

# Hydrogenolysis of Polypropylene and Mixed Polyolefin Plastic Waste over Ru/C to Produce Liquid Alkanes

Julie E. Rorrer, Clara Troyano-Valls, Gregg T. Beckham, and Yuriy Román-Leshkov\*

Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 11661–11666

Read Online

ACCESS |



Metrics &amp; More



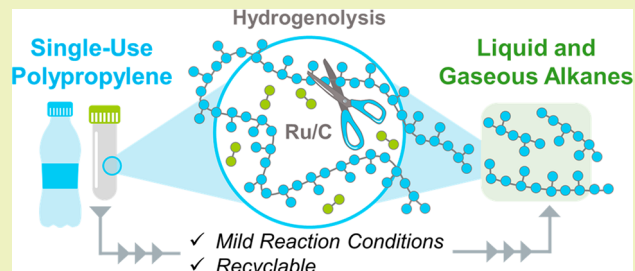
Article Recommendations



Supporting Information

**ABSTRACT:** Catalytic depolymerization of polyolefins is a promising chemical recycling strategy to create value-added products from waste plastics, which are accumulating in landfills and the natural environment at unsustainable rates. The cleavage of strong C–C bonds in polyolefins can be performed using a noble metal and hydrogen via a hydrogenolysis mechanism. Previously, we identified ruthenium nanoparticles supported on carbon (Ru/C) as a highly active heterogeneous catalyst for the conversion of polyethylene into liquid and gaseous *n*-alkanes under mild conditions. In the present study, we investigated the catalytic depolymerization of polypropylene (PP) under mild conditions (200–250 °C, 20–50 bar H<sub>2</sub>). We demonstrate that Ru/C produces C<sub>5</sub>–C<sub>32</sub> iso-alkane yields above 68% in the absence of solvent and identify trade-offs between product yield and temperature, hydrogen pressure, and reaction time. We apply a rigorous analytical method to quantify all liquid and gaseous alkane products. The characterized catalyst was found to be recyclable after the complete depolymerization of high molecular weight PP (*M<sub>w</sub>* ~ 340,000 Da) to liquid and gaseous hydrocarbons and after depolymerization of a postconsumer PP centrifuge tube. Further, the catalyst was shown to be effective in depolymerizing a mixture of high-density polyethylene and PP to produce a mixture of linear and branched liquid alkanes, demonstrating feasibility for the depolymerization of streams of mixed polyolefin waste.

**KEYWORDS:** Plastic upcycling, Hydrogenolysis, Polypropylene, Polyethylene, Mixed plastics, Depolymerization, Ruthenium



## INTRODUCTION

The global consumption of single-use plastic has caused massive accumulation of plastic waste in landfills and the environment, adversely affecting the ecosystem and human health. Each year, approximately 380 million tons of plastics are generated,<sup>1</sup> and projections estimate that plastic production will reach over 1.1 billion tons per year by 2050.<sup>2</sup> In the U.S. alone, plastics consumption accounts for 3.2 quads of annual energy use and 104 MMT of CO<sub>2</sub>e in annual greenhouse gas emissions.<sup>3</sup> Globally, plastics consume 6% of today's fossil carbon use.<sup>4</sup> Polyolefins are the most widely produced plastic, as polyethylene (PE) and polypropylene (PP) make up 36% and 21% of global plastics production, respectively.<sup>1</sup> Mechanical recycling can offer a second life to waste plastics, but only around 16% of plastic is actually recycled.<sup>5</sup> These recycled materials often exhibit inferior properties such as lower mechanical stability and contamination from dyes and additives.<sup>6</sup>

Chemical recycling offers an opportunity for plastic waste streams to be converted into higher value chemicals which could be used as drop-in fuel additives, integrated into chemical refineries, or used as synthons to produce the next generation of recyclable-by-design polymers.<sup>7–11</sup> Existing pathways such as pyrolysis and thermal cracking can enable the conversion of polyolefin waste into fuel-range chemicals,

but they require high operating temperatures (400–900 °C) and suffer from low product selectivity.<sup>12–14</sup> Recent efforts in chemical recycling have identified methods of activating the strong C–C bonds of PE at lower temperatures (200–300 °C) through both thermochemical and electrochemical routes.<sup>9,15–18</sup> Platinum-based catalysts have been shown to be effective for PE depolymerization via hydrogenolysis<sup>19,20</sup> and hydrocracking<sup>21</sup> and through tandem dehydrogenation/metathesis with a SnPt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Re<sub>2</sub>O<sub>7</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst system.<sup>22</sup>

