured to increase sorting yield. Both fractions were first investigated separately. For further upgrading trials, the fractions were then combined to provide a sufficient material quantity. The mixture was mechanically shredded and subjected to a second NIR sorting step in which 2D PO/PS films were specifically separated. The isolated 2D PO/PS fraction was subsequently agglomerated in a disc agglomerator.
All samples were dried and milled to < 0.5 mm. Thermogravimetric analysis was performed based on DIN 51005/51006 using a Linseis STA PT1600. Samples were heated under nitrogen at 10 K/min to 500 °C and then held isothermally for 30 min.
In parallel, continuous gas-phase analysis was carried out by FTIR (Gasmet CX4000), measuring CO, CO_2, hydrocarbons and other relevant components. The combination of TGA and FTIR allows assignment of the released gaseous decomposition products to the respective thermal decomposition ranges.

Results

The TGA curves in Fig. 1 show clear differences between the unsorted reject (Input) and the sorted polymer-rich fractions (PO, PO/PS). The first mass-loss step up to about 350 °C is much less pronounced for the polymer-rich fractions and is almost completely reduced for the additionally sorted and agglomerated PO/PS fraction. This is a consequence of the reduced fiber content. This is followed by the typical decomposition range of polyolefins between 350 and 450 °C [4, 6].

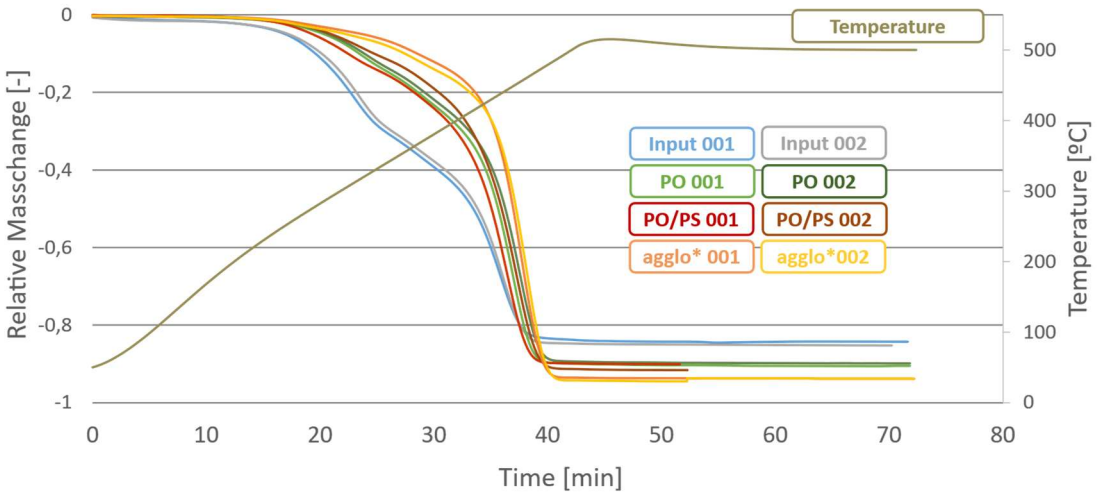


Figure 1. TGA of OCC Paper reject (Input), the sorted fractions and the additionally sorted and agglomerated fraction (agglo*) under N_2. (10 K/min to 500 °C, 30 min hold).

The corresponding FTIR gas-phase analysis (Fig. 2) of the feed material (Input) shows elevated CO_2 and CO concentrations and indications of nitrogen compounds in the region of the first mass-loss step (300-350 °C). In the temperature range of polyolefin decomposition (350-450 °C), CH_4, higher hydrocarbons and BTEX increase strongly. In addition, small amounts of styrene occur.

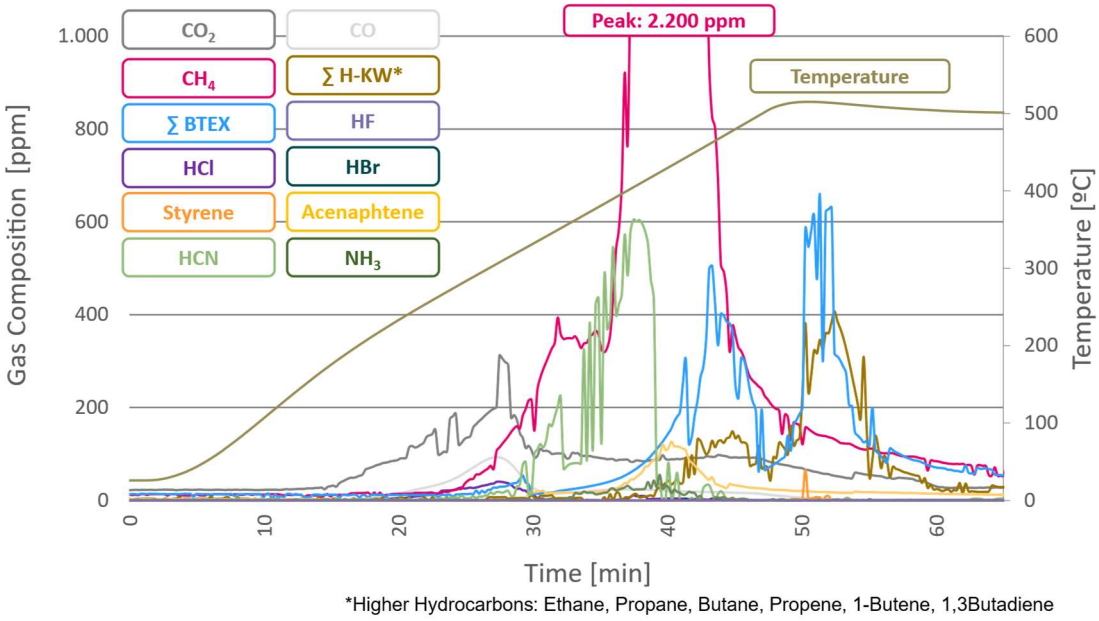


Figure 2. TGA-FTIR product gas analysis of sample Input 001.

The product gas composition of the PO/PS fraction (Fig. 3) confirms that the CO_2 and CO concentrations observed in Fig. 2 are related to the decomposition of paper-based constituents. These concentrations no longer occur in the product gas of the PO/PS fraction, while CH_4, higher hydrocarbons and aromatic compounds dominate. The thermal decomposition behavior of the fiber and polymer fractions differs fundamentally.
However, there are overlaps in certain temperature ranges so that complete separation is not possible. This should be investigated in more depth in order to evaluate the approach of a two-stage pyrolysis.

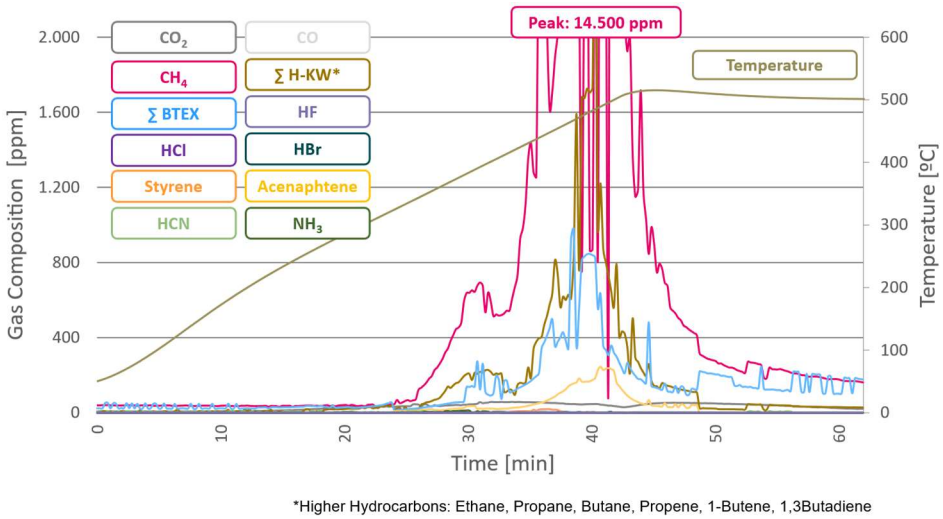


Figure 3. TGA-FTIR product gas analysis of sample agglo 001.

Conclusions and Outlook

The investigations confirm that, during pyrolysis, the paper rejects decompose in two distinct stages. Fiber-based constituents react predominantly at 250-350 °C, and polymer-based constituents at 350-450 °C. The ratio of these components has a decisive influence on the quality of thermochemical products. [5, 6, 7]

NIR sorting significantly reduces the paper-dominated mass loss and leads to a degradation behavior of polymer-rich fractions that is close to that of pure polyolefins. Using a two-stage pyrolysis, the products from fiber and polymer decomposition could be obtained separately.

Further work will investigate additional sorting options as well as batch and continuous pyrolysis experiments to assess pollutant transfer and the quality of larger condensate quantities. Based on this, aa suitable process concept for recycling OCC reject streams will be developed.

References

This abstract was originally published in German in:
Klüttermann, J., Kaphahn, I., Quicker, P.: *Bewertung des thermochemischen Verhaltens von Papierrejekten*
In: Deutsche Gesellschaft für Abfallwirtschaft e.V.; Hochschule Pforzheim - Institut für Industrial Ecology - Fachgebiet Ressourcenmanagement und Abfalltechnik (Hrsg.): 15. Wissenschaftskongress Kreislauf- und Ressourcenwirtschaft am 24. - 25. Februar 2026 an der Hochschule Pforzheim

[1] CEPI, Confederation of European Paper Industry: Cepi Key Statistics 2024. European pulp & paper industry. URL: https://www.cepi.org/cepi-key-statistics-2024/ [Stand: 06.12.2025]

[2] Statistisches Bundesamt: Abfallentsorgung: Deutschland, Jahre, Abfallarten. Erhebung der Abfallentsorgung in Deutschland. EAV 03 03. URL: https://www-genesis.destatis.de/genesis/online [Stand: 03.10.2025]

[3] Quicker, P. und Seitz, M.: Abschätzung der Potenziale und Bewertung der Techniken des thermochemischen Kunststoffrecyclings. Umweltbundesamt. Dessau-Roßlau, Januar 2024

[4] Johansson, A.-C.; Selander, A.; Soleimanisalim, A. H.; Nordsvahn, R.; Shafaghat, H.: Chemical recycling of complex reject streams from the paper industry via thermal and catalytic pyrolysis. In: Journal of Analytical and Applied Pyrolysis. 181. Jg., 2024, S. 106572

[5] Quicker, P.; Weber, K. (Hrsg.): Biokohle. Herstellung, Eigenschaften und Verwendung von Biomassekarbonisaten. Wiesbaden, Heidelberg: Springer Vieweg, 2016

[6] Matsuzawa, Y.; Ayabe, M.; Nishino, J.: Acceleration of cellulose co-pyrolysis with polymer. In: Polymer Degradation and Stability. 71. Jg., 2001, Nr. 3, S. 435–444

[7] Burhenne, L.; Messmer, J.; Aicher, T.; Laborie, M.-P.: The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. In: Journal of Analytical and Applied Pyrolysis. 101. Jg., 2013, S. 177–184

Catalytic hydropyrolysis of low-density polyethylene in a fluidized bed with Ni-based catalysts

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Introduction

To reduce the pollution from plastic waste, there is a strong demand for improvements to plastic recycling efficiency. Catalytic hydropyrolysis at elevated temperatures and pressures can turn plastics into short-medium chain length hydrocarbons and remove heteroatoms, which can be used in various industrial applications, from fuels to raw materials for new plastics. Fluidized beds are suitable for such process for its capability to be operated continuously at high temperature and pressure [1]. **Figure 1** shows the conceptual vision of the process, with hydrogen supplied from electrolysis using renewable energy, catalytic hydropyrolysis of the plastic feed in a fluidized bed and downstream fixed bed reactor for further adjusting the product composition via hydrocracking/hydrogenation.

Ni-based hydrocracking catalysts are promising alternatives to noble-metal catalysts due to their much lower cost and considerable hydrogenation activity. This work investigated the outcome of the catalytic hydropyrolysis of LDPE, one of the most common plastic wastes [2], with different catalytic and non-catalytic bed materials and operating conditions. The aim was to maximize the yield of n-paraffinic condensable hydrocarbons (C_{4+} excluding wax) for fuel and input to steam crackers.

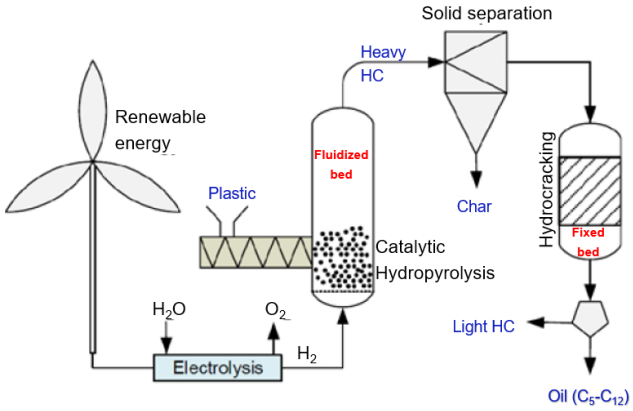


Figure 1. Schematic of catalytic hydropyrolysis of plastics coupled with green H_2 source.

Experimental

A laboratory scale fluidized bed system was used for initial hydropyrolysis and a downstream fixed bed reactor provided further hydrocracking of the heavy vapors and hydrogenation of olefins. The Ni-based catalysts employed were a commercial hydrocracking catalyst (HC) and two different Ni/Al_2O_3 catalysts (NAC) with 7 wt% and 20 wt% Ni loading, respectively. All catalysts were provided by Topsoe. To examine different extents of cracking, sand, catalyst and their mixtures were used in the fluid bed. The particles of sand and catalyst were crushed to sizes of 150-250 μm and 200-300 μm respectively, for good

fluidization. In the downstream fixed bed reactor, the catalyst was used as extrudates (diameter ~1 mm and length 1-6 mm). The feed was low-density polyethylene (250-600 µm) fed by a screw feeder and pneumatically transported into the fluidized bed reactor by a gas stream composed of 70 vol% H_2 and 30 vol% N_2. The feed entered the reactor above the fluidized bed to avoid plugging of the feed tube and cooling of the bed by the cold feed gas. Experiments were operated at 11 or 15 bars at temperatures of 530 °C - 580 °C (fluidized bed) and 270 °C - 330 °C (fixed bed) for 3-6 hours. The liquid products were condensed stepwise from ambient temperature to −30 °C. Gas products were measured online by a GC-TCD+FID analyzer and condensed oils were collected and analyzed by GC-VUV.

Results and discussions

To achieve a high yield and a high quality in the liquid product, different process conditions were tested as listed in **Table 1**. Single-step hydropyrolysis with pure sand (exp. 1) or pure catalyst (exp. 2) in the fluid bed led to either under-cracking, with a significant fraction of wax as the product, or over-cracking and hydrogenation forming exclusively methane, respectively. Applying a sand and catalyst mixture (5-10 wt% catalyst) in the fluid bed and secondary hydrocracking in the fixed bed (exp. 4 & 5) provided a reasonable extent of cracking leading to product distributions with liquid yield up to 33 wt% and total C_{4+} hydrocarbons (excluding wax) up to 80 wt%. Compared with the other catalysts, the 20-NAC was too reactive under fluid bed temperatures and thus is only suggested for the fixed bed. Therefore in exp. 3, there was only sand in the fluid bed. It led to a 22 wt% liquid yield but lowered the mass balance to 71 wt% because inadequate initial cracking caused condensation before the fixed bed.

Table 1. Polyethylene hydropyrolysis experiments and results.

Exp:	1	2	3	4	5
Fluid bed material	Sand	20-NAC	Sand	95 % sand 5% HC	90% sand 10% 7-NAC
Fluid bed temperature (°C)	580	530	580	530	580
Fixed bed material	/	/	20-NAC	HC	7-NAC
Fixed bed temperature (°C)	/	/	270	300	310
Pressure (barg)	15	15	11	11	11
Total flow (Nl/min)	75	80	70	70	70
PE consumption (g)	116	216	126	286	288
Yields (wt% of daf feed)					
Gas	27.8	101.8	45.3	54.9	38.3
Liquid	3.0	0	22.8	33.5	33.2
Wax	38.4*	0	3.0*	3.0	17
Mass balance	69.2	101.8	71.1	91.4	88.5
Gases yields					
Methane	1.0	101.8	9.8	0.5	9.3
Ethane	1.9	0	5.1	1.1	6.4
Propane	1.5	0	5.4	5.6	5.0
Butane	0.7	0	5.2	13.3	4.2
Pentane	0.2	0	4.4	12.9	3.4
C_{6+}	15.0	0	15.4	21.5	10.0
C_{2-5} Olefins	7.6	0	0	0	0
Liquid & C_{4+}	21.2	0	47.8	81.2	50.8

*: wax yields were significantly underestimated due to condensation in the tubing before the fixed bed

The catalyst type had significant impact on the liquid hydrocarbon composition as shown in **Figure 2**. The commercial hydrocracking catalyst (exp. 4) led to a high fraction of *iso*-paraffinic hydrocarbons (over 60 wt%) with further 10-20% of each of *n*-paraffins, naphthenes and aromatics, which meets the hydrocarbon composition requirement of jet fuel. According to boiling point analysis, roughly 70 wt% of the oil was within C_8-C_{16} (125 ºC - 290 ºC), the jet fuel range. In comparison, the 7 wt.% Ni/Al_2O_3 catalysts favored the formation of n-paraffins. Thus, *n*-paraffins made up over 55 wt% of the liquid, while the *iso*-paraffins were reduced to 23 wt% and aromatics were about 12 wt%. However, due to insufficient cracking in the fixed bed, only 31 wt% of the oil was within C_5-C_{12} (< 220 ºC) and can be used directly in steam crackers.

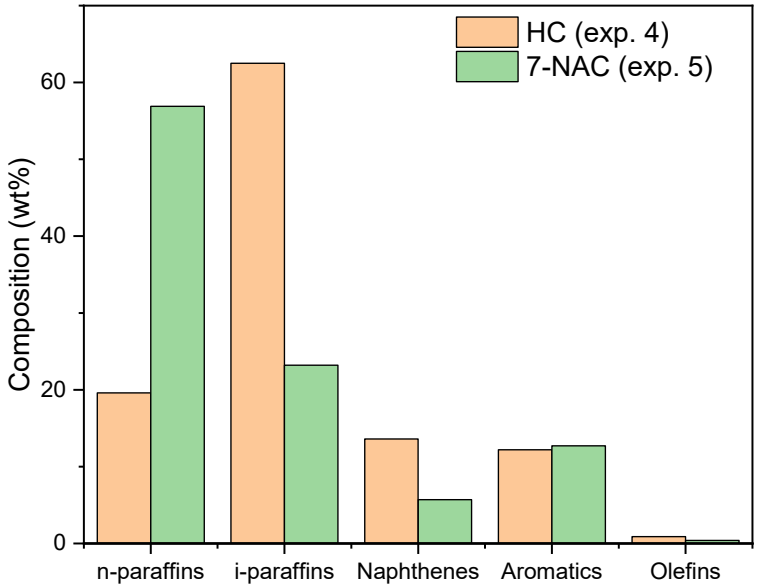


Figure 2. Relative hydrocarbon distribution in liquid products when using the hydrocracking catalyst (exp. 4) and the 7%Ni/Al_2O_3 catalyst (exp. 5).

Conclusions

This work proves the feasibility of recycling polyethylene to a variety of hydrocarbons through catalytic hydropyrolysis by using a fluidized bed with a downstream fixed bed reactor. By using the staged hydropyrolysis process, the liquid hydrocarbon yield was significantly improved under the tested conditions. Ni-based catalysts showed good cracking and hydrogenation activity and especially the Ni/Al_2O_3 catalysts favored the production of n-paraffins suitable as feed for steam crackers.

References

[1] Al-Salem, S. M., Antelava, A., Constantinou, A., Manos, G., Dutta A.: *A Review on Thermal and Catalytic Pyrolysis of Plastic Solid Waste (PSW)*. J. Environ. Manage, 197 (1408), 177–198, 2017.

[2] Musa, A., Jaseer, E. A., Barman, S., Garcia, N.: *Review on Catalytic Depolymerization of Polyolefin Waste by Hydrogenolysis: State-of-the-Art and Outlook*. Energy and Fuels, 38 (3), 1676–1691, 2024.

Effects of High Hydrostatic Pressure Treatment on Paramylon Nano-Fibrillation and The Resultant Oil Gelation Behavior

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Background

The demand for oil gelling agents has been expanding across a wide range of industrial fields, including cosmetics, pharmaceuticals, paints, and spilled heavy oil recovery agents. These agents play a vital role in converting liquid oils into semi-solid (gel) states, thereby improving storage stability and functionality. Currently, mainstream low-molecular-weight gelling agents, such as 12-hydroxystearic acid, require heating and cooling processes for gelation. This heating process poses risks of thermal denaturation of heat-sensitive active ingredients and leads to increased energy costs. Furthermore, the limitation on the polarity of compatible solvents is also a challenge, creating a strong need for the development of novel gelling agents that are compatible with a wide range of solvents without requiring heating.

In this study, we focused on paramylon (β-1,3-glucan) derived from the microalga *Euglena gracilis*. Paramylon is a structural isomer of cellulose nanofibers (CNF), which are already advancing in industrial applications. Due to its distinct triple-helical structure[1)], it is suggested that paramylon has the potential to form physical gels in organic solvents. Unlike the rigid crystalline network of CNF, the flexible helical structure of paramylon holds potential as a novel functional material; however, natural paramylon granules possess high crystallinity and low dispersibility, preventing the full realization of their functions.

Nanofibrillation (PNF conversion) is effective for increasing the specific surface area to resolve this issue[2)]; however, conventional water jet (WJ) treatment alone often results in incomplete defibrillation due to the strong crystal structure. Therefore, in this study, we introduced "High Hydrostatic Pressure (HHP) processing" as a pretreatment for WJ. By impregnation water molecules into the granules and inducing swelling under a high pressure of 100 MPa, we aimed to enhance defibrillation efficiency, create uniform "high-functionality paramylon nanofibers (HHP-PNF)," and evaluate their gelation ability in organic solvents.

Methods

Paramylon granules extracted from *E. gracilis* powder were dispersed in pure water (1 wt%), subjected to ultrasonic treatment and stirring, and then sealed in a polyethylene pouch. HHP treatment was performed using a pressure device (HP-500, Shin Corporation) at 25°C and 100 MPa for 10 minutes. Subsequently, both the HHP-treated samples and untreated samples (Control) were subjected to defibrillation treatment using a wet micronization device (Star Burst minimo, Sugino Machine) under conditions of a discharge pressure of 200 MPa and 30 collision passes. The resulting suspension was freeze-dried and used for SEM observation and gelation tests.

The prepared nanofibers (PNF, HHP-PNF, CNF) and paramylon granules were added to jojoba oil, a vegetable oil, at predetermined concentrations (1.0 wt% and 1.5 wt%). After stirring for 1 minute with a vortex mixer, the sample bottles were inverted and left to stand (inversion test), and gelation was determined based on the presence or absence of fluidity in the contents.

Result and Discussion

SEM observations confirmed that HHP-PNF, which underwent combined HHP treatment, had finer fiber diameters and was more highly defibrillated compared to untreated PNF (Fig. 1). The morphology of HHP-PNF was extremely similar to that of CNF. This suggests that the water impregnation effect

induced by HHP treatment effectively relaxed the strong hydrogen bond network within the paramylon granules, thereby significantly reducing the resistance to defibrillation during the subsequent physical impact of WJ treatment.

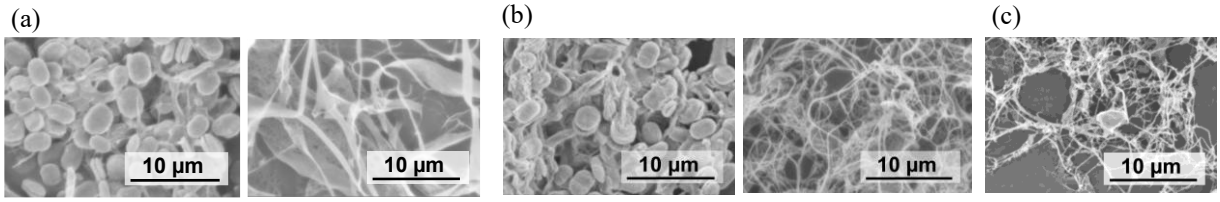


Fig. 1. SEM images of paramylon: (a) control (left: 0 passes, right: 30 passes), (b) high hydrostatic pressure –treated sample (left: 0 passes, right: 30 passes), and (c) CNF.

In the gelation test using jojoba oil, gelation was not confirmed with untreated paramylon granules, but all nanofibrillated samples (PNF, HHP-PNF, CNF) exhibited gelation (Fig. 2). Black arrows indicate the position of the gel. This is attributed to the increase in specific surface area and the improvement in network formation ability due to nanofibrillation. In particular, regarding the difference due to HHP treatment, while normal PNF showed concentration-dependent behavior, HHP-PNF lost fluidity and confirmed clear gelation even at a low concentration of 1.0 wt%. This is presumed to be because the fibers were refined by HHP treatment, allowing for the construction of a strong network that efficiently holds oil even with a small amount. This result indicates that HHP-PNF is promising as a highly efficient oil gelling agent that functions at low concentrations.

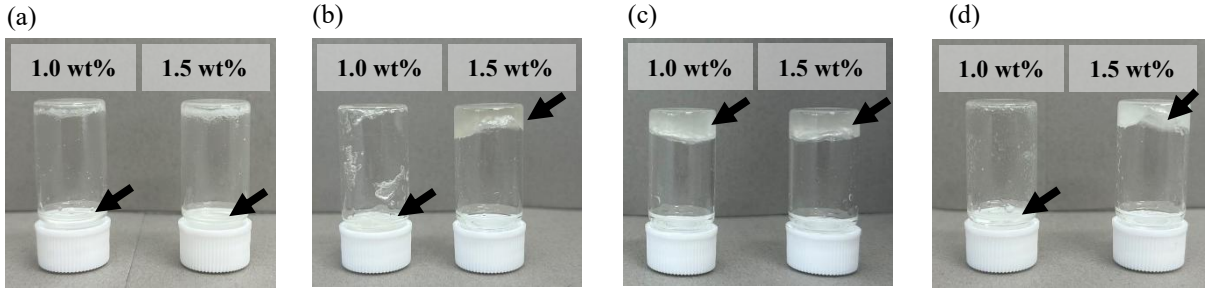


Fig. 2. Photographs of jojoba oil mixed with paramylon after standing for two weeks: (a) control (0 passes), (b) control (30 passes), (c) high hydrostatic pressure–treated paramylon, and (d) CNF.

Conclusion

This study revealed that introducing HHP treatment as a pretreatment for WJ promotes the nanofibrillation of paramylon, yielding a fine structure comparable to CNF. Furthermore, the obtained HHP-PNF possesses the ability to gel jojoba oil with only room-temperature stirring, without the need for heat dissolution, and demonstrated superiority in gelation ability especially at a low concentration (1.0 wt%). The high gelation ability for organic solvents demonstrated in this study suggests its potential application to low-polarity solvents and mixed solvent systems, which have been difficult to handle with conventional gelling agents. This technology is expected to become a key foundational technology not only for contributing to energy saving in manufacturing processes but also for the development of next-generation cosmetics and pharmaceutical formulations containing heat-sensitive functional ingredients.

References

[1] Kazutaka Miyatake: "Properties of Paramylon: Bio-particles Produced by Protozoa", Journal of the Society of Powder Technology, Vol. 32, No. 8, pp. 569-574, 1995.

[2] Takefumi NARITA, Juna KOIZUMI, Kasumi WADA, Ryo NAKADA, Ikuhiro TANIDA, Satoshi OSAWA: "Enhancing Dispersibility of Paramylon Nanofiber Suspensions through Water-Jet Defibrillation Treatment", material technology, Vol. 41, No. 5, pp.31-38, 2023.

Development of a Methodology for the Comparative Assessment of Chemical Recycling Routes

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Introduction

In Germany, approximately 5.6 million tonnes of plastic waste are generated annually [1]. A substantial fraction is mechanically recycled. However, the applicability of these recyclates is limited as contaminants often prevent their reuse in the original application areas (e.g. food packaging). In addition to mechanical recycling, chemical recycling processes like pyrolysis and gasification are promoted to obtain chemical feedstocks. These thermochemical conversion routes differ considerably with respect to reactor design, process operation, and waste pretreatment, which complicates environmental assessment and hinders meaningful comparability across technologies [2]. The type and purity of the plastic waste also directly influence the composition of the resulting pyrolysis oils.

Although numerous life cycle assessments of individual processes are available, they are often difficult to interpret and scarcely comparable due to differing system boundaries, assumptions, and databases. For this purpose, a methodology was developed that systematically captures and appropriately accounts for all relevant influencing factors required for the assessment. This methodology, which is essentially based on a mass and energy balance, can in principle be transferred to other process evaluations and used as a reference approach for more advanced analyses like the basket of products method [3].

Assessment

Within the study "Assessment of the potentials and evaluation of techniques of thermochemical plastic recycling" [3] conducted by the German Environment Agency (Umweltbundesamt), two practical processes each for liquefaction and for pyrolysis were investigated, using different plastic waste streams with in some cases strongly varying quality. All processes were quantified with respect to their yields on the basis of mass balances. However, the quality of the pyrolysis oils for further processing has not yet been taken into account. According to this, in addition, the quality of the input waste streams and of the produced products were analysed and regarded in a system expansion by a downstream upgrading chain. As a uniform target product, so-called high-value chemicals (HVCs) – including ethylene, propylene, butenes, butadiene, and aromatics – as well as by-products were defined. In this way, a consistent system boundary was established for all processes, thereby enabling a systematic comparison of the accounting routes of the investigated chemical recycling technologies. The assumptions regarding the downstream processing steps, such as hydrogenation of the pyrolysis oils and the use in naphtha cracking, are based on the current state of the art of petroleum-based chemistry [4-9]. The selected system boundary represents, within a gate-to-gate approach, a fictitious plant (**Figure 1**) that does not exist in reality or only exists in parts.

The fossil naphtha route from crude oil, including its upstream chain to HVCs, served as the reference pathway within this gate-to-gate framework. Consequently, the environmental assessment is carried out along the entire process chain – from plastic waste, without consideration of sorting and transport, to the target products (high-value chemicals, HVC). By-products are accounted for on the basis of their energy content and can be included in further analyses (e.g. the basket of product method) [10].

The basis is a simplified global mass, energy, and greenhouse gas balance resulting from the summation of all relevant subprocesses – including thermochemical conversion, hydrogenation, cracking, and downstream upgrading – referenced either to the input (e.g. plastic waste) or to the target product (HVC). This balance is implemented in a Python-based, parametrized computational model with a database-backed, standardized data structure for feedstock properties, process parameters, and subprocess inventories, enabling transparent generation, storage, and comparison of process chains under consistent assumptions.

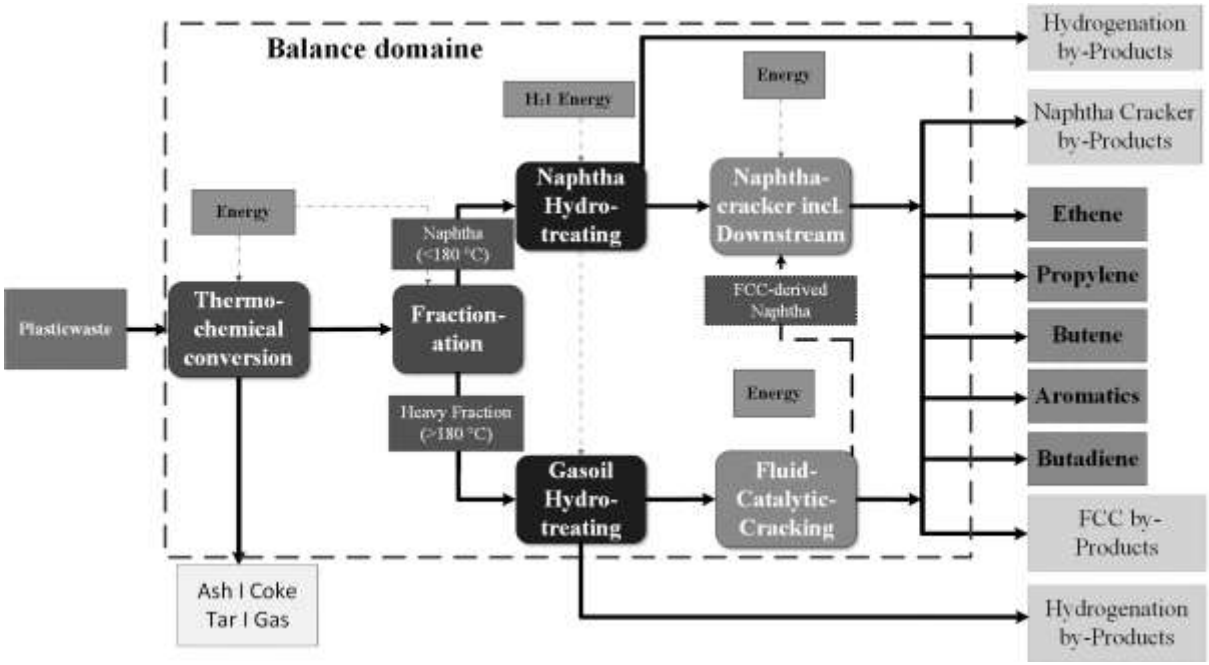


Figure 1. Balance domain for the chemical recycling of plastic waste including downstream processing.

Results

In this study, two liquefaction routes and two conventional pyrolysis routes were investigated. The liquefaction routes were operated using an oil tank, whereas the conventional pyrolysis routes followed standard operational regimes in a rotary kiln like reactor. The pyrolysis oil of all considered processes yields were between 77 % and 56 % relative to the input mass. The quality of the obtained oils was different quality, regarding the content of olefins, aromatics and contaminants and the molecular weight of the hydro carbons. According to the properties of the oil, the processes for downstream operation with usual yields was chosen and the hydrogen demand was calculated. On the basis of the analysed plastic waste streams, the resulting pyrolysis oils and the associated mass and energy balances – including the respective modelled downstream processes – the investigated process routes can be systematically and comparably evaluated.

Liquefaction I, with a pyrolysis oil yield of 77 %, exhibits the highest HVC yield at 50 %. Liquefaction II performs significantly worse, although its total oil yield is comparable to that of liquefaction I. The reduced performance of Liquefaction II results from increased losses associated with the high heavy oil fraction in the downstream processing using propene-enhanced Fluid-Catalytic Cracking (FCC). Consequently, the pyrolysis oil yield alone cannot be used as a suitable criterion for a comparative assessment. Pyrolysis I and II achieve HVC yields of around 40 %, whereas liquefaction II RDF (50 % pyrolysis oil yield), based on low-quality waste, attains only 32 %. At this point it has to be questioned whether the yield of HVC related to the waste feed is suitable for comparison, as the heating value of the waste stream were different.

When the energy content of the feedstocks is additionally considered on a lower heating value (LHV) basis, the differences between the processes become significantly smaller. Regardless of the material used – whether high-calorific, polyolefin-rich waste with an LHV of around 40 MJ kg^{-1} or the so-called refuse-derived fuel (RDF) with an LHV of around 28 MJ kg^{-1} (with an ash content of 18%) – the energy yield of HVC products based on the lower heating value is approximately 0.5 MJ_HVC MJ_feed^{-1} in relation to the lower heating value of the raw material. This indicates that the product-based energy yield of the investigated processes is comparable despite differences in feedstock quality.

Since the energy efficiencies of pyrolysis and liquefaction cannot yet be validated on the basis of industrial-scale data, they have to be derived from assumptions and literature values. In this context, effective heat integration appears to be indispensable for future implementations of these processes.

These parameters have a substantial influence on both the greenhouse gas emissions and the energy demand of the investigated process routes.

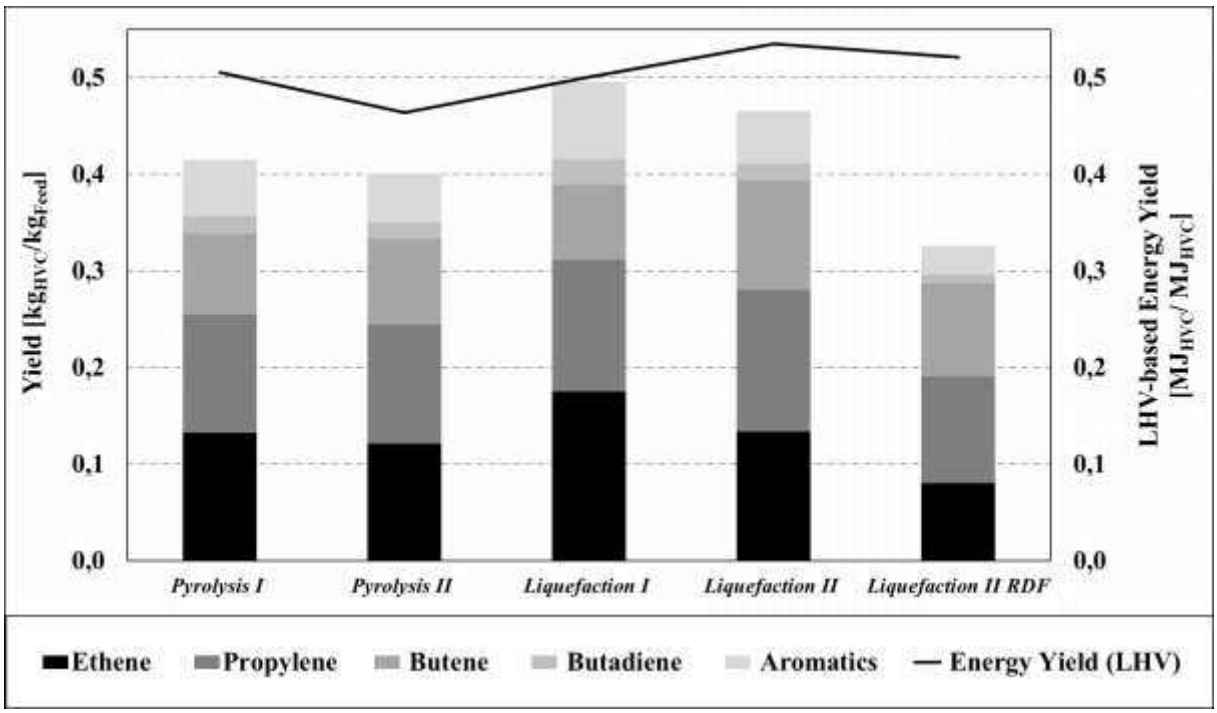


Figure 2. Pyrolysis oil yield for four different processes and plastic waste streams.

Conclusion

The computational model developed within the framework of this work provides the basis for an engineering-grounded reference methodology for the assessment of thermochemical conversion pathways of plastic waste. In this context, it enables the consistent accounting of new processes under uniform assumptions and is equally suitable for the comparative analysis of already published environmental assessments. On the basis of the model's uniform data structure and parameterization, external studies – provided that raw data are available – can be systematically reanalysed.

References

[1] Fischer, E., Hein, J.: *Stoffstrombild Kunststoffe in Deutschland 2023: Zahlen und Fakten zum Lebensweg von Kunststoffen*, Conversio Market & Strategy GmbH, Mainaschaff, 2024.

[2] Butler, E., Devlin, G., McDonnell, K.: *Waste polyolefins to liquid fuels via pyrolysis: Review of commercial state-of-the-art and recent laboratory research*, Waste and Biomass Valorization, 2(3), 227–255, 2011.

[3] Quicker, P., Seitz, M.: *Abschätzung der Potenziale und Bewertung der Techniken des thermochemischen Kunststoffrecyclings*, Umweltbundesamt, Dessau-Roßlau, 2024.

[4] Parkash, S.: *Refining Processes Handbook*, Gulf Professional Publishing, Burlington, 2003.

[5] Haydary, J.: *Chemical Process Design and Simulation: Aspen Plus and Aspen HYSYS Applications*, Wiley, Hoboken, 2019.

[6] Parkash, S.: *Petroleum Fuels Manufacturing Handbook: Including Specialty Products and Sustainable Manufacturing Techniques*, McGraw-Hill, New York, 2010.

[7] Zimmermann, H., Walzl, R.: Eth*ylene,* Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, 2000.

[8] Pascal, B., Chaugny, M., Sancho, L. D., Roudier, S.: *Best Available Techniques Reference Document for the Refining of Mineral Oil and Gas*, European Commission, Sevilla, 2015.

[9] Zhou, X., Zhai, Q., Chen, C., Yan, H., Chen, X., Zhao, H., Yang, C.: *Technoeconomic Analysis and Life Cycle Assessment of Five VGO Processing Pathways in China*, Energy & Fuels, 33(11), 12106–12120, 2019.

[10] Rothgänger, T., Schröter, S., Quicker, P., Seitz, M.: M*ethodenentwicklung zur vergleichenden Beurteilung technischer Verfahren anhand des chemischen Recyclings von Kunststoffabfällen*, Umweltinformationssysteme – Digitale Innovationen für eine nachhaltige Zukunft, Springer Vieweg, Wiesbaden, 2026.

Recycling of Waste-Derived Mattresses Foam through Pyrolysis

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Introduction

In Germany, approximately 8.27 million waste-derived mattresses are generated annually. Assuming an average mass of 20 kg per mattress, this corresponds to 165,400 tons of mattress waste per year, including approximately 16,540 tons of latex mattress foam [1]. Of particular interest is styrene–butadiene rubber (SBR), a sulfur-vulcanized copolymer [3]. At present, recycling of latex mattress foams is not established at an industrial scale. However, rising EU recycling targets for municipal waste necessitate a shift from energy recovery towards material recycling to improve resource efficiency [2]. Whether mechanical recycling is feasible seems unlikely due to the polymer's chemical structure, contamination, and its use in composite assemblies [4]. An alternative to thermal treatment is feedstock recycling aimed at replacing primary raw materials within a circular economy.

Pyrolysis may provide an option for recycling SBR-containing waste. In pyrolysis, the material is heated under an inert atmosphere, causing polymer chains to thermally fragment and release volatiles that form permanent gases and condensable hydrocarbons with oily-to-wax-like consistency. With optimized process control and sophisticated downstream upgrading, these condensates can be reintegrated into material use, substituting fossil feedstocks and supporting circularity.

Methodology

The compaction of waste-derived latex mattress foam aimed to produce stable agglomerates with good conveying properties. Bulk density was increased to improve transport and feeding into the pyrolysis unit while minimizing the fine fraction. To this end, pelletization and agglomeration processes were tested, and the resulting pellets and agglomerates were evaluated for conveyability and abrasion resistance. Without additives, neither agglomeration nor pelletization was feasible. For pelletization, waste-derived additives included polystyrene yogurt cups and polyethylene films obtained from lightweight packaging sorting. For agglomeration, additional additives were used, namely a sorting fraction derived from lightweight packaging waste consisting of expanded polystyrene (EPS) and polystyrene (PS), along with pure EPS from commercial waste. A key focus was to maximize the share of latex mattress foam in the agglomerates. The effect of the additives on chemical composition was assessed by proximate and elemental analysis.

The thermochemical decomposition behavior was first investigated by thermogravimetric analysis (TGA). Based on the TGA results, initial conditions for batch-reactor scale-up experiments were defined. Batch experiments were performed in duplicate. For each run, 200 g of latex mattress foam was charged under nitrogen and heated at 5 $K \cdot min^{-1}$ to 450 °C. This temperature was maintained for 60 min and the resulting pyrolysis gases were directed through cold traps to separate condensable components. Gas-phase products were monitored by Fourier-transform infrared spectroscopy (FTIR). Condensates and char were collected for quantification and further analysis. The composition of the pyrolysis condensates was analyzed by gas chromatography–mass spectrometry (GC–MS). The char was characterized by proximate, elemental analysis and by X-ray fluorescence (XRF) to identify constituents with recovery potential.

Results and Discussion

During compaction of latex mattress foam, agglomeration showed a more stable process than pelletization and produced agglomerates with better stability and conveying properties. Therefore, only agglomerates are considered in the following. In total, 18 agglomerate formulations were produced using different mixing ratios of additive and latex mattress foam. Agglomerate 17 had the highest content and comprised 60 wt% latex mattress foam, 20 wt% EPS from commercial waste, and 20 wt% of the EPS/PS sorting fraction from lightweight packaging waste. Figure 1 compares the elemental and proximate analysis of the latex mattress foam, the additive EPS/PS and Agglomerate 17.

Overall, agglomeration and additive incorporation caused only minor changes in the chemical composition of the latex mattress foam compared with Agglomerate 17.

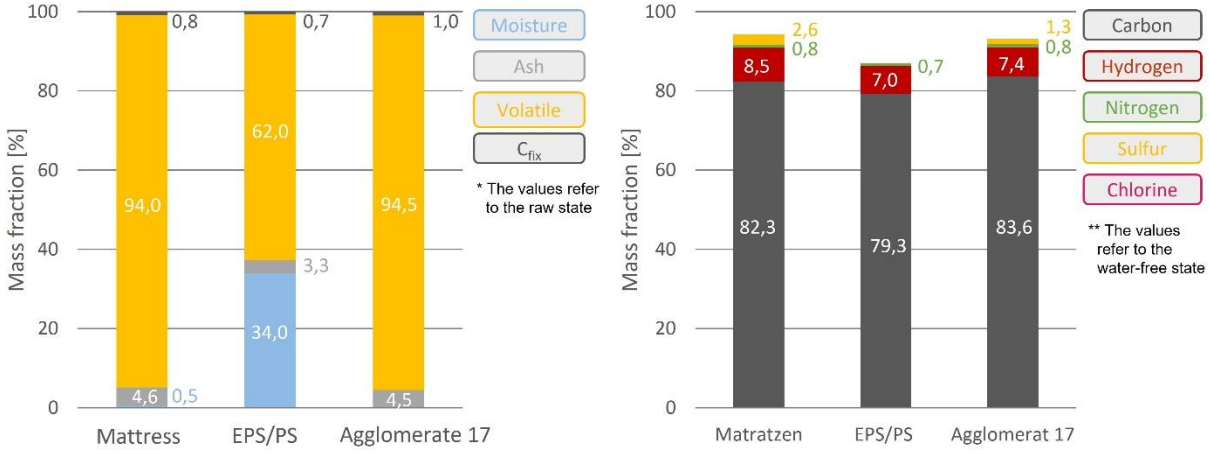


Figure 1. Comparison of proximate and elemental analysis of latex mattress foam, the EPS/PS additive, and Agglomerate 17.