Recently, our group identified ruthenium nanoparticles supported on carbon (Ru/C) as a highly active catalyst for PE depolymerization into liquid *n*-alkanes via hydrogenolysis under mild conditions (200–225 °C, 20–30 bar H<sub>2</sub>).<sup>18</sup> This reaction was performed in the absence of solvent, and the catalyst was shown to be recyclable for multiple cycles. Ru-based heterogeneous catalysts are attracting growing interest as materials for the hydrogenolysis of aromatic plastic waste,<sup>23</sup>

Received: June 5, 2021

Revised: July 20, 2021

Published: July 27, 2021

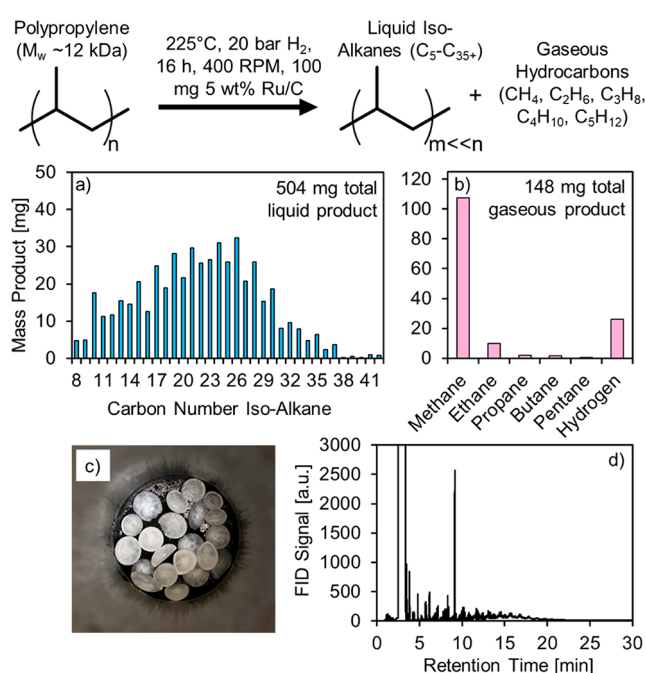


PE,<sup>24–27</sup> and model alkanes.<sup>28</sup> The high activity and stability of Ru-based heterogeneous catalysts in various catalytic systems make them excellent candidates for the hydrogenolysis of realistic waste plastic streams.<sup>29–31</sup> In addition to being recyclable, carbon supports can be sourced sustainably from biogenic carbon or even from the pyrolysis of waste plastics themselves.<sup>32</sup>

Mixed polyolefin (MPO) streams are considered a low-value feedstock for mechanical recycling, as the difference in melting points and processing temperatures between the different polymers present technical challenges concerning the degradation of lower-molecular weight components.<sup>33</sup> Further, blends of PE/PP have different mechanical and thermal properties than their constituent parts.<sup>34,35</sup> While the tertiary carbon–carbon bonds in PP have lower bond dissociation energies than secondary carbon–carbon bonds in PE,<sup>36–38</sup> PP generally also exhibits a higher  $T_m$ ,<sup>35</sup> and thus, the effect of carbon chain branches on hydrogenolysis activity is unclear. To utilize hydrogenolysis for the chemical upcycling of waste plastic, we must understand how the reaction proceeds over polymers with varying molecular weights and carbon chain branches. To this end, challenges include quantifying products and identifying product distributions obtained from varying feeds and optimizing conditions and feed stream compositions to achieve targeted product distributions and properties. In this study, we demonstrate PP hydrogenolysis to iso-alkanes over Ru/C by identifying suitable reaction conditions for PP depolymerization and performing rigorous quantification of liquid and gaseous products. We then demonstrate the proof of concept for catalyst recoverability and recyclability, as well as the hydrogenolysis of mixed streams of PE and PP waste.