Compaction of the latex mattress foam was only achievable with additives, because the elastomeric foam degrades upon heating instead of softening. The EPS/PS additive initially contained 34 wt% moisture, which was reduced as a result of the agglomeration process, likely due to heat generation and friction. In subsequent work, pyrolysis experiments will be conducted using Agglomerate 17. For continuous operation, agglomeration was selected to ensure reliable conveying and feeding behavior.

After the pyrolysis experiments, mass balances were established, which are shown in Figure 2.

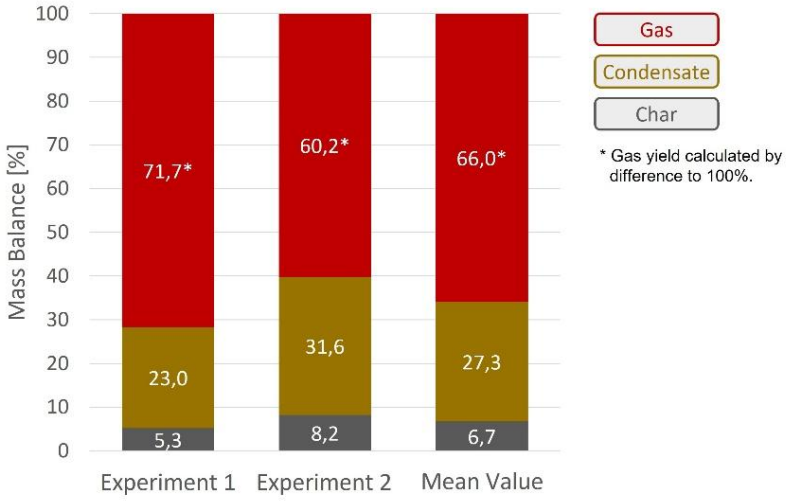


Figure 2: Mass balance for Experiments 1 and 2 and the corresponding mean values under the following conditions: 200 g feed, target temperature 450 °C, holding time 60 min.

Mean yields of 6.7 wt% char, 27.3 wt% condensate, and 66.0 wt% permanent gas were determined. The permanent-gas fraction was calculated by difference to 100%. Given the variability between the two experiments, additional runs at different temperatures and holding times are planned to optimize the operating parameters. GC–MS analysis of the condensate identified styrene, limonene, and ethylbenzene among other compounds. The char contained 25.25 wt% zinc. The initial batch-reactor pyrolysis experiments yielded measurable product fractions. However, the analysis of the output materials requires further verification. Potential utilization pathways for the condensate include use as steam-cracker feedstock, processing in an entrained-flow gasifier, or recovery of selected compounds. In the longer term, the char will undergo further treatment to obtain defined substances (e.g., zinc) and to identify and evaluate suitable utilization routes.

Conclusions and Outlook

The investigations show that latex mattress foam can be compacted using additives, improving handling for transport and process feeding. In addition, initial batch-reactor pyrolysis experiments yielded condensate in the range of 20–30%. The resulting product fractions were chemically characterized, enabling initial conclusions on the product spectrum and potential utilization options. The next step will focus on scaling up the pyrolysis process. For this purpose, operating parameters will be further optimized to achieve higher condensate yields and the agglomerate will be pyrolyzed in the batch reactor in comparison with the latex mattress foam. Subsequently, the process chain will be transferred to continuous pilot-scale operation to validate the results under practically relevant conditions and to establish the basis for later implementation at larger scale.

References

This abstract was originally published in German in:

Clemens, L., Kaphahn, I., Quicker, P.: *Chemisches Recycling von abfallstämmigem Matratzenschaum durch Pyrolyse.* In: Deutsche Gesellschaft für Abfallwirtschaft e.V.; Hochschule Pforzheim - Institut für Industrial Ecology - Fachgebiet Ressourcenmanagement und Abfalltechnik (Hrsg.): 15. Wissenschaftskongress Kreislauf- und Ressourcenwirtschaft am 24. - 25. Februar 2026 an der Hochschule Pforzheim

[1] Dornbusch, H.-J., Hannes, L., Santjer, M., Böhm, C., Wüst, S., Zwisele, B., Kern, M., Siepenkothen, H.-J.: *Vergleichende Analyse von Siedlungsrestabfällen aus repräsentativen Regionen in Deutschland zur Bestimmung des Anteils an Problemstoffen und verwertbaren Materialien*; Abschlussbericht, Umweltbundesamt, 2020.

[2] Europäisches Parlament: *Richtlinie (EU) 2018/ des Europäischen Parlaments und des Rates vom 30. Mai 2018 zur Änderung der Richtlinie 2008/98/EG über Abfälle*.

[3] Garrido, M.A., Font, R., Conesa, J.A.: *Thermochemical study of the briquetting process of mattress foams*, Fuel Processing Technology,159:88–95, 2017.

[4] Zanchet, A., Sousa F.D.B.: *Elastomeric Composites Containing SBR Industrial Scraps Devulcanized by Microwaves: Raw Material, Not a Trash*, Recycling, 5(1):3, 2020.

Influence of metal-modified ZSM5 on pyrolysis and in-line catalytic cracking of HDPE

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Introduction

Plastics have become an essential product of the current lifestyle, because of their excellent properties and versatility. Consequently, annual plastic waste world generation has increased and will continue to increase in the future. For this reason, the management or recovery of this waste is indispensable. Chemical recycling, and especially catalytic pyrolysis, is a promising option to recover high value-added products from plastics. The use of catalyst is necessary to increase the selectivity of these products, and ZSM5 zeolite has demonstrated a great selectivity to olefins and aromatics. In addition, the modification of zeolite through the addition of metal can enhance catalyst selectivity [1-3].

In this work, three synthesized catalysts have been tested in the pyrolysis and in-line catalytic cracking of HDPE. The zeolites (ZSM5) were impregnated with different metals (Co, Mo, Ga) using wet impregnation method and they were agglomerated with alumina and bentonite. Specifically, the aim of this work is to evaluate the influence of catalyst type has on the distribution of product yields at zero time on stream

Methodology

The plastic (HDPE) used in this study have been supplied by Dow Chemical Company (Tarragona, Spain) are the main characteristics are displayed in Table 1.

Table 1. Characteristics of the plastics used.

Plastic	Molecular weight (kg mol^{-1})	Polydispersity	HHV (MJ kg^{-1})	Ultimate analysis (wt %)	
				C	H
HDPE	46.2	2.89	43	85.7	14.3

The plastics pyrolysis step (500 ºC) has been carried out in a conical spouted bed reactor (CSBR), and the volatile stream has been fed in-line to a fixed bed catalytic reactor (550 ºC, 15 $g_{catalyst}$ min $g^{-1}_{plastic}$) at feed rate of 1 g min^{-1} and fluidizing agent rate of 2 L min^{-1}. The determination of product distribution at zero time has been carried out by gas chromatography. The scheme of the bench scale plant used is shown in Figure 1.

The solid feeding system consists of a vessel equipped with a vertical shaft connected to a piston placed below the plastic bed. This feeding system allows a continuous feeding of plastic between 0.2 and 5 g min^{-1}. The plastic is fed into the reactor by raising the piston at the same time as the system is vibrated by an electrical motor that facilitates the plastic dosing. In addition, the tube between the feeder and the reactor is cooled with tap water to prevent the plastic from melting before entering the reactor. A very small nitrogen flow rate introduced into the vessel stops the volatile stream entering the feeding system. Nitrogen has been used as spouting agent in the CSBR, and its flow rate is controlled by mass flow controller.

The CSBR is made of stainless steel and equipped with non-porous draft tube in order to optimize the spouting regime characteristics, improve its stability and reduce the spouting agent (nitrogen) requirements. This reactor is placed inside radiant oven. The HDPE pyrolysis at 500ºC led to a

continuous volatile stream composed of 67.0 wt% of waxes, 25.6 wt% of C_{12}–C_{21}, 5.9 wt% of C_5–C_{11} and 1.5 wt% of C_1–C_4. These compounds were transferred in line into the reforming reactor, and no solid residue remained in the pyrolysis reactor.

The products of the pyrolysis step were fed to fixed bed reactor, which is located inside an electric oven. Both reactors are located inside a forced convection oven heated at 300ºC in order to avoid the condensation of heavy compounds before their analysis.

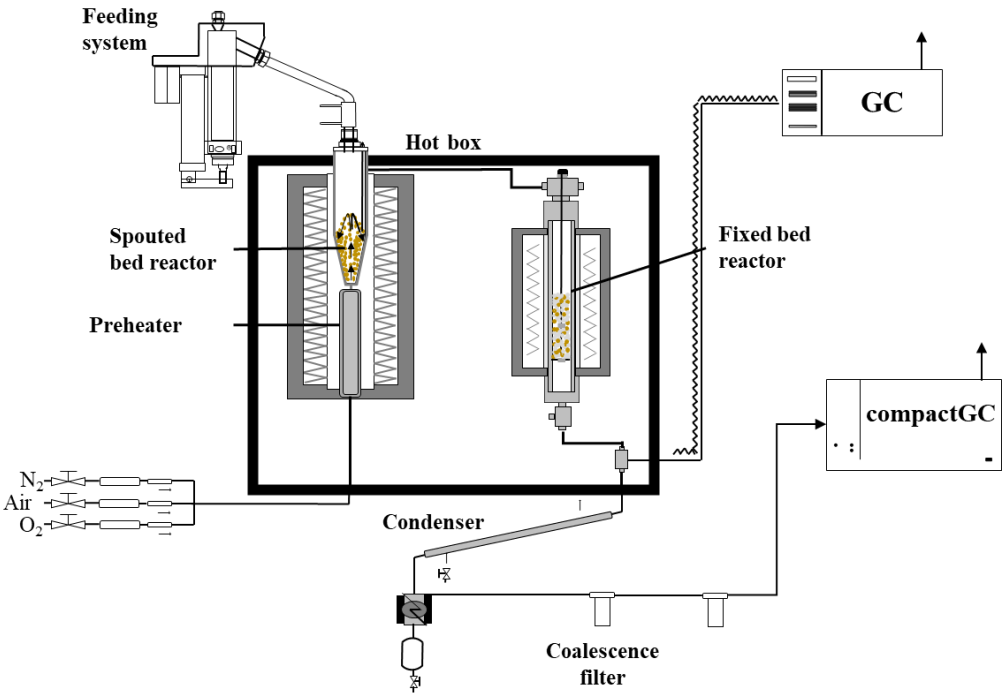


Figure 1. Scheme of the bench scale plant.

The gases leaving the fixed bed reactor circulate through a volatile condensation system consisting of a double-shell tube condenser cooled with tap water and coalescence filters that ensure the cleaning of permanent gases before they are introduced into the chromatograph.

The product stream leaving the FBR is analysed by an on-line Agilent 8890 GC equipped with a flame ionization detector (FID) and a HP PONA column. The sample is conducted to the GC by thermostated line at 230 ºC to avoid condensation of some compounds. Moreover, the stream of permanent gases was collected downstream in a Tedlar gas sample bag and analysed in G.A.S. Compact GC4.0 provided with two detectors (FID and TCD) and three columns.

Results

Figure 2 shows the product yields obtained in the HDPE pyrolysis and in-line cracking process using different metal-modified ZSM5 catalysts. As observed, Ga loading has a great impact on product distribution, reducing the light olefins yields while increasing that of BTX comparing to ZSM5. In fact, the light olefin yield obtained with ZSM5 was 80 % while using Ga-ZSM5 catalyst the yield was 52 %. The other two catalysts (Co-ZSM5 and Mo-ZSM5) have a similar light olefins yield of ZSM5, with a yield of 77.6 % and 79.5 %, respectively. However, the maximum yield of BTX was obtained with Ga-ZSM5, whose yield was 35.9 %. This is a significant improve of BTX yield comparing with 9.6 % obtained with non-modified zeolite. Conversely, the Co and Mo loading in ZSM5 catalysts did not significantly influence the BTX yields (around 12 % in both catalysts). In addition, Ga-ZSM5 improve a little the yield of light alkanes with a value of 6.2 %.

Regarding the gas fraction, propylene is the main compound in all catalyst, with a minimum of 25.4 % (Ga-ZSM5) and a maximum of 42.6 % (ZSM5). The main compound in the liquid fraction was C_7 due to the toluene yield, as toluene is the main aromatic in the product stream.

In view of these results, it can be concluded that, all catalysts have shown a great capacity for obtaining high value products, such as light olefins and aromatics, with a low yield of C_{12+} hydrocarbons. Specifically, ZSM5 impregnated with Ga is the best catalyst for producing BTX, whereas non-impregnated zeolite is better for producing light olefins. Finally, the loading of Co and Mo into ZSM5 does not significantly affect the distribution of product yields compared to the bulk ZSM5 catalyst.

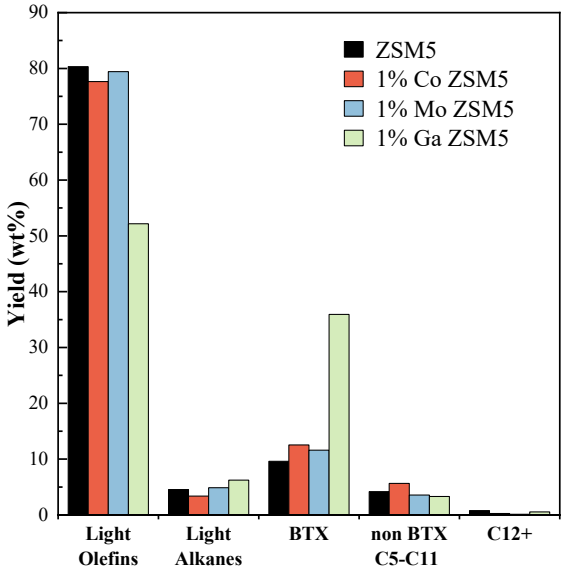


Figure 2. Effect of metal modification over product distribution the pyrolysis and in-line catalytic cracking of HDPE.

References

[1] Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., Olazar, M.: *Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review*, Renewable and Sustainable Energy Reviews, 73, 346-368, 2017.

[2] Artetxe, M., Lopez, G., Amutio, M., Elordi, G., Bilbao, J., Olazar, M.: *Light olefins from HDPE cracking in a two-step thermal and catalytic process*, Chemical Engineering Journal, 207, 27-34, 2012.

[3] Yuan, H., Li, C., Shan, R., Zhang, J., Wu, Y., Chen, Y.: *Recent developments on the zeolites catalyzed polyolefin plastics pyrolysis*, Fuel Processing Technology, 238, 107531, 2022.

Evaluation of the catalyst-to-adsorbent ratio influence on waste plastic pyrolysis and in-line sorption enhanced steam reforming

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Introduction

More than 350 million tonnes of plastic waste are generated worldwide every year, accounting for a significant fraction of solid waste, with a continuously increasing generation trend despite the implementation of policies aimed at its progressive reduction. In this context, both industry and academia have intensified their efforts to mitigate the environmental impact of this residue, with energy valorization emerging as a promising strategy. There are different routes available for hydrogen (H_2) production as an energy vector, including electrochemical, photocatalytic, chemical and biological processes, among which thermochemical technologies are considered the most mature which includes processes like gasification, pyrolysis, and pyrolysis coupled with in-line steam reforming (SR), the latter constituting the focus of the present work [1].

This study is part of the ongoing work of the Catalytic Processes & Waste Valorization (CPWV) research group, which consists of a first stage of continuous pyrolysis of waste plastics followed by an in-line reforming stage of the volatile compounds generated during pyrolysis [2]. One of the main drawbacks of this process lies in the high energy demand associated with elevated operating temperatures, as well as the significant carbon dioxide (CO_2) content in the resulting product gas. To optimize the process, this work proposes the integration of in situ CO_2 capture during the SR stage, this requires an adsorbent that can withstand the conditions of reforming while being compatible with the Ni-Al_2O_3-based catalyst, to prevent partial catalyst deactivation. Additionally, the adsorbent must provide sufficient CO_2 uptake to maintain an extended effective capture period. In this context, dolomite is identified as a suitable candidate due to its availability, low cost, and compatibility with the process requirements [3]. Moreover, the CO_2 capture promotes the displacement of the water–gas shift reaction, resulting in a product gas with higher H_2 purity and concentration compared to SR, particularly during periods when this component is fully or partially absent in the outlet stream. Therefore, the objective of this work is to compare the gas streams obtained from conventional SR and steam reforming with *in situ* CO_2 capture, as well as to investigate the effect of the catalyst-to-adsorbent ratio in the fixed-bed reforming reactor on conversion and product gas composition.

Experimental

The experiments were carried out in a bench-scale plant previously and successfully used by the research group CPWV. The experimental setup consists of two main stages, as schematically shown in **Figure 1**. In the first stage, waste plastic pyrolysis is carried out at 550°C in a conical spouted bed reactor (CSBR). The plastic feedstock, in this case is HDPE (Dow Chemical) continuously fed into the reactor using a piston dosing tube assisted by a vibration mechanism, ensuring a stable and continuous solid supply. Therefore, the pyrolysis reactor produces a continuous volatile stream composed of 60.9 wt% of waxes, 30 wt% of C_{12}–C_{21}, 6.7 wt% of C_5–C_{11} and 2.4 wt% of C_1–C_4. These volatile products are transferred in line into the reforming reactor, that operates with a fixed bed which contains Ni–Al_2O_3-based catalyst (Süd-Chemie) and dolomite as the CO_2 adsorbent (Calcinor), and no solid residue remained in the pyrolysis reactor. Here the steam reforming occurs at 650°C, yielding a product gas mainly composed of H_2, CO_2, CO, and CH_4. Both reactors are heated by independent electric furnaces

and are housed within a thermally insulated box that maintains the internal temperature above 250°C. Heat is distributed by forced convection using a fan, thereby preventing gas condensation inside the system.

A fraction of the product gas stream is diverted through a heat-traced line and analyzed using a gas chromatograph equipped with a flame ionization detector (GC-FID, TRACE 1300/1310, Thermo Fisher Scientific). Downstream of the system, the gas stream passes through a condenser to remove unreacted water, followed by a stainless-steel filter and a coalescing filter then the gas continues to an online gas analyzer (GenTwo V2.4) to monitor the evolution of CO_2, CO, and CH_4, and to a micro gas chromatograph (μGC, COMPACTGC 4.0) for the analysis of permanent gases and volatile compounds.

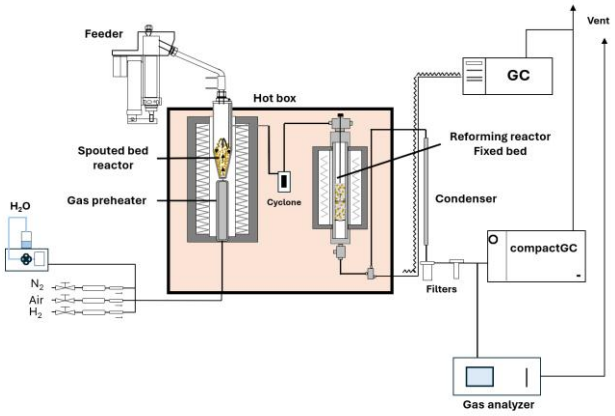


Figure 1. Experimental setup of the plant.

In order to fulfill the objective of this work, the experimental conditions summarized in **Table 1** were established and different adsorbent space times were evaluated.

Table 1. Experimental conditions

Parameter	Value
T_{pyro}(°C)	550
T_{reform}(°C)	650
Plastic fed (g/min)	0.5
$\tau_{catalyst}$ (g catalyst/g plastic)	40
$\tau_{adsorbent}$ (g adsorbent/g plastic)	40, 80, 120
S/P	3.5
$T_{preheater}$ (°C)	550

Results

After performing the experiments for the different catalyst-to-adsorbent ratios, the results shown in **Figure 2** were obtained. **Figure 2a** presents the yields of the main components of the reforming product gas for four experiments corresponding to zero time on stream. One of these experiments corresponds to SR while the remaining three were performed with Sorption Enhanced Steam Reforming (SESR) at different catalyst-to-adsorbent ratios. H_2 yields above 97% are achieved in all SESR experimental runs, representing a clear improvement compared to conventional SR (88% H_2). Moreover, the higher H_2 production (g H_2 per 100 g of plastic fed) further confirms the enhanced performance of SESR increasing 37.8wt% for SR to approximately 42.0 wt% in the three SESR tests. This is accompanied by the production of a purer gas stream due to a substantial reduction in the remaining major components, in particular, the CO_2 content is reduced by up to 94% compared to the value observed under conventional SR conditions.

Figure 2b shows the evolution of CO_2 concentration with time on stream for the different reactions, displaying values consistent with the theoretically determined adsorbent saturation time in all cases. Increasing the adsorbent leads to smoother saturation behavior. For instance, in the case of a catalyst-

to-adsorbent ratio of 1:3, the CO_2 concentration stabilizes after approximately 1 h of reaction, whereas for the 1:1 ratio, the maximum CO_2 concentration is reached after only 18 min. On the other hand, almost full conversion (> 99.9%) was observed for all the experimental runs except for the 1:3 ratio. Analysis at advanced reaction times revealed that complete conversion is not achieved under this condition, and volatile compounds start to appear in the reforming gas stream, reaching up to 0.1 % of light volatiles. This behavior may be attributed to partial catalyst deactivation caused by the higher CaO content in the adsorbent, which interacts with the active sites of the Ni catalyst, leading to the formation of inactive compounds and therefore reducing the catalyst's activity in reforming reactions. Thus, the 1:3 ratio exhibits better performance in terms of CO_2 capture, the 1:2 ratio was selected as the optimal operating condition as it provides a better compromise when the objective is to obtain a reforming gas stream with the highest possible H_2 purity.

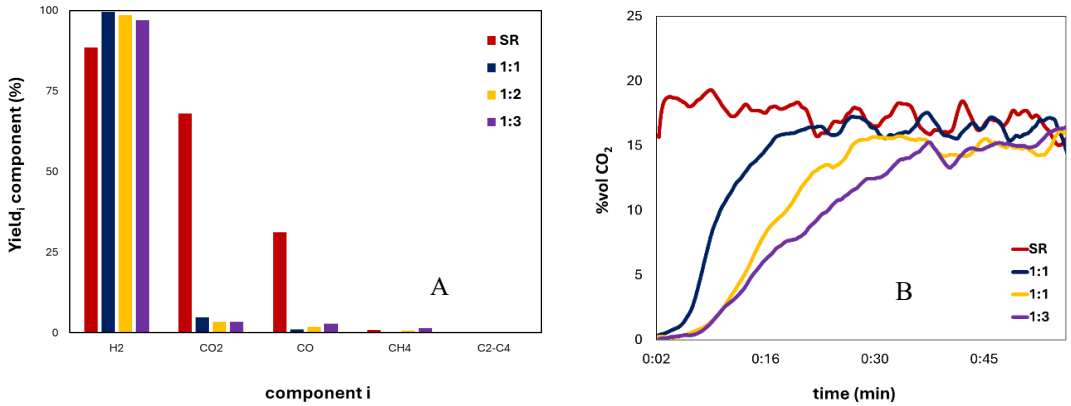


Figure 2. Effect of catalyst-to-adsorbent ratio on the reaction: (a) yields of H_2, CO_2, CO, CH_4 and hydrocarbons (C_2-C_4) at zero time on stream; and (b) evolution of the CO_2 concentration as a function of reaction time.

Conclusions

In this work, experiments were performed using different catalyst-to-adsorbent ratios, demonstrating that, in all cases, process performance is significantly improved compared to SR as an integration of *in situ* CO_2, resulting in a product gas with a higher H_2 concentration. However, increasing the adsorbent proportion is limited by the interaction between the catalyst and the CaO present in the adsorbent, which can lead to partial catalyst deactivation and negatively affect both conversion and product gas purity. Therefore, under the studied experimental conditions a catalyst-to-adsorbent ratio of 1:2 was identified as the most suitable option, providing the best balance between hydrogen concentration and purity at these conditions with H_2 yield of 98.52 %.

References

[1] Niu, F., Wu, Z., Chen, D., Huang, Y., Ordomsky, V., Khodakov, A.,Van Geem, K.: *State-of-the-art and perspectives of hydrogen generation from waste plastics*, Royal Society of Chemistry, 54(10), 4948-4972, 2025.

[2] Santamaria, L., Lopez, G., Fernandez, E., Cortazar, M., Arregi, A., Olazar, M., Bilbao, J.: *Progress on Catalyst Development for the Steam Reforming of Biomass and Waste Plastics Pyrolysis Volatiles: A Review*, Energy & Fuels, 35(21), 17051–17084, 2021.

[3] Comendador, P., Cortazar, M., Artetxe, M., Santamaria, L., Olazar, M., Lopez, G.: *Insights into the cyclic operation of sorption enhanced steam reforming of biomass pyrolysis volatiles: Role of contact mode and sorbent to catalyst ratio*, Fuel, 410, 2026.

Development of Antibacterial Protamine-Containing Cotton Fibers via High Hydrostatic Pressure or Cellulase Pretreatment

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Background

Hospital-acquired infections caused by drug-resistant bacteria are a serious medical issue that complicates the treatment of infectious diseases and leads to severe illness and death. Methicillin-resistant Staphylococcus aureus (MRSA), in particular, accounts for a large proportion of pathogens causing nosocomial infections, with contact transmission via linens contaminated with patient droplets being the primary route[1]. As a countermeasure, we attempted to create antimicrobial fibers using protamine (PRO), a naturally derived antimicrobial substance. PRO is extracted from salmon milt and is a strong basic peptide composed of more than two-thirds arginine. It possesses high safety, also used as a food additive, and has a lower environmental impact compared to existing metal-based antimicrobial agents. Furthermore, it exhibits high antimicrobial activity in the neutral to alkaline range where MRSA readily proliferates and is less prone to inducing resistant strains compared to antibiotics [2–3]. In this study, two strategies were investigated to stably incorporate PRO into cotton fibers: physical treatment using high hydrostatic pressure (HHP) to promote impregnation into the fiber interior, and chemical treatment using cellulase to modify the fiber surface. The objective was to clarify the effects of these treatments on the amount of PRO incorporated and the resulting antimicrobial properties.

Methods

Test fabrics were made of cotton fabric (Kanakin No. 3) conforming to JIS L 0803. They were immersed in 1,000 ppm and 5,000 ppm PRO solutions for 10 min and 24 h, respectively, at 30°C to adsorb PRO. To enhance adsorption capacity, methods were attempted: first, cellulase treatment to increase the number of adsorption sites (-OH groups), followed by 24 h immersion in PRO solution; second, HHP treatment at 100 MPa for 10 min to improve protamine impregnation into the fibers. Surface analysis by XPS analyzed the peak intensity of the nitrogen (N 1s) orbital, using the nitrogen content derived from proteins as an indicator to semi-quantify the adsorption amount. Antibacterial activity value was calculated based on the degree of bacterial growth inhibition before and after cultivation, using *Staphylococcus epidermidis* NBRC100911 (*S. epidermidis* NBRC100911), a BSL1 microorganism belonging to the same genus as MRSA, as a reference, following JIS L 1902.

Results and Discussion

Fig. 1 shows the XPS analysis results of PRO-adsorbed cotton fabrics subjected to various treatments, while Fig. 2 presents their antibacterial activity value. Fig. 1 indicates that PRO adsorption was confirmed even with untreated cotton fabric during immersion, but the adsorption amount increased under 10 min high-pressure immersion compared to untreated and cellulase-treated cotton fabric. The adsorption amount decreased in cellulase-treated cotton fabric compared to untreated fabric. This is thought to be due to sodium acetate, used as the buffer solution, remaining on the adsorption sites and inhibiting adsorption. Fig. 2 shows that cotton fabric without PRO showed no antibacterial activity value, whereas fabric immersed in a 5,000 ppm PRO solution exhibited strong antibacterial activity value with an antibacterial activity value of 3.8. Notably, cotton fabric immersed in a 5,000 ppm PRO solution and subjected to HHP treatment demonstrated strong antibacterial activity value with a value of 3.9, equivalent to that of untreated fabric after 24 h, despite only a 10 min treatment. The higher antibacterial activity value of 4.4 observed in cotton fabric treated with cellulase followed by immersion in a 5,000

ppm PRO solution compared to other conditions is thought to result from a synergistic effect due to the action of residual acetic acid and sodium acetate. The significant results achieved by applying HHP treatment are related to the adsorption model of protamine and cotton fabric. PRO, a cationic protein, is expected to form hydrogen bonds with the -OH groups of cotton fabric (cellulose) and adsorb. Under high-pressure conditions, PRO penetrates the fiber structure, facilitating hydrogen bond formation. This increased adsorption led to enhanced antibacterial activity value.

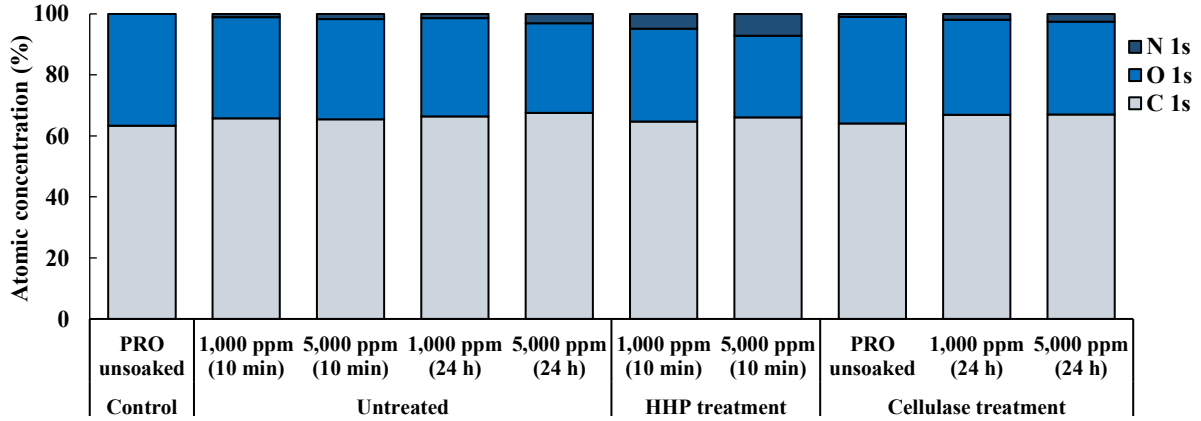


Fig. 1. XPS analysis results of PRO-adsorbed cotton fabrics subjected to various treatments.

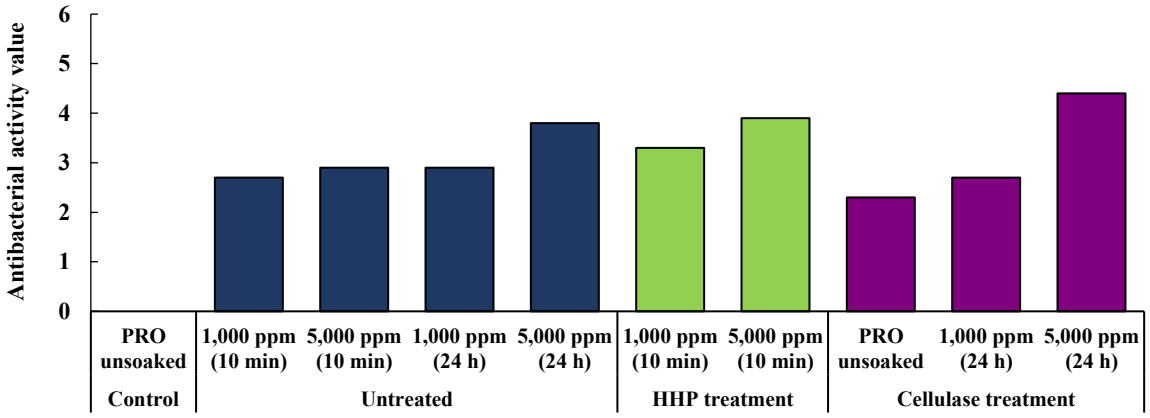


Fig. 2. Antibacterial activity value of PRO-adsorbed cotton fabrics subjected to various treatments.

Conclusion

This study demonstrated that incorporating PRO, a naturally derived antimicrobial substance, into cotton fabric enables the production of fibers with high antimicrobial properties. Specifically, using HHP treatment promoted PRO adsorption in a short processing time, achieving a high antimicrobial activity (3.9) equivalent to that of untreated fabric after 24 h immersion. This is thought to result from PRO penetrating into the fiber interior under high pressure conditions, promoting the formation of hydrogen bonds with cellulose. Therefore, the combined use of HHP treatment and PRO is expected to be an effective, environmentally friendly, and efficient method for producing antimicrobial fibers. Future studies will include evaluating wash resistance for practical applications and observing the surface modification state.

References

[1] Takamine, M., Huruse, K.: *Bactelial Contamination of Laundly in Hospital: Actual State of the Contamination and Preventive Measures Against it*, Journal of the Japanese Academy of Nursing Science, 14(1), 48-53, 1994.

[2] Kazuhiko, N.: *Antibacterial properties of Protamine and its applications*, Journal of antibacterial and antifungal agents, 23(10), 635-642, 1995.

[3] Zasloff, M.: Antimicrobial peptides of multicellular organisms, Nature, 415(6870), 389-395, 2002.

Film Formation and Evaluation of γ-Zirconium Phosphate/Gemini-Type Quaternary Ammonium Salt Complexes

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Background and aims

Since the 1990s, hospital-acquired infections, food poisoning incidents, and microbial damage have garnered significant attention. Demand for antimicrobial-treated products has also surged, and antimicrobial processing has been applied to plastic products.

Gemini-type quaternary ammonium salts (QAS), which possess a structure where two monomeric surfactant molecules are linked by a spacer at or near the hydrophilic group, exhibit high antibacterial activity and a broad antimicrobial spectrum[1)]. However, QAS are water-soluble, causing them to lose their antibacterial effect under running water and limiting their applications due to low heat resistance.

To address the above issues, we focused on the inorganic layered compound γ-zirconium phosphate (γ-ZrP). γ-ZrP exhibits intercalation properties, enabling reversible reactions where cations are exchanged and adsorbed, allowing other elements to invade the voids between molecules or molecular clusters. Complexation with γ-ZrP is expected to enhance the heat resistance and water resistance of gemini-type QAS.

In this study, gemini-type QAS was intercalated into γ-zirconium phosphate to create an antibacterial film using a plastic substrate. The antibacterial properties, water resistance, heat resistance, and mechanical properties of the resulting film will be evaluated to develop sustainable materials.

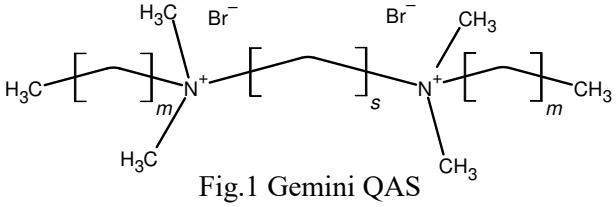


Fig.1 Gemini QAS

Methods

Intercalation of gemini-type QAS and γ-ZrP was performed by adding 0.5 mmol of gemini-type QAS. Next, γ-ZrP was added and adjusted to a molar ratio of gemini-type QAS:γ-ZrP of 2:1.5, followed by the addition of 1000 mL of RO water. After stirring at room temperature for 24 hours, the product was recovered by vacuum filtration and dried in a fume hood.

The prepared composite was subjected to thermogravimetric-differential thermal analysis (TG-DTA) to evaluate its thermal stability.

The antibacterial film was fabricated using polypropylene (PP) as the base material. Samples were prepared with a PP to QAS/ZrP weight ratio of 96:4 by weight. These samples were then processed into antibacterial film using a heating press (IMC180℃, Imoto Manufacturing Co., Ltd.). The film was subsequently cooled between aluminum plates. The fabricated antibacterial film underwent antibacterial water resistance evaluation using the shake method. Antibacterial activity value of 2.0 or higher, demonstrating antibacterial properties

Results and Discussion

Fig. 2 shows the TG-DTA measurement results for 12-5-12, 12-8-12 alone,and their respective γ-

ZrP composites. For 12-5-12 (A), an endothermic peak is observed around 230°C, indicating thermal decomposition. Furthermore, for the composite (B) supported with γ-ZrP, an exothermic peak is observed around 310°C, confirming weight loss. This indicates that supporting γ-ZrP increased the decomposition temperature by approximately 80°C, thereby improving heat resistance. Similarly, in 12-8-12(C), an endothermic peak is observed around 300°C, indicating thermal decomposition. In 12-8-12 γ-ZrP (D), an exothermic peak is observed around 350°C, indicating weight loss. This indicates that the decomposition temperature increased by approximately 50°C, demonstrating improved heat resistance.

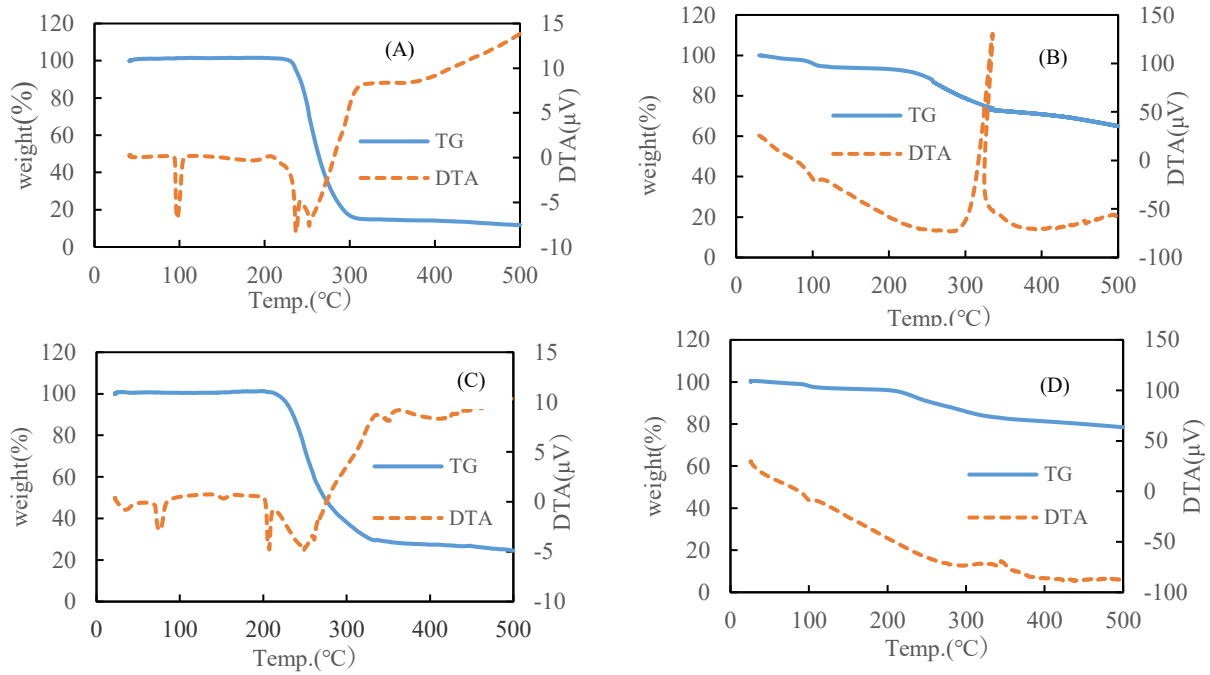


Fig.2 TG-DTA measurement results
(A)12-5-12 (B)12-5-12 γ-ZrP (C)12-8-12 (D)12-8-12 γ-ZrP

The results of the water-resistance evaluation are summarized in **Table 1**. All composites exhibited antibacterial activity values of ≥2.0, indicating that the films satisfy the performance requirements for application categories 0, 1, and 2. Although 12-5-12 alone shows poor resistance to water and readily loses antibacterial functionality, incorporation of γ-ZrP imparted clear water resistance to the composite material. These findings demonstrate that γ-ZrP plays a significant role in improving the water resistance and maintaining the antibacterial performance of the gemini-type QAS. The improvement in heat resistance of each sample contributes to the stability of molding processability.

Table1 shake method results

Category	Water temperature (ºC)	Soaking time (hr)	12-5-12 γ-ZrP	12-6-12 γ-ZrP	12-8-12 γ-ZrP
0	-	-	2.4	2.8	2.4
1	5~35	16~18	2.5	2.5	2.5
2	45~55	16~18	2.6	2.6	2.5

Conclusion

We successfully supported Gemini-type QAS on γ-ZrP and formed the complex into a film. To confirm the films' antibacterial properties, a shake test was performed, revealing antibacterial activity in all samples: 12-5-12 γ-ZrP, 12-6-12 γ-ZrP, and 12-8-12 γ-ZrP. Furthermore, a water resistance test via shaking confirmed that the films maintained their antibacterial properties within grades 0, 1, and 2.

References

1) Shilpa Tyagi,Vinod Kumar tyagi :Tenside surfactants Detergents Vol.51-5,2014,p.379

Application of compact electrostatic precipitators for collection of pyrolysis oil

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Introduction

The study is dedicated to the development of compact electrostatic precipitators (ESPs) for collection of pyrolysis oil from pyrolysis of biomass, plastic, wastes, etc. The review is focused on ESP design and operation conditions, as well as, on the ESPs application and perspectives for enhancement of collection efficiency of pyrolysis oil using electrostatically augmented condensation system (EACS).

Electrostatic precipitation of pyrolysis oil

In the modern society, plastics provide a decisive contribution to different kinds of daily activities. The increase in plastic wastes (PWs) has a negative impact on the environment. Landfills and incineration are common ways for PWs disposal, but they are not the crucial solution. The alternative approach to upgrade PWs can be achieved through the use of pyrolysis technology. The PWs could be treated in the pyrolysis reactor, what results in generation of high temperature pyrolysis gases, which exit from the reactor and pass through the coolers, installed in series downstream the reactor [1].

ESP design

To ensure effective collection of pyrolysis oil, the ESPs are used, being installed downstream the coolers or combined with them [2-4]. Usually, an ESP includes a casing with a cover, which supports a high voltage (HV) electrode. The casing can be manufactured from conductive or dielectric material. In the last case, a grounded conductive tube is axially installed inside the dielectric casing. The gas input and output are orthogonal or are installed with an angle to the lateral wall of ESP casing. The gas can flow in the ESP upstream or downstream. A high voltage, being applied to HV electrode, is used to generate corona discharge on the top of sharp electrodes' points. Oil droplets are electrostatically charged in the corona discharge. The electric field in the ESP ensures precipitation of electrostatically charged condensed oil droplets. The collected oil flows out from the ESP through the output for the condensate. If necessary, an ESP can be heated or cooled.

ESP operation

The collection efficiency of an electrostatic precipitator depends on the design of ESP casing (preferably tube form), HV electrode (wire, needle, star-form, etc.), number of corona discharge points, electrode gap width, loading of corona discharge and grounded electrodes with precipitated material (spark-over discharges), electrohydrodynamic (EHD) phenomena (EHD-spraying of collected oil in the ESP), polarity and value of applied voltage (corona discharge onset, operation and spark-over voltages), corona discharge current polarity and value (efficiency of particle charging), corona discharge suppression phenomena, which depend on the distance between corona discharge points and aerosol space charge in the electrode gap. Among the design parameters, the efficiency of an electrostatic precipitator depends on operation conditions, such pyrolysis gas flow rate, particle concentration in gas flow, gas temperature, pressure and chemical composition. The long-term operation stability of the ESP depends on the level of protection of high voltage insulator against the loading with particles (uncharged and charged), on the cleaning interval of the ESP, clogging of ESP with condensed and/or solidified materials, etc. An important role plays the algorithms for operation control of ESP parameters, especially, for dynamic regulation of voltage (reduced frequency of spark-over discharges). Being equipped with heat exchanger, the control procedures of the ESP parameters need to take into consideration the change in gas flow density and velocity in dependence on gas temperature.

Compact electrostatic precipitators for collection of pyrolysis oil

The compact electrostatic precipitator (see **Figure 1**) was designed for effective collection of condensed oil from pyrolysis of biomass [5,6]. A single-stage ESP was designed, being installed downstream the 5-stage cooling system C1-C5. The ESP operated on the principle of unipolar particle charging in corona discharge and particle precipitation in the grounded collector under the influence of aerosol own space charge. In the tests, flow rate of biomass (rape pellets, rape fruit, wood chips) was 15-30 kg/h. The main part of pyrolysis oil was collected in the first (C1) cooler. Fine oil mist fraction was precipitated in the ESP (U=10-12 kV, I=0,1 mA). The mass collection efficiency of a single-stage ESP was 97-99,5% depending on gas composition, temperature and flow rate. To ensure effective collection of pyrolysis oil at gas flow rates up to 100 m³/h, a two-stage ESP was designed (see **Figure 2, left**) and applied. The design view of a four-stage ESP, which was developed for collection of oil mist from the pyrolysis gases at flow rates up to 500 m³/h, is shown in **Figure 2, right.**

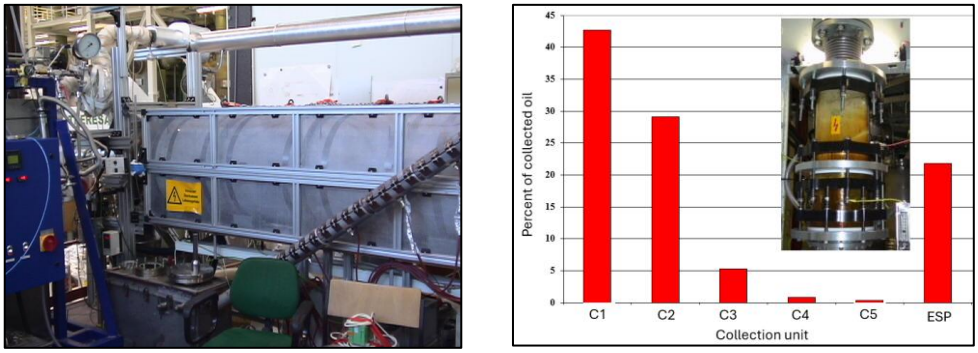


Figure 1. Application of single-stage compact ESP for biomass pyrolysis.