## RESULTS AND DISCUSSION

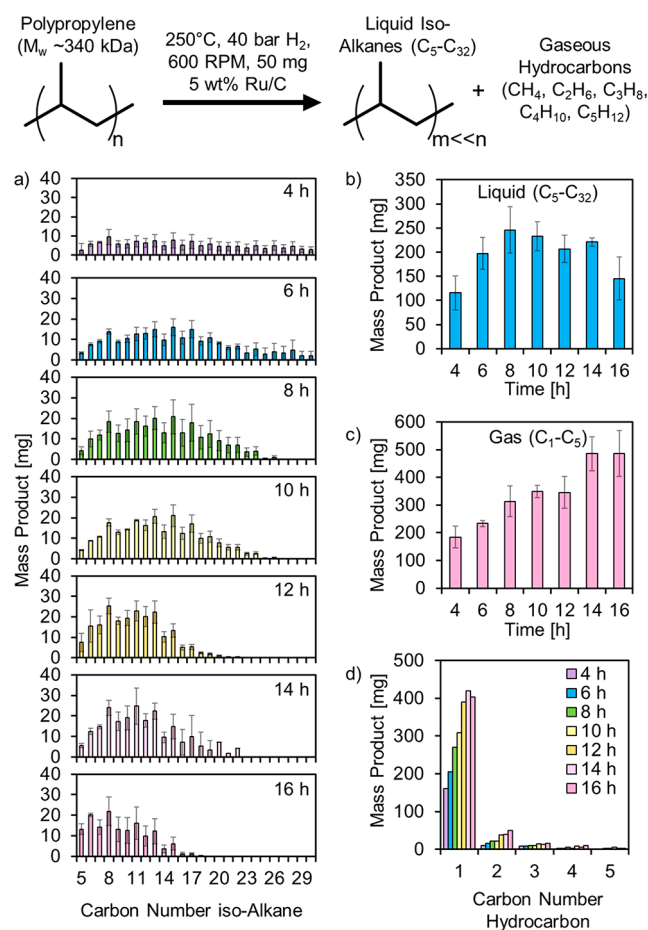
The first goal of this study was to identify suitable reaction conditions for PP hydrogenolysis to maximize the yield of liquid hydrocarbons, defined here as  $C_5$ – $C_{32}$  iso-alkanes. We started by investigating the hydrogenolysis of model PP (isotactic,  $M_w$  12,000 Da) using the optimal conditions identified in our previous study for the hydrogenolysis of linear low-density polyethylene (i.e., using a 5 wt % Ru/C at temperatures and pressures ranging from 200 to 225 °C and 20–30 bar  $H_2$ , respectively, with substrate to catalyst ratios ranging from 8:1 to 28:1).<sup>18</sup> PP beads were added directly to a 25 mL Parr reactor along with the catalyst and pressurized with hydrogen gas. The reactor was placed in an insulated aluminum block with a temperature-controlled heater. After the specified reaction time, the reactor was cooled to room temperature by quenching in an ice bath. Gaseous products were collected from the headspace and analyzed with GC-FID and GC-TCD to quantify  $C_1$ – $C_5$  alkanes and  $H_2$ . Liquid products were dissolved in acetone or toluene, then identified and quantified with GC-MS and GC-FID using 1,3,5-triisobutyl benzene as an external standard. Additional experimental details are provided in the [Supporting Information](#), along with a rigorous quantification scheme for the analysis of liquid and gaseous products ([Scheme S1](#)). As shown in [Figure 1](#), liquid iso-alkane yields of over 68% by mass were obtained from 700 mg of PP at 225 °C, 16 h, 20 bar  $H_2$ , 400 rpm, and 100 mg of 5 wt % Ru/C catalyst. From [Figure 1a](#), the liquid product distribution exhibited a yield of branched alkane products ranging from  $C_8$ – $C_{42}$  with a peak at around  $C_{24}$ . Gaseous products ([Figure 1b](#)) primarily comprised methane, with small amounts of ethane, propane, and butane. The



**Figure 1.** Hydrogenolysis of PP ( $M_w \sim 12,000$  Da,  $M_n \sim 5000$  Da) over ruthenium nanoparticles (5 wt %) supported on carbon: (a) liquid products quantified by GC-FID, (b) gaseous products quantified by GC-FID and GC-TCD, (c) picture of initial substrate, and (d) GC-MS spectra of liquid iso-alkane products dissolved in toluene. Reaction conditions: 225 °C, 16 h, 20 bar  $H_2$ , 400 rpm, 700 mg of isotactic PP, and 100 mg of catalyst. Raw data and the detailed quantification scheme are provided in the [SI](#), as well as additional reaction conditions screened.

gaseous product distribution is similar to that observed for PE hydrogenolysis over Ru/C,<sup>18</sup> however, the liquid products comprised a range of alkanes with varying degrees of branching ([Figure S1](#)).