Figure 2. Compact two-stage (left) and four-stage (right) electrostatic precipitators for pyrolysis oil.

Electrostatically augmented condensation system

The next stage of the development included the design and test of the electrostatically augmented condensation system. The first step of the study involved the investigation of the laboratory compact electrostatic precipitator with integrated heat exchanger (see **Figure 3,a**). The ESP included the tube-form casing through which the pyrolysis gas flue in the downstream direction. The ESP was equipped with a jacketed cooler. An external system was applied for cooling/heating of the heat transfer liquid (HTF). Due to jacked cooler, the laboratory ESP could be operated at gas input temperatures. A direct current negative polarity corona discharge was used for particle charging. The star-form shaped corona discharge electrodes were maintained on a high voltage rod, connected with the output of HV power supply unit. To ensure long-term operation stability, the corresponding measures were taken to protect the high voltage insulator against loading with aerosol.

Before the test with pyrolysis gases, the ESP was investigated at air flow rates up to 3 m³/h and T=0-80°C. With increase in air temperature, at U=const, the corona current increased. The increase of air flow up to 3.0 m³/h resulted in decrease of the spark-over voltage and operation corona current.



Fig. 3,a



Fig. 3,b



Fig. 3,c

Figure 3. Electrostatically augmented condensation system.

The set of experiments was carried out with the laboratory ESP, which was installed downstream the pyrolysis reactor (see **Figure 3,b,** pyrolysis of plastic wastes). In the reactor, the nitrogen was used as carrier gas. The results of the tests have proved the efficiency of collection of the pyrolysis oil in the design apparatus at various gas temperatures. The collection efficiency of the test unit reached the values up to 99%.

The next step of project development included the design of the multi-stage electrostatically augmented condensation system (see **Figure 3,c**). The EACS included four tube-in-shell coolers, connected into a row. The 1st module become hot gases from pyrolysis reactor. The gas was in step-mode cooled in the forthcoming modules. The last module was operated at T~0°C. The 2nd, 3rd and 4th modules were equipped with corona discharge ionizers. The HV insulators were protected against the loading with pyrolysis oil. The HV star-form electrodes were maintained orthogonal to the lateral wall of coolers. The study with EACS was devoted to investigation of the influence of pyrolysis gas parameters on the system operation stability, as well as, fractional collection efficiency.

The scaling of the EACS system is in plan of forthcoming research. The three-stage EACS should be installed downstream the pyrolysis fluidized bed reactor. The reactor, as well as, the EACS itself, are currently in the maintenance phase.

References

[1] Papari, S., Hawboldt K.: *A review on condensing system for biomass pyrolysis process*, Fuel Processing Technology, 180, 1-13, 2018.

[2] Gooty A.T., Li D., Briens C., Berruti F.: *Fractional condensation of bio-oil vapors produced from brick bark pyrolysis*, Separation and Purification Technology, 124, 81-88, 2014.

[3] Nygard H., Olsen E.: *Molten salt pyrolysis of milled beech wood using an electrostatic precipitator for oil collection*, AIMS Energy, 3(3), 284-296, 2015.

[4] Bedmutha R.J., Ferrante L., Briens C., Berutti F., Inculet I.: *Single and two-stage electrostatic demisters for biomass pyrolysis application,* Chemical Engineering and Processing, 48, 1112-1120, 2009.

[5] Bologa A., Hornung A., Seifert H., Woletz K., Paur H.-R.: *Application of space-charge electrostatic precipitator for collection of oil mist from pyrolysis gases*, Proceedings of 16th IEEE International Conference on Dielectric Liquids, (ICDL-2008), Poitiers, France, 2008.

[6] Bologa A., Paur H.-R., Seifert H., Woletz K.: *Collection of oil droplets from pyrolysis gases by an electrostatic precipitator*, Proceedings Intern. Conf. & Exhib. for Filtration and Separation Technology, Wiesbaden, Germany, 2009.

[7] Bologa A., Gehrmann H.-J., Woletz K., Stapf D.: *Development of electrostatically enhanced condensation system for pyrolysis gases*, Proceedings of European Aerosol Conference (EAC-2022), Malaga, Spain, 2022.

Towards Circular Polystyrene usage, comprising Pyrolysis in a Pilot Scale Fluidized Bed Reactor Rectification and Styrene Polymerization

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General Information

Polystyrene (PS) is a versatile polymer which is used for many purposes involving isolation, packaging, consumer good parts and so is a fundamental part of everyday life.[1] Its high consumption encompasses also the risk of environmental pollution due to the non-biodegradable properties of PS. At the same time, its fossil-resource-based origin puts stress on its production and use too. Consequently, there is growing interest in recycling of the single-use polystyrene found in collection systems. One of the challenges is to maintain product quality and material properties as effectively as possible even after multiple cycles. This study aims to examine the changes in material properties of a circular system of recycling polystyrene to styrene monomer through pyrolysis, styrene rectification and repolymerization.[2]



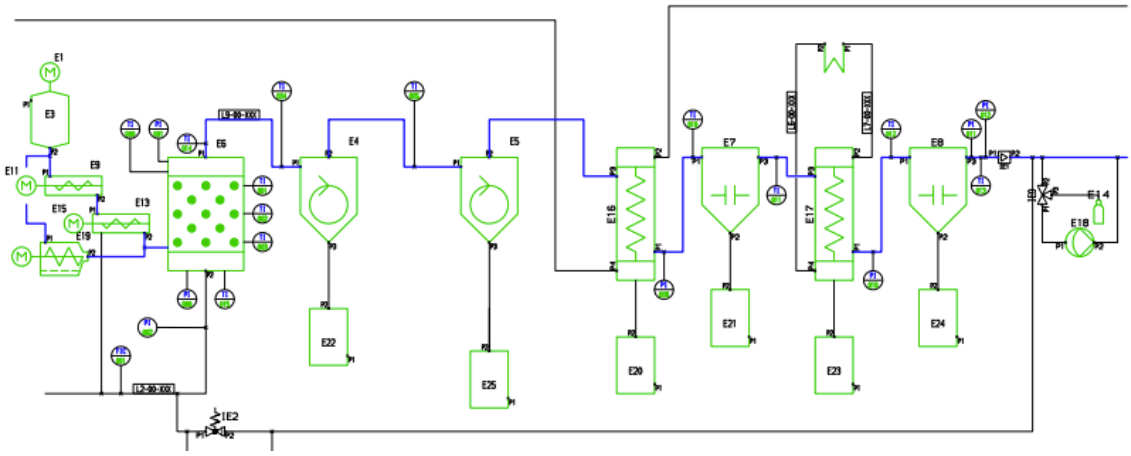


Figure 1. pyrolysis plant and flow diagramm

Work overview

The cycle is to be run not less than 4 times, and analysis of side products in reclaimed styrene. An initial feed of virgin polystyrene was pyrolyzed in a fluidized bed reactor (**Figure 1**), then rectified and re-polymerized. This now is in repetition. Each time the products of the pyrolysis (styrene oil), the purity of the rectification product (polymerization grade styrene), its polymerization and the polystyrene material property profile will be mapped. The target is to investigate for build-up of cycle compounds and its effects on the property profile of repolymerized styrene.

The starting point is virgin polystyrene (TOTAL POLYSTYRENE CRYSTAL 1160) 5 kg of which were pyrolyzed using the fluidized bed reactor operated at 600 °C (residence time of ~3 s). The produced pyrolysis gas was cooled down and the aerosol was electrostatically separated. The mass balance was closed to find over 90% of the input feed recovered as pyrolysis oil (**Figure 2)**. Its composition by GC-FID shows that next to styrene, monoaromatic species as toluene, ethylbenzene or α-methylstyrene are formed. (**Figure 3**) Recent work at our institute showed that the styrene recovery fraction is 73%.[3]

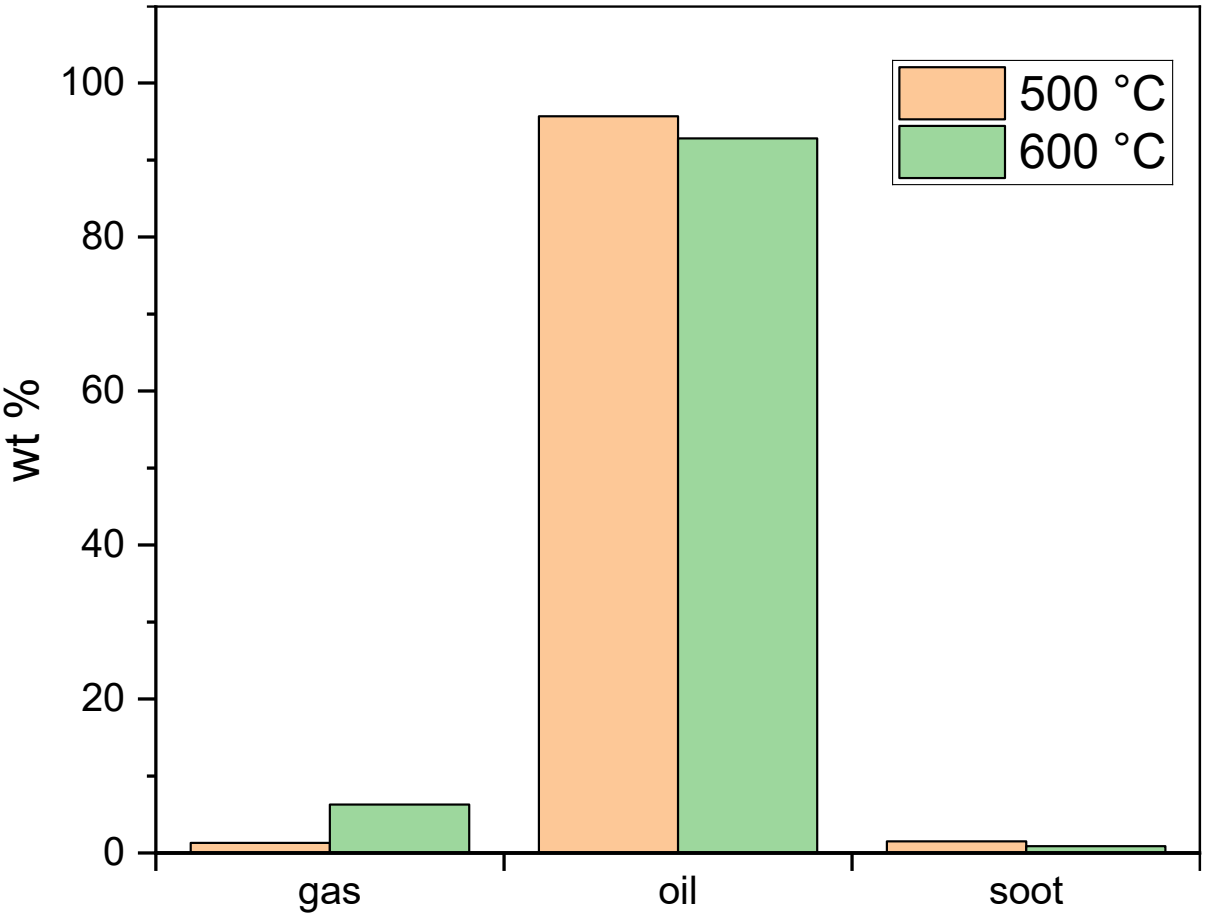


Figure 2. Standardized product composition of the pyrolysis experiments at different temperatures.

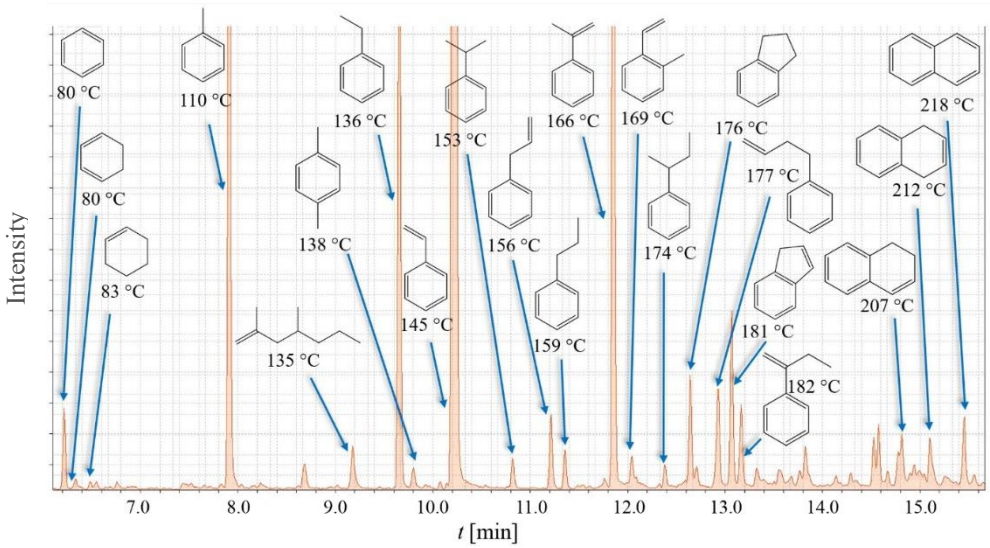


Figure 3. GC-FID of pyrolysis oil of virgin PS.

The task that remains for a circular polystyrene is to isolate the styrene at a sufficient purity for repolymerization to a general useful polystyrene. This generally achievable by distillation as was prior shown.[3] More relevant to industrial praxis is a rectification: a report has been published that gives an achievable purity of 99.7%.[4] Thus reclaimed styrene oil will have certain byproducts that could remain in the cycle and influence product properties.[5,6] Practical knowledge on the byproduct spectrum will

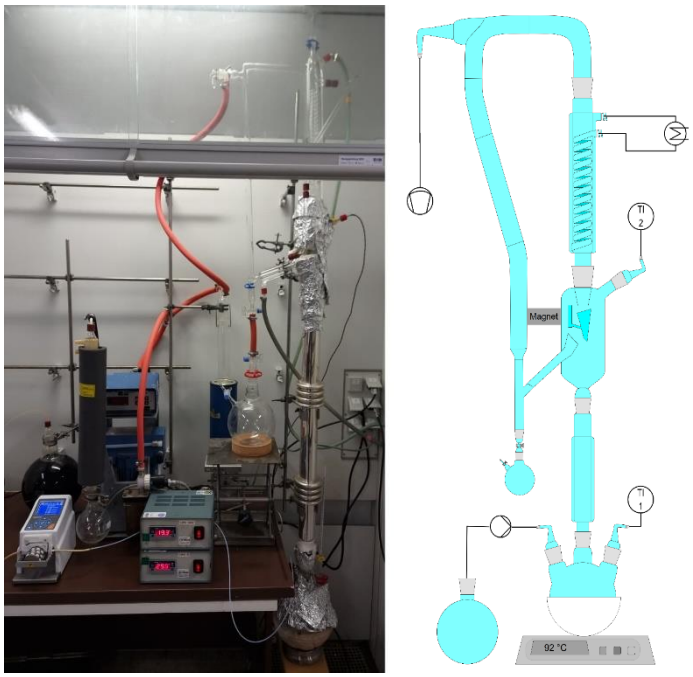


Figure 4. Rectification plant and schematic set up.

be gathered by a circular approach involving pyrolysis, rectification and polymerization. A rectification pilot set up was therefore also installed and operated under various pressures (**Figure 5**). The rectification plant consists of a pump, a collector flask heated by a heating mantle and connected to a rectification column. To control the reflux rate, there is a column top with an integrated automated reflux splitter. Attached to the column top is a vacuum pump to rectify at different pressures.

Further Work

Results will be shown of the first cycle of pyrolysis, rectification and repolymerization. Product properties as rheological, thermal and mechanical properties of the recycled polystyrene will be reported.

References

1. *Modern styrenic polymers*: *Polystyrenes and styrenic copolymers;* Scheirs, J., Ed.; Wiley: Chichester, 2003, ISBN 0-471-49752-5.
2. Mo, Y.; Zhao, L.; Chen, C.-L.; Tan, G.Y.A.; Wang, J.-Y. Comparative pyrolysis upcycling of polystyrene waste: thermodynamics, kinetics, and product evolution profile. *J Therm Anal Calorim* **2013**, *111*, 781–788, doi:10.1007/s10973-012-2464-6.
3. Plessing, L. Untersuchungen zur pyrolytischen Monomerrückgewinnung von Polystyrol, Polyethylen und Polypropylen in einer indirekt beheizten Wirbelschicht. Doktorarbeit, to be submitted; Universität Hamburg, Hamburg, 2024.
4. Liu, Y.; Qian, J.; Wang, J. Pyrolysis of polystyrene waste in a fluidized-bed reactor to obtain styrene monomer and gasoline fraction. *Fuel Processing Technology* **2000**, *63*, 45–55, doi:10.1016/S0378-3820(99)00066-1.
5. Merkel, A.; Plessing, L.; Luinstra, G.A.; Grünewald, M.; Biessey, P. Development of a Separation Sequence for the Integration of a Styrene Recyclate into Polystyrene Production. *Chemie Ingenieur Technik* **2023**, *95*, 1323–1331, doi:10.1002/cite.202100210.
6. Holtkamp, M.; Renner, M.; Matthiesen, K.; Wald, M.; Luinstra, G.A.; Biessey, P. Robust downstream technologies in polystyrene waste pyrolysis: Design and prospective life-cycle assessment of pyrolysis oil reintegration pathways. *Resources, Conservation and Recycling* **2024**, *205*, 107558, doi:10.1016/j.resconrec.2024.107558.

From Technology Comparison to System Design: Integrated Assessment of Waste Plastic Sorting and Recycling

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Introduction

To achieve plastic resource circulation, increasing attention has been paid to the design of recycling systems that effectively integrate mechanical recycling (MR), chemical recycling (CR), and energy recovery (ER) [1,2]. Although numerous studies have reported the environmental impact of these technologies using life cycle assessment (LCA), most existing evaluations focus on individual technologies, resulting in an insufficient understanding of an integrated plastic recycling system that incorporates upstream sorting processes. Specifically, there are few quantitative studies examining how the design and performance of sorting processes affect the choice of downstream recycling technologies. Previous LCA studies have also pointed out methodological challenges and differences in system boundary settings when evaluating circular processes, indicating that frameworks for the integrated assessment of waste plastic treatment systems, including sorting and pre-treatment processes, are not yet sufficiently established [3,4].

Against this background, this study aims to clarify not the relative superiority of individual recycling technologies, but rather how environmental impacts and costs vary at the system level, including sorting. In addition, the factors that govern these variations during integrated assessment of sorting and recycling processes are identified. A model was developed that incorporates sorting machines arranged across multiple layers and positions, together with downstream MR, CR, and ER options (Fig. 1). Greenhouse gas (GHG) emissions and total system cost were adopted as evaluation indicators for an integrated system-level assessment. For MR and CR technologies, both GHG emissions and cost inventories were corrected in a unified manner using the technology reports [5-7] for commercially implemented processes.

The configuration of sorting machines and the selection of recycling options for each output stream were treated as decision variables. Accordingly, a bi-objective optimization was performed to derive a Pareto-optimal solution set with respect to GHG emissions and cost. The Pareto solutions were analyzed by examining the patterns of change in GHG emissions and costs.

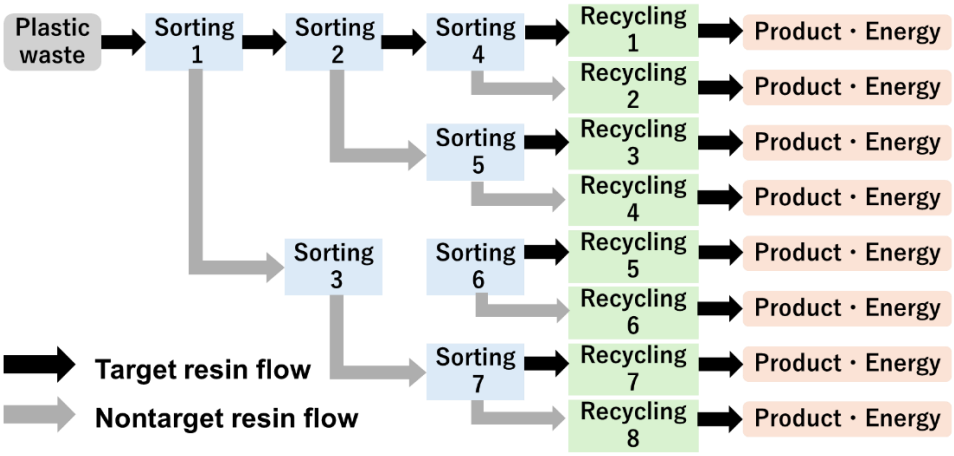


Fig. 1 System Overview

Methods

Case study

In this study, waste plastics generated in Sendai City were considered as the target feedstock, and a small-scale recycling system with an annual treatment capacity of 7,307 t/y was assumed. The input composition consisted of five polymer types (polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyvinyl chloride (PVC)). MR, CR, and ER were defined as downstream processes, while the purity requirements and technology applicability conditions for each polymer were incorporated as model constraints.

Modeling of the System Configuration

The sorting process was modelled as a three-layer, seven-position arrangement of sorting machines to represent a realistic multi-stage, parallel sorting structure. Each sorting stage was assumed to achieve an 80% separation accuracy for the target polymer. The eight output streams were subsequently assigned to MR, CR, or ER. This structure enabled the representation of an integrated combinatorial framework linking the sorting and recycling processes.

Evaluation Indicators

The total system cost and GHG emissions were defined as the evaluation indicators. The total cost was calculated as the sum of capital expenditures (CAPEX), annualized using the annuity method for both sorting and recycling facilities, and operating expenditures (OPEX). GHG emissions were estimated on an annual basis by accounting for emissions from each process as well as substitution effects. A bi-objective optimization was then performed using these two indicators as objective functions.

Optimization algorithm: NSGA-II

The total system cost and GHG emissions were adopted as objective functions, and Pareto-optimal solutions were obtained using the non-dominated sorting genetic algorithm II (NSGA-II). The decision variables included the presence or absence of sorting machines, the type of sorting machines used, and the treatment options selected after sorting (CR, MR, ER). The NSGA-II parameter settings are summarized in the table below.

Table 1 NSGA-II parameter settings

Population Size	Iteration	Crossover	Mutation
20	20	0.7	0.3

Results and discussion

In the GHG emission range of approximately 5,000–10,000 t-CO_2/y, GHG emissions varied over a relatively wide range without substantial changes in total cost (**Fig. 2**). In contrast, as GHG emissions decreased from around zero to negative values, a steep increase in total cost was observed. By comparing the detailed breakdown of each Pareto solution, the influences of sorting system configuration, combinations of MR, CR, and ER on the sensitivity of environmental impacts and costs were systematically identified (**Tables2-3**). In **Tables 2-3**, S1-7 and R1-8 correspond to Sorting1-7 and Recycle1-8 in **Fig. 1**, respectively. A total of 177 Pareto-optimal solutions were obtained. The two extreme solutions (minimum cost and minimum GHG) and four additional solutions exhibiting structural transitions along the Pareto front were selected for detailed analysis. A comparison of **Tables 2 and 3** indicates that even with similar sorting machine configurations, variations in the selected recycling options can lead to significant differences in total cost and GHG emissions.

This study presents a framework that reconceptualizes waste plastic treatment not as a comparison of individual technologies, but as an integrated system design problem encompassing both sorting and recycling processes. By visualizing the trade-off structure between GHG emissions and cost, the proposed approach provides insights into the key factors governing environmental and economic performance, thereby supporting decision-making for the design of sustainable plastic resource circulation systems.

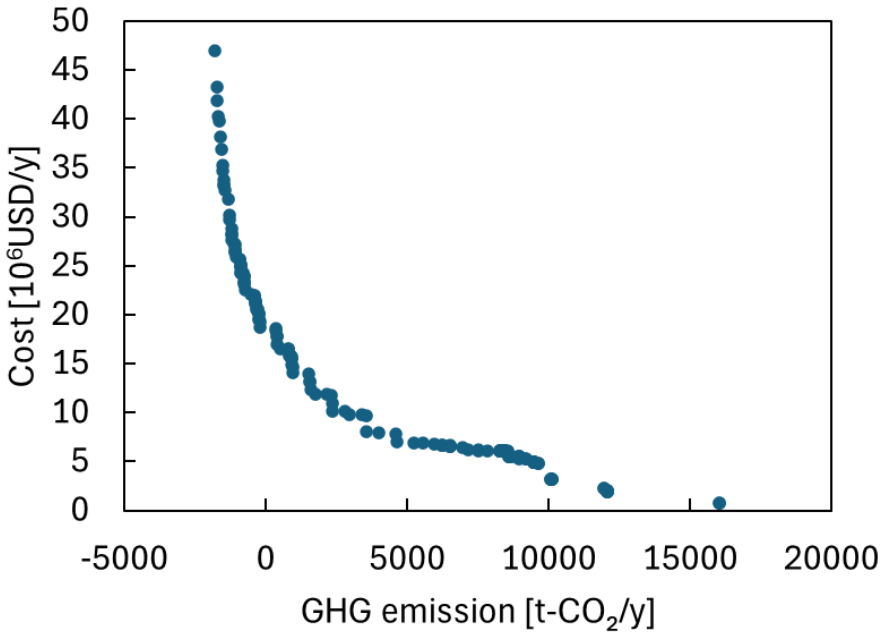


Fig. 2 Pareto solutions for the integrated sorting–recycling system

Table 2 Sorting machine configurations (**S1-7**) in the Pareto solutions (The solutions are arranged in ascending order of total cost)

	S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
$Cost_{min}$	-	-	-	-	-	-	-
Bi-objective	PE	PE	PET	PE_PP	PP	-	-
	PE	PE	PET	PE	PET	-	PET
	PE	PE	PET	PE_PP	PET	-	PE_PP
	PE	PE	PET	PE_PP	PET	-	PE_PP
GHG_{min}	PE	PE	PET	PE	PP	-	PE_PP

Table 3 recycling options (**R1-8**) selected in the Pareto solutions

	R1	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**	**Total Cost [10^6USD/y]**	**Total GHG [t-CO_2/y]**
$Cost_{min}$	ER	-	-	-	-	-	-	-	0.81	16040
Bi-objective	MR1	ER	CR3	ER	ER	-	ER	-	4.85	9641
	MR1	ER	ER	ER	ER	-	ER	CR4	6.87	5556
	MR1	CR1	ER	CR3	ER	-	CR1	CR4	15.5	921
	MR1	CR1	ER	CR1	CR4	-	CR4	CR5	25.7	-912
GHG_{min}	MR1	CR5	CR5	CR4	CR4	-	CR5	CR5	47.0	-1804

References

[1] Improving Plastics Management, *Organisation for Economic Co-operation and Development (OECD)*, 2018.
[2] *European Commission*: A European Strategy for Plastics, European Commission, 2018.
[3] Nordahl, S. L., Scown, C. D.: Recommendations for life-cycle assessment of recyclable plastics in a circular economy, *Chem. Sci.*, **15**, 9397-9407, 2024.
[4] Uusitalo, T., Toukoniitty, E.: Environmental impacts of plastic recycling – a literature review, *VTT Research Report*, VTT-R-00604-24, 2024.
[5] S&P Global. (2019). *Post Consumer Plastic Recycling* (PEP Report 199C), Process Economics Program.
[6] S&P Global. (2021). *Large-scale Pyrolysis-Plastic Chemical Recycling* (PEP Report 199G), Process Economics Program.
[7] S&P Global. (2021). *Mechanical Recycling of Waste Polymers* (PEP Report 199F), Process Economics Program.

Influence of chemical structures in unconventional liquid feedstocks on cracking in fluidized beds.

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Introduction

Industrial-scale usage of recycled feedstock into today's chemical clusters require knowledge of the decomposition of post-consumer wastes as they are processed in thermochemical conversion processes, such as steam cracking or pyrolysis. Pyrolysis oil produced today have strict specification on the amount of poly-olefinic content (PO%) in the feedstock used, sometimes as much as 90-95% pure polyolefins[1]. The pyrolysis operators are making one big assumption; that pyrolysis oil is going to be cracked in traditional steam cracking furnaces, which are sensitive to contaminants, aromatics and olefinic content [2]. This limits the potential for true recycling, i.e. going from post-consumer waste back to virgin quality, as the rejected fraction (PO% < 90%.) will be burned for energy recovery. Steam cracking in a dual fluidised bed (DFB) is an alternative to traditional steam cracking in tubular reactor. The process utilises a dual fluidised bed configuration, where the steam cracking reactor fluidized bed reactor and can handle heavy coking and contaminants, as well as liquid (such as untreated pyrolysis oils) and solid feedstocks. The process has been demonstrated at semi-industrial scale at Chalmers University of Technology. For more detail regarding the process the reader is referred to Mandviwala et al [3].

Thermochemical conversion processes are complex and poses challenges when trying to make predictive models, especially for large scale simulations. The decomposition of polymers has been described using kinetics, providing insight into how volatile matter leaves the feedstock. The devolatilization kinetics are not enough to predict the product distribution from the process; therefore, authors have provided kinetics for individual radical reactions and modelled the assumed global decomposition pathway of the polymer [4]. By building the modelling from bottom-up, one can capture nuances of the process, but it requires significant computational resources and poses challenges with radical reactions selection.

An alternative to the complexity of radical reaction modelling is to simplify, or lump, reactions together to describe broader chemical processes, instead of radical interactions. Netzer et al. modelled combustion of municipal solid waste utilising surrogate species. They did so by using representative compounds which captures key reaction products, such NOx, tar etc., with great results[5]. Forero Franco et al. proposed a similar, but more general, approach for describing steam cracking of solid feedstocks in fluidized bed. Instead of relying of specific surrogate species, they simplified the feedstock complexity by describing it in terms of carbon atoms with specific bonds, such as aliphatic carbon (C-Al), aromatic carbon (C-Ar), and oxygenated carbon (C-X). To specify the bonds, the polymeric composition of the feedstock was estimated based on properties of the feedstock, such as elemental analysis and LHV. By using a top-down modelling, sufficient resolution to describe the process could be obtained. They showed clear correlations between the type of carbon bond groups and product yields. By simplifying into broad groups, predictions become less prone to overfitting. The prediction has limitations and makes no claim to completely resolve the intricacies of thermochemical conversion, but it is robust to make good predictions. It is a framework which allows for parametric modelling of highly complex processes[6].

The chemical structure of liquid feedstocks differs from that of solids in the possibility for a higher fraction of double bonds (olefin), branching (iso-paraffin), or aromatic rings per chain-length. Following the top-down modelling approach presented by Forero-Franco, this work aims to explore the relationship between chemical structures in liquid feedstocks and their cracking products. The chemical structures explored in the preliminary work are non-saturated, iso-paraffinic, and aromatic chains. The work will aid in the understanding of thermochemical conversion processes and utilisation of parametric and correlational modelling.

Preliminary work

Three liquid feedstocks were included in the preliminary work: Naphtha, rapeseed oil, and pyrolysis oil. The data used for the preliminary work comes from Mandviwala et al [3,7]. Liquid feedstocks are commonly classified by the PIONA, which provides insight regarding the saturated and non-saturated carbons, as well as branching in the liquid. The PIONA analysis presented for the pyrolysis oil and naphtha is based of measurements in a GC-VUV, see **Table *1***. The PIONA of the rapeseed oil was approximated based on the mass fraction of saturated and non-saturated fatty acid chains (FA). The FAs was classified as paraffins and olefins respectively, data was collected from Mandviwala et al [7]. The feedstocks can contain oxygenated species, however, the PIONA analysis does not capture this detail of the feedstock. **Table *1*** also contain the average chain length of the feedstocks.

Table 1. Characterisation of selected feedstocks via PIONA and avg. chain length (number of carbon)

Hydrocarbon type, %wt.	Paraffin	Iso-paraffin	Olefin	Naphthene	Aromatics	Avg. Chain length, number of carbons
Naphtha	32	47.1	0	17.7	3.2	4.5
Py-oil	3.5	24.1	50.6	14.2	7.1	12.1
Rapeseed oil	10	0	90	0	0	17.8

The experiment for cracking of rapeseed oil was conducted in a bubbling bed at lab-scale, while the rest was conducted in Chalmers Dual fluidized bed (semi-industrial-scale). Both setups utilized a bed temperature (eq. to coil temperature in traditional steam cracking) of ~750°C. The severity, here defined by methane yield, in accordance with Van Geem et al.[8], have an average value of 10.4 %C with a standard deviation of 0.41 percentiles, thus the conditions for the different experimental runs are deemed to be equivalent enough to compare.

Preliminary results

Preliminary results of the cracking process are shown in **Figure 1**, where chemical structures in the feedstock are shown to influence the product yields. Iso-paraffinic content, shown in **Figure 1a)**, is shown to correlate with both the olefinic and aromatic yields. Due to the branching present in iso-paraffins, additional side chain scissions occur, thus promoting creation of double bonds. Double bonds can promote cyclisation and aromatisation, which is also indicated by the increase of aromatic yields for olefinic content in the fuel, seen in **Figure 1b)**. The path from iso-paraffin to double bond to aromatic is not as dominant as the path straight from olefin to aromatic. Counterintuitive, the increase in aromatic content of the feedstock, decreases the yield of aromatic in the cracking products, as shown in **Figure 1c)**. This decrease might be attributed to the average chain length, as shown in **Table *1***, which might promote the aromatisation when breaking up by producing longer secondary chains with double bonds in it. Cracking of rapeseed oil yields significantly higher aromatic products, while having no aromatic chemical structures, but it has the longest average chain length. Additionally, the CO_x yield from the rapeseed oil cracking is higher due to the oxygen present in the feedstock, a characteristic which is not included in the PIONA analysis. The CO_x production from the other feedstock comes from oxygen transport of the bed, the reader is referred to the work by Mandviwala et al. for this topic[3].

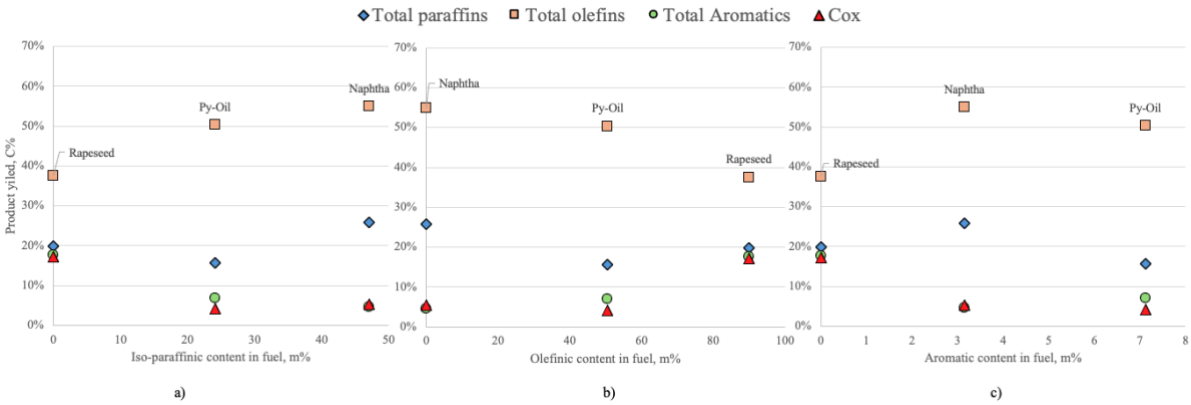


Figure 1.Influence of a) iso-paraffinic, b) olefinic, and aromatic c) content in feedstock (m%) on product yields.

Initial conclusions and continued work

The results showed that there is a correlation between the types of structures found in feedstocks and the product distribution from a cracking process. Traditional characterisation methods of liquids, like the PIONA analysis works well for easy communication between industrial parties, but fails to capture some aspects of the feedstocks, like oxygen in the rapeseed oil. Unconventional feedstocks, like pyrolysis oils, can contain oxygenates and higher amount of double bonds and aromatics than traditional feedstocks. Thus, it is important to explore how to sufficiently describe unconventional feedstocks as they are introduced into existing petrochemical industries. To aid with this task, the continuation of this work will focus on lab-scale experiments with liquid feedstocks, including characterization of the liquid feedstock and the cracking products. The aim is to further investigate the influence of key bond structures such as single carbon bonds, aromatic bonds, double bonds (conjugated and non-conjugated), and chain length, all which can be found in liquids.

[1] Eisele, P.: *A Chemical Recycling Process to Turn Non-recyclable Waste into High Grade Chemical Materials.*, Advanced recycling conference, Cologne, Germany, 2025.

[2] Kusenberg, M.,Eschenbacher, A.,Djokic, M. R.,Zayoud, A.,Ragaert, K.,De Meester, S.,Van Geem, K. M.: *Opportunities and challenges for the application of post-consumer plastic waste pyrolysis oils as steam cracker feedstocks: To decontaminate or not to decontaminate?* Waste Manag. *138*, 83–115, 2022.

[3] Mandviwala, C.,Forero Franco, R.,Berdugo Vilches, T.,Gogolev, I.,González-Arias, J.,Cañete Vela, I.,Thunman, H.,Seemann, M.: *Steam cracking in a semi-industrial dual fluidized bed reactor: Tackling the challenges in thermochemical recycling of plastic waste.* Chem. Eng. J. *500*, 156892, 2024.

[4] Wei, X.,Zhong, H.,Yang, Q.,Yao, E.,Zhang, Y.,Zou, H.: *Studying the mechanisms of natural rubber pyrolysis gas generation using RMD simulations and TG-FTIR experiments.* Energy Convers. Manag. *189*, 143–152, 2019.

[5] Netzer, C.,Li, T.,Løvås, T.: *Surrogate Reaction Mechanism for Waste Incineration and Pollutant Formation.* Energy Fuels *35*(9), 7030–7049, 2021.

[6] Forero-Franco, R.,Cañete-Vela, I.,Berdugo-Vilches, T.,González-Arias, J.,Maric, J.,Thunman, H.,Seemann, M.: *Correlations between product distribution and feedstock composition in thermal cracking processes for mixed plastic waste.* Fuel *341* 2023.

[7] Mandviwala, C.,González-Arias, J.,Seemann, M.,Berdugo Vilches, T.,Thunman, H.: *Fluidized bed steam cracking of rapeseed oil: exploring the direct production of the molecular building blocks for the plastics industry.* Biomass Convers. Biorefinery *13*(16), 14511–14522, 2023.

[8] Geem, K. M. V.,Reyniers, M. F.,Marin, G. B.: *Two severity indices for scale-up of steam cracking coils.* Ind. Eng. Chem. Res. *44*(10) 2005.

Thermogravimetric Investigation of Calcium-Based Additives for Halogen Capture during Pyrolysis of Electronic Waste Plastic

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Introduction

The Global E-Waste Monitor 2024 states that the quantity of the world's e-waste was 62 million tonnes in 2022, an 82 wt.% increase over 2010 [1]. By 2030, 74.7 million tonnes of e-waste are estimated to be generated worldwide [2], and could reach approximately 120 million tonnes by 2050 [3].

In Germany, the collection of e-waste is controlled by Elektro- und Elektronikgerätegesetz (ElektroG), which implements the European Union Waste Electrical and Electronic Equipment Directive (EU WEEE Directive). The collected devices are classified and processed either manually or mechanically to obtain valuable materials, particularly metals. Although much focus has been on recovering precious and base metals from e-waste due to their economic value [4], the non-metallic fractions, including plastics, that remain are challenging to recover [5].

E-waste plastics are not easily mechanically recycled due to their material heterogeneity and hazardous substance content, such as brominated flame retardants (BFRs) and other halogenated compounds, including chlorine (Cl) compounds, such as polyvinyl chloride (PVC) [6-8]. Chemical recycling, such as pyrolysis, can decompose materials at high temperatures (300-900 °C) under inert conditions to produce gases, liquids, and solids [9]. In this temperature range, most plastic components decompose into condensable vapours (pyrolysis oil) and non-condensable gases, while inorganic materials remain in the solid residue. By introducing calcium-based additives into the pyrolysis process, it is possible to capture released halogens and form stable calcium halides, thereby reducing halogen emissions [10-11]. This process is a promising approach not only for treating e-waste plastic to remove hazardous substances, but also for recovering valuable resources [10].

Although previous studies on the use of calcium additives in the pyrolysis of simulated e-waste plastics have been extensive [12-13], research on real e-waste plastic non-Printed Circuit Board (PCB) streams remains limited. In this experiment, the feedstock material is sink fraction (SF) of WEEE recycling, which is a real mixed post-consumer e-waste stream of plastic. Therefore, further research is needed.

Materials and Methods

The e-waste plastic fraction under investigation was first cryogenically milled before analysis to achieve a size distribution mainly below 1 mm, with minor coarse particles up to about 2 mm. The feedstock was characterized by halogen content (Br and Cl), heating value, proximate analysis (moisture, ash and volatile matter) and elemental analysis (C, H, N and S) to establish its physicochemical properties prior to thermogravimetric investigation.

TGA was conducted for each calcium-based additive and SF using 20–25 mg of sample in 3 mL Al_2O_3 crucibles under a N_2 atmosphere at a heating rate of 10 K/min to 1000 °C, with purge and reaction gas flows of 75 and 50 mL/min, respectively.

To directly assess halogen release, TGA-FTIR experiments were subsequently conducted on mixtures of e-waste plastic and the selected calcium-based additive at a stoichiometric Ca/(Br+Cl) molar ratio. The calcium-based additive powders were physically premixed with the milled feedstock prior to thermogravimetric analysis.

Data were evaluated using Linseis TA Evaluation software, and the presented curves represent averaged measurements smoothed using the Savitzky–Golay algorithm. Measurements were conducted at least in duplicate, with additional runs performed if deviations exceeded 3%.

Preliminary Results

The material characterization results are summarized in Table 1. The presence of ash in SF points to residual inorganic constituents after thermal treatment. The volatile content indicates that the composition is mostly polymeric. The measured lower heating value presents a considerable energy content typical of WEEE plastic [14]. The detected halogen content in SF is consistent with values reported in the literature for WEEE plastic fractions, where total Cl and Br concentrations typically range between approximately 0.6 and 4 wt.% [14].

Table 1. Proximate and elemental analysis of SF (raw state)

Parameter	Value	Parameter	Value
Ash (815°C)	16.21 wt.%	H	6.23 wt.%
Volatile matter	75.70 wt.%	N	1.43 wt.%
Moisture	6.80 wt.%	S	0.15 wt.%
LHV	24.17 MJ/kg	Cl	1.22 wt.%
C	53.00 wt.%	Br	0.50 wt.%

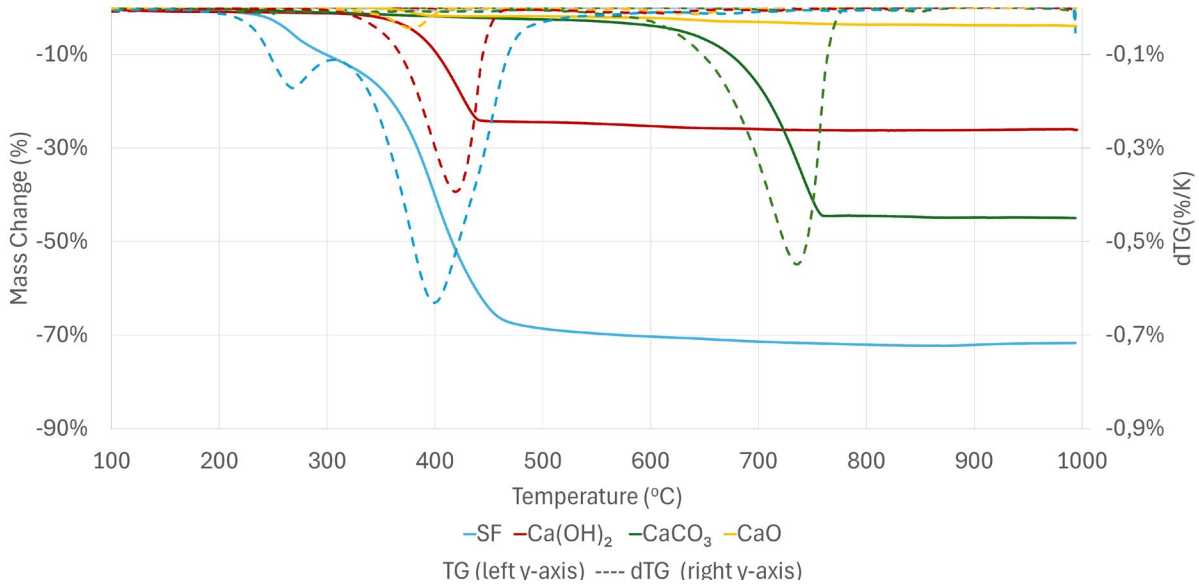
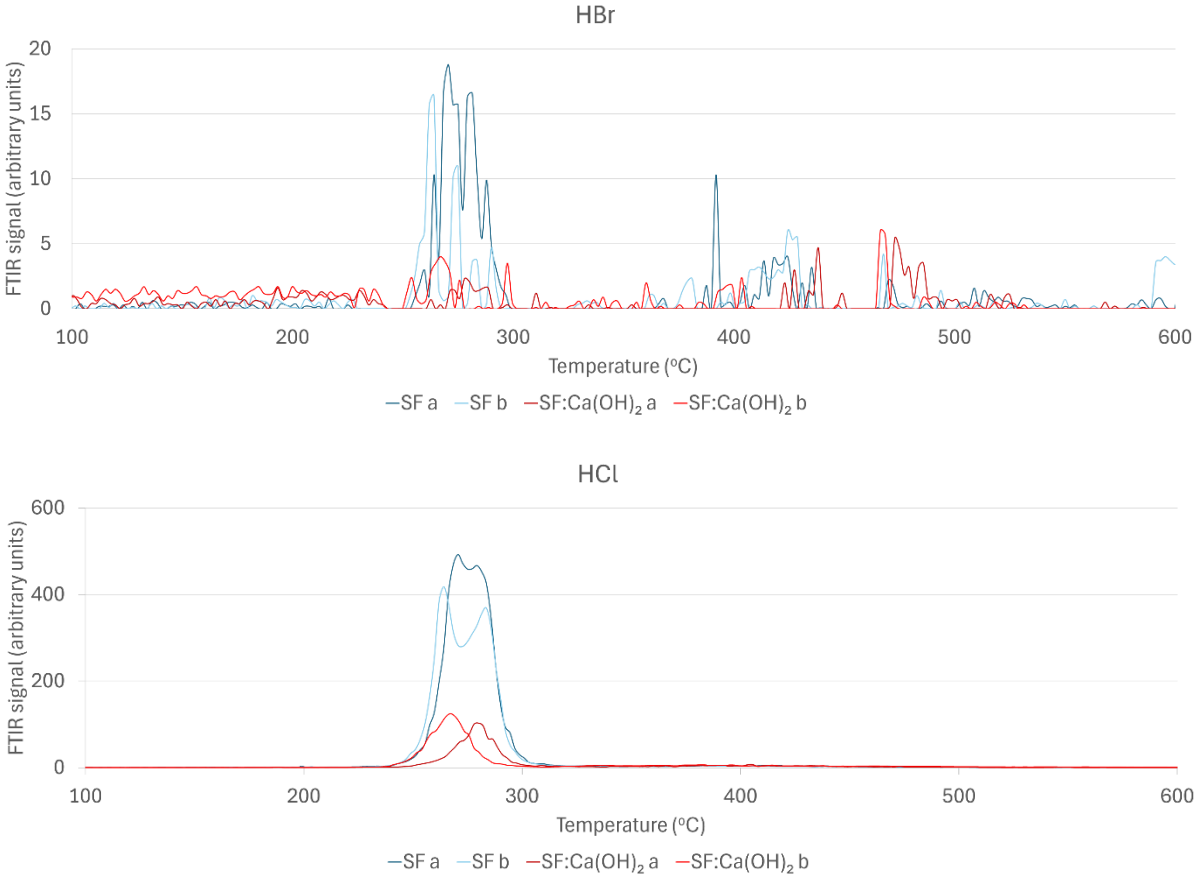


Figure 1. TGA of SF and Calcium-based additives

Based on the TGA results in Figure 1, two degradation stages were observed during SF pyrolysis. A mass loss of 17 wt.% was observed in the temperature range of 180-310°C, with the maximum mass-loss rate occurring at 268°C. This degradation step may involve scission of weak links within thermally sensitive functional groups in the mixture [15], as well as PVC dehydrochlorination and HCl release [16]. TGA studies of WEEE plastics report PVC degradation at approximately 223–300 °C [16]. The second degradation stage of SF occurred in the temperature range of 310-580°C, corresponding to a mass loss of 63 wt.%. The DTG curve indicated a maximum mass-loss rate of 400 °C during this stage. The second stage was much more significant and complicated, possibly due to the decomposition of several polymeric components that frequently appear in plastics from e-waste, such as polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), acrylonitrile–butadiene–styrene (ABS), and PVC [17].