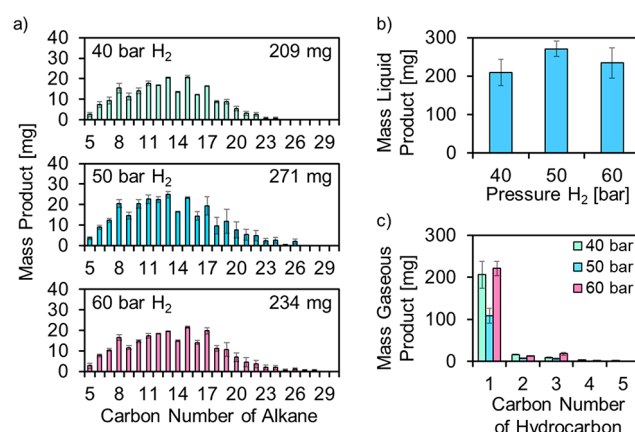
Depending on the application, PP is used in vastly different molecular weight ranges; thus, we turned our investigation to the hydrogenolysis of isotactic PP with an average molecular weight ( $M_w$ ) of 340,000 Da. To investigate the hydrogenolysis of this substrate over Ru/C, a series of reactions were performed with varying reaction time, temperature, and hydrogen pressure. [Figure 2](#) shows the product distributions as a function of time between 4 to 16 h for the hydrogenolysis of 340,000 Da PP beads (700 mg) under reaction conditions of 250 °C, 40 bar  $H_2$ , and 600 rpm. The liquid product distributions are shown in [Figure 2a](#). At early reaction times (4 h), the product distribution is very broad, ranging from  $C_5$ – $C_{32}$  hydrocarbons, with a significant fraction (62%) of insoluble iso-alkanes in the lubricant/wax range ( $C_{33+}$ ). As the reaction time is increased, the solid fraction is consumed, and the product distribution shifts to shorter alkanes. Eventually, between 8 and 12 h, the product distribution reaches a maximum yield of liquid products centered around  $C_{12}$ – $C_{15}$ , past which the C–C bonds continue to cleave, and the fraction of gaseous hydrocarbons increases ([Figure 2c](#)). The gaseous hydrocarbons are primarily composed of methane, which results from the cleavage of terminal C–C bonds. As shown in [Figure 2d](#), the masses of methane, ethane, propane, and butane produced increase with increasing extent of reaction. Indeed, under harsher reaction conditions (250 °C, 24 h, 50 bar  $H_2$ , 100 mg of 5 wt % Ru/C, 700 mg of PP, 600



**Figure 2.** Effect of reaction time on PP hydrogenolysis product distributions over Ru/C: (a) liquid product distributions as a function of time, (b) total liquid products obtained ( $\text{C}_5\text{--C}_{32}$ ), (c) total gaseous products ( $\text{C}_1\text{--C}_5$ ), and (d) gaseous product distributions as a function of time. Reaction conditions:  $250^\circ\text{C}$ ,  $40$  bar  $\text{H}_2$ ,  $600$  rpm,  $700$  mg of PP ( $M_w$   $340,000$  Da,  $M_n \sim 97,000$  Da), and  $50$  mg of  $5$  wt % Ru/C. Raw data are provided in the SI.

rpm), the PP substrate is completely converted to methane, ethane, and propane (Figure S2). Under slightly milder conditions for the complete conversion of PP into gaseous hydrocarbons ( $225^\circ\text{C}$ ,  $48$  h,  $50$  mg of  $5$  wt % Ru/C,  $40$  bar  $\text{H}_2$ ,  $700$  mg of polypropylene,  $600$  rpm), the selectivity toward ethane and propane relative to methane can be increased (Figure S2).