TGA of the calcium additives showed different decomposition behaviours consistent with literature reports [18]. $Ca(OH)_2$ exhibited a single major mass-loss step at 380-470°C, due to dehydration and CaO formation. The $CaCO_3$ was found to be stable to about 650°C and decomposed within the range of 670-780°C as a result of calcination. Conversely, the mass loss of CaO was insignificant (3-4%) over the temperature range studied, which demonstrates thermal stability. The minor mass loss is attributed to residual moisture and slight surface carbonation/hydration during storage, rather than to intrinsic thermal decomposition of CaO. Overall, the obtained TGA curves are in good agreement with the theoretical mass loss calculated from the stoichiometry of the respective calcium compound decomposition reactions, confirming the reliability of the measurements. These findings determine the

temperature range over which reactive CaO is released and show that $Ca(OH)_2$ enables earlier CaO generation than $CaCO_3$ in pyrolysis.
For subsequent TGA-FTIR experiments, $Ca(OH)_2$ was selected because it forms active CaO earlier than $CaCO_3$ and produces newly formed CaO with a larger specific surface area than sintered CaO [11]. TGA-FTIR was coupled to monitor the evolution of hydrogen halides (HBr and HCl) in the gas phase and to evaluate relative changes in their release profiles. As shown in Figure 2, gas-phase FTIR analysis indicates that SF releases more HBr and HCl than a mixture of SF and $Ca(OH)_2$ at the stoichiometric molar ratio Ca/(Br+Cl). $Ca(OH)_2$ can suppress HBr and HCl release by reacting with these acidic gases to form stable calcium halides, such as $CaBr_2$ and $CaCl_2$.



*FTIR signals are shown as semi-quantitative trends. The evaluation method is currently under refinement.

Figure 2. FTIR HBr and HCl gas analysis of SF and SF-$Ca(OH)_2$

Conclusions and Outlook

The results show that SF contains a major polymeric component with Cl and Br content, requiring effective mitigation strategies. TGA further showed that $Ca(OH)_2$ allows the formation of active CaO earlier than $CaCO_3$. Gas-phase FTIR results indicate reduced gas-phase HBr and HCl release in the presence of $Ca(OH)_2$ consistent with the capture of hydrogen halides by calcium-based species. The selected conditions from the TGA-FTIR experiment will be transferred to semi-technical-scale pyrolysis experiments to investigate the effect of calcium-based additives at larger scale.

References

[1] Baldé, C.P., Kuehr, R., Yamamoto, T., McDonald, R., D'Angelo, E., Althaf, S., Bel, G., Deubzer, O., Fernandez-Cubillo, E., Forti, V., Gray, V., Herat, S., Honda, S., Iattoni, G., Khetriwal, D.S., di Cortemiglia, V.L., Lobuntsova, Y., Nnorom, I., Pralat, N., Wagner, M.: *The Global E-waste Monitor 2024*, International Telecommunication Union (ITU) and United Nations Institute for Training and Research (UNITAR), Geneva/Bonn, 2024.

[2] Forti, V., Baldé, C., Kuehr, R., Bel, G.: *The Global E-waste Monitor 2020*, *Quantities, flows, and the circular economy potential,* United Nations University (UNU), United Nations Institute for

Training and Research (UNITAR), SCYCLE Programme, International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Rotterdam, 2020.

[3] Vishwakarma, S., Kumar, V., Arya, S., Tembhare, M., Rahul., Deblina, Kumar, S.: *E-waste in Information and Communication Technology Sector: Existing scenario, management schemes and initiatives*, Environmental Technology & Innovation, 27, 102797, 2022.

[4] Schwartz, E., He, H., Frost, K., Nguyen, B.H., Ogunseitan, O.A., Schoenung, J.M.: *Comparative life cycle assessment of copper and gold recovery from waste printed circuit boards: Pyrometallurgy, chemical leaching and bioleaching,* Journal of Hazardous Materials, 473, 134545, 2024.

[5] Guo, J., Guo, J., Wang, S., Xu, Z.: *Asphalt Modified with Nonmetals Separated from Pulverized Waste Printed Circuit Boards*, Environmental Science & Technology, 43(2), 503–508, 2019.

[6] Wäger, P. A., Schluep, M., Müller, E., Gloor, R.: *RoHS regulated substances in mixed plastics from waste electrical and electronic equipment*, Environmental Science & Technology, 46(2), 628–635, 2012.

[7] Wagner, F., Peeters, J.R., De Keyzer, J., Janssens, K., Duflou, J.R., Dewulf, W.: *Towards a more circular economy for WEEE plastics–Part B: Assessment of the technical feasibility of recycling strategies*, Waste Management, 96, 206–214, 2019.

[8] Chaine, C., Hursthouse, A.S., McLean, B., McLellan, I., McMahon, B., McNulty, J., Miller, J., Viza, E.: *Recycling Plastics from WEEE: A Review of the Environmental and Human Health Challenges Associated with Brominated Flame Retardants*, International Journal of Environmental Research and Public Health, 19, 766, 2022.

[9] Miandad R., Barakat, M.A., Aburiazaiza, A.S., Rehan, M., Nizami, A.S.: *Catalytic pyrolysis of plastic waste: A review*, Process Safety Environ Protection, 102, 822–838, 2016.

[10] Gao, R., Xu, Z.: *Pyrolysis and utilization of nonmetal materials in waste printed circuit boards: Debromination pyrolysis, temperature-controlled condensation, and synthesis of oil-based resin*, Journal of Hazardous Materials, 364, 1–10, 2019.

[11] Gao, R., Liu, B., Zhan, Lu., Guo, Jie., Zhang, Jie., Xu, Zhenming, *In-situ debromination mechanism based on self-activation and catalysis of $Ca(OH)_2$ during pyrolysis of waste printed circuit boards*. Journal of Hazardous Materials, 392, 122447, 2020.

[12] Charitopoulou, M.A., Vouvoudi, E.C., Achilias, D.S., *Isoconversional Analysis of the Catalytic Pyrolysis of ABS, HIPS, PC and Their Blends with PP and PVC*, Polymers, 16(16), 2024.

[13] Vouvoudi, E.C., Rousi, A.T., Achilias, D.S.: *Effect of the catalyst type on pyrolysis products distribution of polymer blends simulating plastics contained in waste electric and electronic equipment,* Sustainable Chemistry and Pharmacy, 34, 2023.

[14] Beccagutti, B., Cafiero, L., Pietrantonio, M., Pucciarmati, S., Tuffi, R., Vecchio, C.S.: *Characterization of Some Real Mixed Plastics from WEEE: A Focus on Chlorine and Bromine Determination by Different Analytical Methods*, Sustainability, 8(11), 1107, 2016.

[15] Vouvoudi, E.C., Rousi, A.T., Achilias, D.S.: *Thermal degradation characteristics and products obtained after pyrolysis of specific polymers found in Waste Electrical and Electronic Equipment*, Frontiers of Environmental Science and Engineering, 11(5), 9, 2017.

[16] Sahle-Demessie, E., Mezgebe, B., Dietrich, J., Shan, Y., Harmon, S., Lee, C.C.: *Material recovery from electronic waste using pyrolysis: Emissions measurements and risk assessment,* Journal of Environmental Chemical Engineering, 9(1), 2021.

[17] Gulshan, S., Shafaghat, H., Wang, S., Dai, L., Tang, C., Fu, Wenming, F., Wen, Y., Wang, C-H., Evangelopaulos, P., Yang, W.: *Kinetic investigation on the catalytic pyrolysis of plastic fractions of waste electrical and electronic equipment (WEEE): A mathematical deconvolution approach,* Waste Management, 187, 156–166, 2024.

[18] Carl, K.: *Gasifizierung von halogenhaltigen Kunststoffabfällen im Holz-Kalk-Festbett*, Ph.D. Thesis, Rheinisch-Westfälische Technische Hochschule Aachen (RWTH Aachen University), 2023.

Degradation onset of polyethylene under pyrolysis conditions

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Introduction

Thermochemical recycling of polymer feedstocks has emerged as a promising route for treating plastic waste streams unsuitable for conventional mechanical recycling. Molecular modeling approaches are employed to improve understanding of the underlying chemical processes and to further advance the technology. Newly found mechanistic insights are, for example, needed to reduce energy demand through catalyst and predict or control the product distribution. Applied methods are molecular dynamics (MD) simulations using reactive force fields and the development and use of detailed chemical reaction schemes.

A common practical challenge of these simulation approaches is the large molecular size of real polymers with average molecular masses of 350 000 g/mol [1]. For example, in MD studies of polyethylene, chain lengths are typically limited to about $C_{200}H_{400}$ [2] with 2805 g/mol while reaction-mechanism-based approaches use representative molecules such as $C_{40}H_{80}$ [3] with 561 g/mol to ensure computational feasibility and applicability in engineering-scale models. These reduced system sizes represent necessary approximations, although their influence on predicted reaction pathways and kinetics must be carefully considered and evaluated with respect to the early degradation, random chain scission and the statistics of rare events like the first bond cleavage.

The present work aims to experimentally resolve morphological changes and the early stages of polymer decomposition to support the selection of appropriate model system sizes and simulation conditions, particularly for capturing and modelling rare bond-breaking events in computational approaches.

Methodology

Morphological changes and the onset of degradation are characterized by ex-situ heat treatment followed by analysis using inelastic neutron scattering (INS). For the analysis, the neutron vibrational spectroscopy VISION beamline at the Oak Ridge National Laboratory's Spallation Neutron Source is chosen. Polymer samples are melted in a vacuum furnace and held at the target temperature for 60 min. LDPE is heated from 125-400°C in 25-50°C increments. For neutron spectroscopy, 0.5-0.8 g of sample is sealed in vanadium cans, cooled to -263 °C, and measured for 30 min.

Spectra are normalized to the elastic peak, and the empty-can background is subtracted. To enable comparison between samples, a common baseline is defined prior to spectral subtraction.

The investigated materials include low-density polyethylene (LDPE) at different life stages: virgin, extruded and film-blown, and recycled. Virgin and recycled LDPE are fully characterized materials supplied by Ruston Services Ltd, while the films are commercial packaging products. Global degradation behaviour is assessed by thermogravimetric analysis (TGA, Netzsch STA 449 C) using 15 mg samples, a nitrogen flow of 20 ml min^{-1}, and a heating rate of 10 °C min^{-1}.

To gain insight into species evolution, the multi-step reaction mechanism of Locaspi et al. [3] for LDPE is evaluated under identical conditions using the stochastic reactor gasification module implemented in LOGE Research [4].

Results

The experimental mass-loss curves of the different LDPE samples and the corresponding simulation results are shown in ***Figure 1***. All samples exhibit very similar thermal decomposition behavior, with only minor differences in the final residue.

The melting onset at 107°C and the transition to the gas phase are modelled with good accuracy. In the reduced reaction mechanism applied here, the initial bond cleavage and formation of the liquid intermediate $C_{30}H_{60}$ occur at approximately 350°C. The experimentally observed mass losses of 85–95% for the ex-situ melted samples at 400°C, therefore, indicate that these conditions cover the onset of degradation.

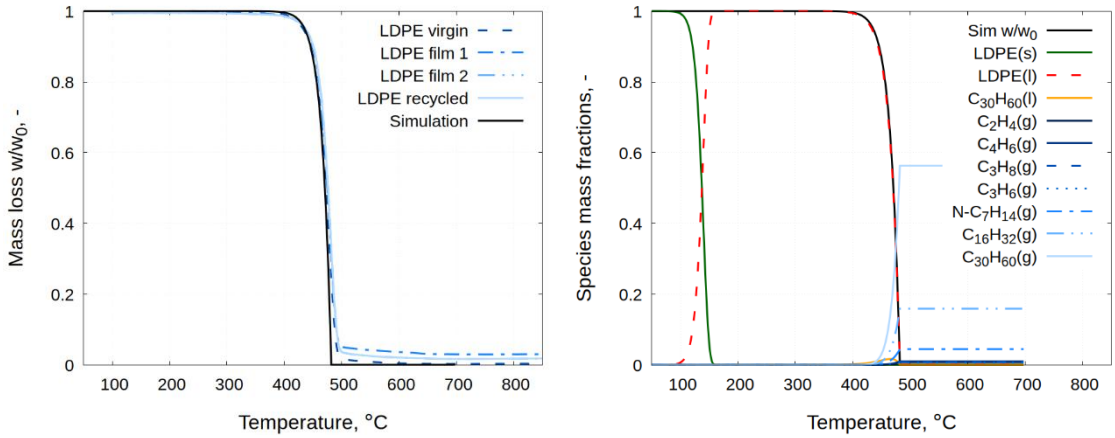


Figure 1: Mass loss curve obtained through TGA on the left and simulated species mass concentrations of the pyrolysis process on the right. The mass loss curve obtained in the simulation serves as a reference in both subplots.

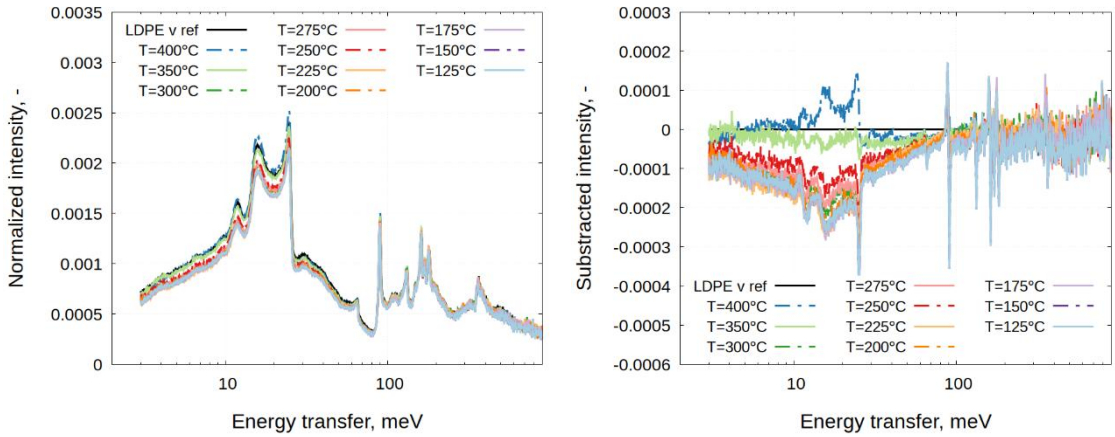


Figure 2: Normalized spectra for the virgin LDPE sample on the left and subtracted spectra on the right. The untreated sample (LDPE v ref) serves as a baseline for the subtraction.

Melting and the onset of degradation are assessed using the relative fraction of amorphous structures, and spectroscopic indicators of early degradation, such as increased disorder and segmental mobility. The spectra of virgin LDPE in **Figure 2:** Normalized spectra for the virgin LDPE sample on the left and subtracted spectra on the right. The untreated sample (LDPE v *r*ef) serves as a baseline for the subtraction. can be grouped according to their temperature-dependent behavior. While clear differences appear in the low-energy region (<80 meV), the high-energy range (> 80 meV), associated with functional groups and backbone saturation, remains largely unchanged. Temperature treatment <300°C leads to lower cooperative motions compared to the not treated sample. This can be caused by lower long-chain entanglement and loss of order and crystalline contribution.

Samples treated at 350°C and 400°C exhibit different behaviour, indicating structural rearrangements and chemical modifications. Both spectra show enhanced low-energy scattering (3–8 meV) and slight peak broadening, indicating a higher fraction of amorphous structures.

The spectra of the 400°C sample exhibit a clear deviation from the other spectra in the 10-30 meV range, suggesting additional scattering contributions from new molecular motions or defect sites. A clear conclusion can, however, not be drawn as in this region indications for an increase in torsional movement caused by more chain ends, shorter crystalline stems and reduced cooperative packaging that indicate degradation and chain scission overlay with low energy CH_2 vibration and bending that can also stem from an increased crystalline structure, formed during the cooling of the samples. Clear indication for bond cleavage and chemical modification would be the formation of vinyl groups at 113-123 meV, which can not be observed here. The change in modes are for the LDPE film and recycled materials more enhanced at 400°C compared to the virgin LDPE (Error! Reference source not found.).

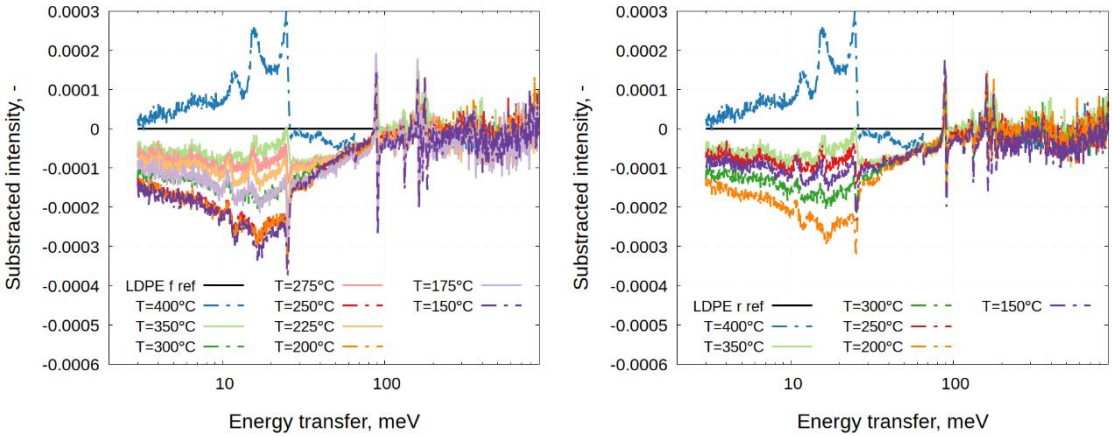


Figure 3: Subtracted spectra for the manufactured LDPE film on the left and the recycled LDPE on the right. The untreated samples (LDPE f ref, LDPE r ref) serve as a baseline for the subtraction.

Conclusions and Future Work

Neutron vibrational spectroscopy was employed to investigate the onset of thermal degradation in different LDPE samples. The analysis focused on identifying morphological changes and the initial bond-breaking processes within the polymer matrix. By combining ex-situ melting with vibrational spectroscopy, structural modifications in the low-energy region were resolved, revealing a progressive increase in amorphous content across the investigated temperature range.

The spectra indicate early-stage decomposition; however, the current temperature resolution does not permit further investigation of the degradation mechanism. Future work will hence cover a proof of reduced crystallinity using differential scanning calorimetry, a better resolution of vinyl formation using spectroscopy methods optimize for the high energy region and reduced temperature stepping.

References

[1] Westerhout, R. W. J., Waanders, J., Kuipers, J. A. M., van Swaaij, W. P. M.: Kinetics of the low-temperature pyrolysis of polyethene, polypropene, and polystyrene modeling, experimental determination, and comparison with literature models and data, Industrial & Engineering Chemistry Research, 36(6), 1955-1964, 1997.

[2] Liu, C., Wang, G., Li, A.: Insights into the evolution mechanism of polyethylene pyrolysis: a combined experimental ReaxFF-MD and DFT study, Fuel, 414, 138333, 2026.

[3] Locaspi, A., Frassoldati, A., Faravelli, T.: Reduced-order condensed-phase kinetic models for polyethylene, polypropylene and polystyrene thermochemical recycling, Chemical Engineering Journal, 500, 156949, 2024.

[4] Weber, K., Li, T., Løvås, T., Perlman, C., Seidel, L., Mauß, F.: Stochastic reactor modeling of biomass pyrolysis and gasification, Journal of Analytical and Applied Pyrolysis, 124, 592-601, 2017.

High-temperature pyrolysis of vulcanized isoprene rubber and liquid isoprene rubber

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Abstract

End-of-life tires (ELT) have been utilized through thermal recovery and material recycling. However, thermal recovery presents challenges in terms of CO_2 emissions and resource circulation. Additionally, material recycling methods such as crumb rubber and reclaimed rubber offer only limited applicability for use as tire materials. Chemical recycling of rubber derived from ELT has gained attention recently via technology of depolymerizing the material back into original monomer. In this direction, the present study is aimed to investigate a method for high yielding isoprene monomer.

Experimentally, vulcanized rubber and liquid polymer feedstocks are pyrolyzed at 750°C and the resulting isoprene yields are measured. Vulcanized rubber compounds according to the formulation shown in **Table 1** are prepared in laboratory based on three kinds of model formulations; liquid polymer is prepared by decomposing vulcanized rubber via a metathesis reaction using ruthenium catalyst [1]. The ratio of isoprene skeleton retention for vulcanized rubber is calculated from the compound formulation ratio, while that for the liquid polymer is determined from 1H NMR analysis. The depolymerization behavior of these samples are evaluated quantitatively by determining isoprene monomer yield in the products by using Py-GC.

Figure 1 shows the relationship between the ratio of isoprene skeleton retention and the isoprene monomer yield for vulcanized rubber and liquid polymers after pyrolysis. It is observed that the isoprene monomer yield after pyrolysis increases with the increasing isoprene skeleton retention in liquid polymer. Further, the liquid polymer exhibits higher monomer yields than vulcanized rubber for the same isoprene skeleton retention. Overall, the findings suggest that liquefaction enhances molecular mobility and thereby improves the isoprene monomer yield by suppressing formation of byproducts. To enhance molecular mobility further, investigations on the pyrolysis of liquid polymers diluted in organic solvents are currently in progress.

Table 1 Vulcanized rubber composition

Material	①	②	③
	Composition(phr)		
Natural rubber	100	60	40
Butadiene rubber		40	60
Carbon black(CB)	50	50	50
Zinc oxide(ZnO)	2.25	2.25	2.25
Sulfur	1.8	1.8	1.8
Steraric Acid	2	2	2
N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine	2	2	2
N-Cyclohexyl-2-benzothiazolylsufenamide	0.6	0.6	0.6
Polymerized trimethyl dihydroquinoline	1	1	1

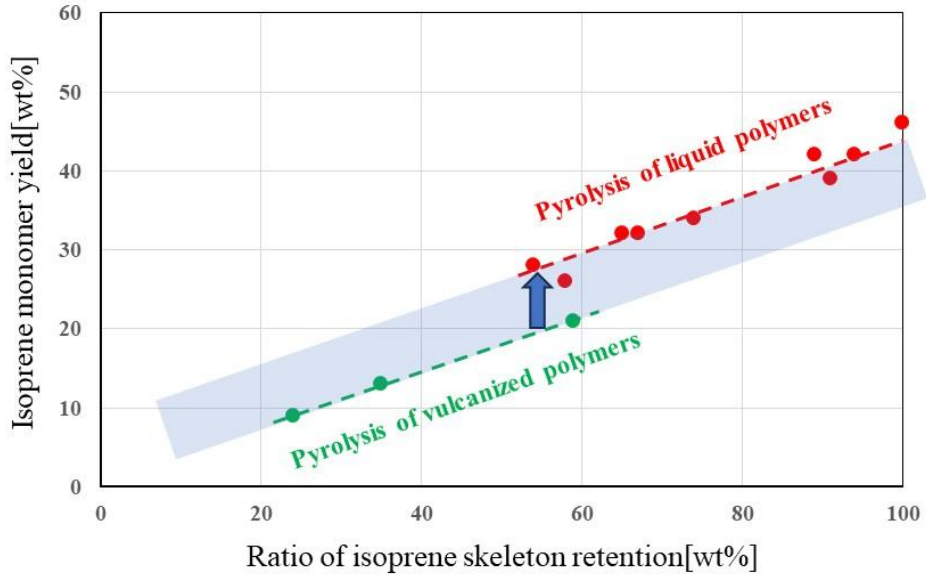


Figure 1 Relationship between the ratio of isoprene skeleton retention and the isoprene monomer yield for vulcanized rubber and liquid polymers after pyrolysis

References

[1] Putro, Wahyu S., Ueda, Y., Yamashita, H., Kamei, N., Faried, M., Hatori, M., Hojo, M.,Tahara, S., Homma, M., Minato, T., Takeuchi, K., Matsumoto, K., Jun-Chul Choi, J., and Fukaya, N.: *Two-Step Chemical Recycling of Tire Rubber to Isoprene*, ACS Catalysis, 15, 20097－20107, 2025

Acknowledgement

This presentation is based on results obtained from a project, JPNP21021, commissioned and subsidized by the New Energy and Industrial Technology Development Organization (NEDO).

Solvent-assisted, $ZnCl_2$-catalyzed conversion of poly(methyl methacrylate) waste into carbon anode materials for lithium-ion batteries

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Introduction

Poly(methyl methacrylate) (PMMA) is among the most widely produced engineering thermoplastics, and its accumulation as post-consumer and industrial waste raises a growing recycling challenge [1, 2]. Unlike polyolefins, PMMA undergoes near-complete unzipping to its monomer upon heating because of its high oxygen content, leaving negligible solid residue. Our thermogravimetric analysis (TGA) confirms a char yield below 1 wt% at 420 °C for neat PMMA, which makes this polymer an inherently poor feedstock for conventional pyrolytic carbonization [3]. Converting PMMA waste into a functional carbon would therefore address two objectives simultaneously: the feedstock valorization of a problematic plastic and the supply of low-cost carbon for electrochemical energy storage [4]. In this work we demonstrate that a solvent-assisted, $ZnCl_2$-catalyzed route transforms PMMA waste into a defect-rich disordered carbon that delivers reversible lithium-storage capacities substantially exceeding the theoretical capacity of graphite (372 mAh g^{-1}).

Experimental

Waste PMMA was cleaned, shredded, and dissolved in ethyl acetate (EA). Zinc chloride was introduced at a PMMA: $ZnCl_2$ mass ratio of 1:1 and homogenized in the polymer solution; the role of $ZnCl_2$ is to act as a dehydrating Lewis-acid catalyst and pore-forming agent that promotes char formation in an otherwise non-carbonizing polymer. After solvent removal, the precursor was pyrolyzed under argon (120 °C for 2 h, then 750 °C for 2 h, heating rate 5 °C min^{-1}), ball-milled (450 rpm, 4 h), washed with 2 M HCl at 80 °C, then rinsed and dried to yield the carbon denoted C-EA-Zn-750..

Materials were characterized by TGA, FTIR, X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Working electrodes were prepared from 80 wt% active carbon, 10 wt% acetylene black, and 10 wt% PVDF binder in N-methyl-2-pyrrolidone, with active-material loadings of approximately 0.5–1.0 mg cm^{-2}. CR2032 half-cells were assembled against lithium metal in an argon-filled glovebox using 1 M $LiPF_6$ in EC: DEC: EMC (1:1:1 v/v) electrolyte and a Celgard 2400 separator. Cells were evaluated by galvanostatic charge–discharge cycling between 0.01 and 3.0 V.

Results and Discussion

TGA results directly demonstrate the catalytic effect of $ZnCl_2$: whereas neat PMMA leaves below 1 wt% residue, the $ZnCl_2$-loaded precursor retains approximately 10 wt% carbon at 750 °C (Figure 1). This confirms that $ZnCl_2$ redirects the decomposition pathway from complete depolymerization toward cross-linking and char consolidation. EDS elemental mapping of the washed product gives 96.5 wt% carbon, 2.7 wt% oxygen, and zinc below the detection limit, indicating that the acid wash effectively removes the catalyst and leaves a high-purity carbon.

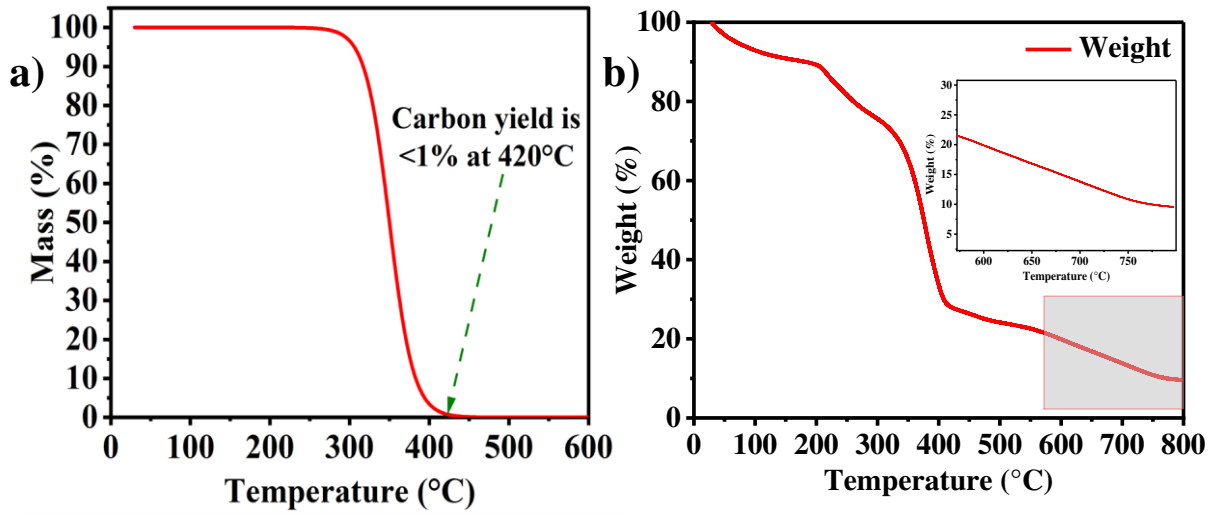


Figure 1. TGA: neat PMMA (<1% char at 420 °C) (a) and $ZnCl_2$-PMMA (~10% carbon at 750 °C) (b), showing the catalytic effect of $ZnCl_2$.

XRD patterns of the washed carbons display two broad reflections near $2\theta \approx 24°$ (002) and $\approx 43°$ (100), characteristic of a highly disordered, hard-carbon-like structure; the sharp crystalline peaks of zinc species observed before washing disappear after acid treatment. Consistently, the Raman spectrum shows the D-band (~1340 cm^{-1}) and G-band (~1580 cm^{-1}) typical of defective carbon, with the intensity ratio decreasing from I_D/I_G = 1.46 before washing to 1.03 after washing (Figure 2), reflecting partial structural reorganization upon removal of zinc residues. SEM reveals an irregular particulate morphology generated during milling.

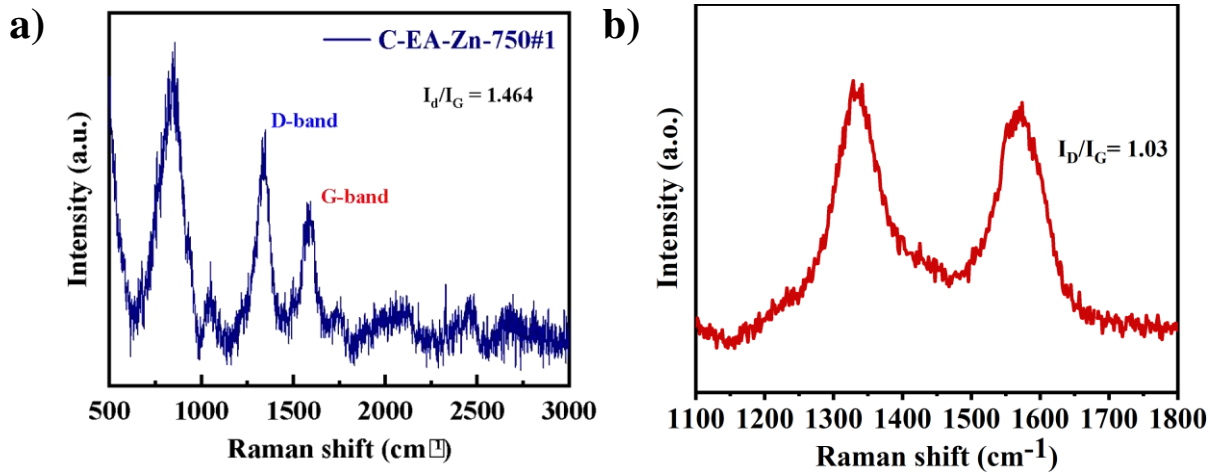


Figure 2. Raman: D- and G-bands, I_D/I_G dropping from 1.46 (before washing) (a) to 1.03 (after HCl wash) (b).

In lithium half-cells, the carbon delivers a high first-discharge capacity of approximately 1000–1300 mAh g^{-1} and a reversible capacity that stabilizes above 600 mAh g^{-1} — reaching 750–850 mAh g^{-1} for the best samples — over about 100 cycles, well above the graphite benchmark (Figure 3). The Coulombic efficiency rises rapidly to ~99% after the initial cycles, and the reversible capacity increases gradually during cycling, indicating progressive electrochemical activation of the disordered structure. The principal limitation is a low initial Coulombic efficiency of approximately 50%, attributed to solid-electrolyte-interphase formation and irreversible lithium trapping at oxygen-containing and defect sites; this is the central target of ongoing optimization through pre-lithiation, surface engineering, and electrolyte tuning.

Conclusions

A solvent-assisted, $ZnCl_2$-catalyzed carbonization route converts otherwise non-charring PMMA waste into a defect-rich carbon that functions as a lithium-ion anode with reversible capacity exceeding 600 mAh g^{-1}. The approach links the feedstock recycling of a difficult plastic with the production of scalable energy-storage materials. Current work focuses on raising the initial Coulombic efficiency and extending the material to sodium-ion anodes, toward a dual lithium-/sodium-ion waste-derived carbon platform.

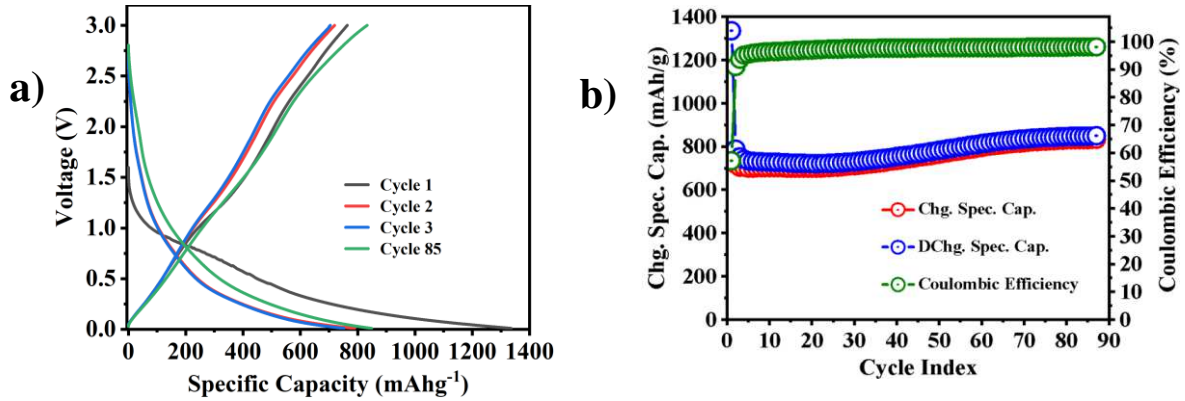


Figure 3. Electrochemistry (Li half-cell): galvanostatic charge–discharge profiles (a) and capacity / Coulombic efficiency (b) vs cycle number.

References

[1] Yang, X. M., Wang, X. Y., & Tang, Y. (2025). The chemical recovery of PMMA into monomer. Chemistry–A European Journal, 31(9), e202404030.

[2] Simoes dos Reis, G., Mayandi Subramaniyam, C., Cárdenas, A. D., Larsson, S. H., Thyrel, M., Lassi, U., & Garcia-Alvarado, F. (2022). Facile synthesis of sustainable activated biochars with different pore structures as efficient additive-carbon-free anodes for lithium-and sodium-ion batteries. *ACS omega*, *7*(46), 42570-42581.

[3] Hwang et al. Upcycling of Waste Polymers into Porous Hard Carbon Anodes for Sodium-Ion Batteries. ChemSusChem, 2026. DOI: 10.1002/cssc.202502183

[4] Issatayev, N., Kalimuldina, G., Nurpeissova, A., & Bakenov, Z. (2021). Biomass-derived porous carbon from agar as an anode material for lithium-ion batteries. Nanomaterials, 12(1), 22.

Challenges of Complex and Unknown Material Compositions in Pyrolysis-Based Recycling of Artificial Turf Waste

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Abstract

Complex plastic waste streams represent a major obstacle to increasing recycling rates. Artificial turf pitches are complex multi-material systems composed of various polymer types and represent a particularly challenging example as can be seen in **Figure 1** [1]. After a service life of 12 to 15 years, these systems exhibit substantial material degradation due to mechanical wear and environmental exposure [2,3]. A standard full-size pitch covers an area of 7,000 m² and has a total mass of around 230 tones, of which roughly 100 tones consist of different plastic fractions [2,4,5]. Added to this is the weight of the elastic base layer underneath the turf carpet, which is sometimes laid without but sometimes with mineral fillers. It has a longer service life and generally lasts for three to four life cycles of an artificial turf pitch [6]. In Europe, 1,000 artificial turf pitches are currently decommissioned each year. Given the continuing demand for synthetic turf systems, a further increase in the associated waste streams can be expected [3,7]. The heterogeneous material composition consisting of different thermoplastics, thermosets and elastomers significantly complicates sorting, separation, and subsequent material recycling, thereby posing a major challenge for the development of applicable end-of-life strategies. Furthermore, unknown components like additives containing substances of concern within these already complex waste streams present an additional challenge to efficient recycling strategies.

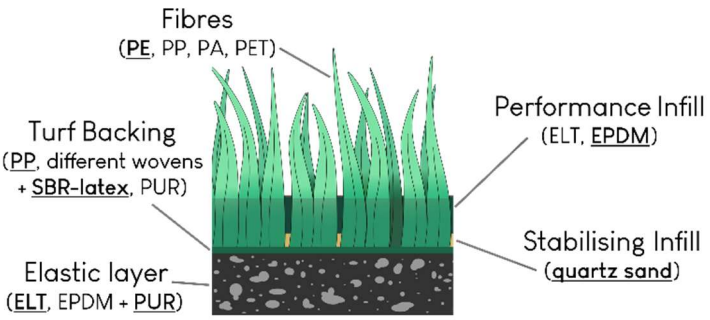


Figure 1. Turf structure [1].

While the applicability of mechanical recycling processes reaches its limits when dealing with complex and contaminated, but particularly with cross-linked plastic waste, chemical recycling and especially pyrolysis is regarded as a promising approach for challenging plastic waste streams. Although pyrolysis is regarded as a promising solution, the quality of the feedstock is a decisive factor in determining the quality of the resulting products. This work identifies the most challenging aspects of recycling complex multi-material systems with regard to pyrolysis based on the example of artificial turf and running track components. Lab-scale pyrolysis experiments are discussed considering their technical feasibility for industrial-scale processes. Various materials from sports flooring including synthetic turf carpet, elastic

infill and bonded running track material were subjected to laboratory tests. Elevated chlorine and nitrogen levels were detected in all samples. Chlorine and nitrogen can lead to a deterioration in the quality of the pyrolysis oil and gas, corrosion of plant equipment and problematic emissions. Depending on the specific process configuration and plant technology, this criterion does not necessarily preclude the applicability of pyrolysis. However, additional process steps must be implemented to improve the pyrolysis oil quality and gas purification. In summary, the pyrolysis of sports flooring waste is possible, but requires greater effort to meet quality and environmental standards.

References

[1] Anna Lena Seibel, Michèle Jampolski, Julia Walz, Mario Schmidt, Katharina Weber and Iman Taha: *End-of-life management of artificial turf: State of the art and future challenges*. Journal of Environmental Management, 406 (2026) 129822. 2026.

[2] EMEA Synthetic Turf Council: *ESTC Guide Processing End of Life Synthetic Turf Sports Surfaces.* https://www.estc.info/wp-content/uploads/2021/07/ESTC-guide-Processing-End-of-Life-Synthetic-Turf-Sports-Surfaces-Edition-2021-FINAL.pdf (accessed Oct 2025). 2021.

[3] PLAYGROUND@LANDSCAPE: *Entsorgung von Kunstrasensystemen - Recyceln statt verbrennen.* https://playground-landscape.com/de/article/2242-entsorgung-von-kunstrasensystemen-recyceln-statt-verbrennen.html (accessed Dec 2024). 2019.

[4] Eunomia Research & Consulting Ltd: *Environmental Impact Study on artificial football turf.* https://eunomia.eco/reports/environmental-impact-study-on-artificial-football-turf/ (accessed Oct 2025). 2017.

[5] EMEA Synthetic Turf Council: *Recycling facilities for synthetic turf systems in Europe.* https://www.estc.info/wp-content/uploads/2023/06/RECYCLING-FACILITIES-FOR-SYNTHETIC-TURF-SYSTEMS-IN-EUROPE-ESTC-Guide.pdf (accessed Mar 2026). 2023.

[6] Polytan GmbH: *Kunstrasen verlegen – Elastische Tragschicht oder Elastikschicht?* https://www.polytan.com/de/blog/kunstrasen-verlegen-elastische-tragschicht-oder-elastikschicht (accessed Aug 2026). 2022.

[7] Tarkett Sports FieldTurf: *Sustainability Commitment – Turf, Innovate.* https://fieldturf.com/en/why-fieldturf/sustainability-commitment/ (accessed Jun 2025). 2025.

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- NH_3-H_2 burner control technology

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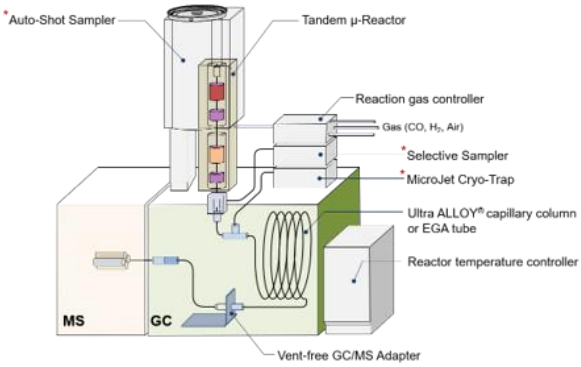
Frontier Laboratories Ltd., founded in 1991 by Dr. Chuichi Watanabe and based in Koriyama (Fukushima), Japan, is a global leader in analytical pyrolysis.

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Frontier Lab is consistently engaged in the research and development of analytical pyrolysis instruments and methods, manufacturing Single- and Tandem Micro-Reactors (Rx-3050TR and Rx-3050SR) alongside associated accessories for a wide range of analytical applications such as **conversion of waste plastics and biomass into fuels and value-added chemicals**, as well as **rapid catalyst screening and characterization**. The development of our micro-reactors was driven by the limitations of conventional catalyst evaluation systems, which feature large reactors and require a significant amount of time (several hours) for temperature stabilization, often taking one to several weeks to evaluate a single catalyst. Rapid development of new catalysts requires a drastic reduction in evaluation time.

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Our analytical pyrolyzers (EGA/PY-3030D or PY-3030S) are used for the physical property evaluation of polymer materials across various advanced scientific fields. Applications include quality control in the aerospace and automotive industries, **characterization of recycled materials and detection of contaminants**, **biomass characterization**, differentiation of rubber, paint, and paper in forensic investigations, and the identification of environmental pollutants such as **microplastics** and **PFAS**.