Comparable liquid hydrocarbon yields from PP ( $M_w$   $340,000$  Da) can be achieved by operating at lower reaction temperatures and extended reaction times. As shown in Figure 3a, the liquid product distribution for PP ( $340,000$  Da) hydrogenolysis at  $225^\circ\text{C}$  for  $24$  h closely resembles the distribution at  $250^\circ\text{C}$  for  $8$  h in Figure 2. The liquid yield at  $225^\circ\text{C}$  was further increased by optimizing the  $\text{H}_2$  pressure. As shown in Figure 3a and b, the liquid yield increases as the pressure is increased from  $40$  to  $50$  bar  $\text{H}_2$ , then decreases slightly from  $50$  to  $60$  bar  $\text{H}_2$ . The gaseous product distribution shown in Figure 3c shows that methane production is minimized at an intermediate pressure of  $50$  bar. In our previous study, we found  $20$  bar to be the ideal pressure for PE ( $M_w$   $4000$  Da) hydrogenolysis over Ru/C. This optimal pressure was thought to be due to the trade-off between suppressed methane formation at higher hydrogen pressures



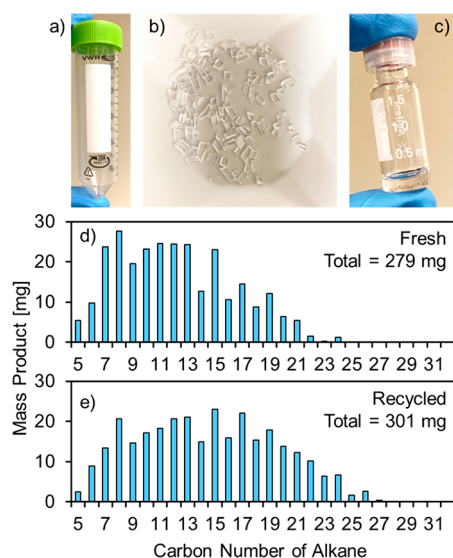
**Figure 3.** Effect of hydrogen pressure on the hydrogenolysis of PP ( $M_w \sim 340,000$  Da,  $M_n \sim 97,000$  Da). Reaction conditions:  $225^\circ\text{C}$ ,  $24$  h,  $600$  rpm,  $700$  mg of PP, and  $50$  mg of  $5$  wt % Ru/C: (a) liquid product distribution at  $40$ ,  $50$ , and  $60$  bar  $\text{H}_2$ , (b) mass liquid produced, and (c) gaseous product distribution. Raw data are presented in the SI.

and inhibiting effects of hydrogen pressure on the reaction rate.<sup>28,39</sup> From a combination of density functional theory and experiments, Hibbits et al. found that over Ir-based catalysts the extent to which hydrogen pressure inhibits hydrogenolysis rates depends on the hydrocarbon structure,<sup>39</sup> suggesting that the hydrogen activation steps, and thus the effect of hydrogen pressure on reaction kinetics, differ from PE to PP. Still, it is important to note that unlike model gas-phase systems which are free of mass transfer limitations, complex polymer melt systems require more careful consideration of hydrogen diffusion through the molten polymer to the Ru surface, suggesting that additional factors are likely important.

Depolymerization of the  $340,000$  Da PP substrate to liquid iso-alkanes ( $225^\circ\text{C}$ ,  $24$  h,  $600$  rpm) required slightly harsher reaction conditions than those used for the  $12,000$  Da PP sample ( $225^\circ\text{C}$ ,  $16$  h,  $400$  rpm). In addition to requiring more C–C bonds to be cleaved, polymer properties such as viscosity, melting point, and diffusivity may be responsible for this difference in activity. It is also worth noting that across Figures 1–3, the quantities of iso-alkanes with an even number of carbons are slightly lower than that of iso-alkanes with odd numbers of carbons, resulting in a lower concentration of alkanes terminating in  $\text{C}_2\text{--C}_1$  bonds relative to  $\text{C}_3\text{--C}_1$  bonds. This could be explained by differences in bond cleavage activity at tertiary–secondary C–C bonds relative to secondary–primary C–C bonds.<sup>28</sup>

With these optimized reaction conditions for the depolymerization of high molecular weight ( $340,000$  Da) PP ( $225^\circ\text{C}$ ,  $24$  h,  $600$  rpm,  $700$  mg of PP,  $50$  mg of  $5$  wt % Ru/C), we investigated the recyclability of the catalyst for PP depolymerization. To account for some loss of catalyst during the reaction workup, spent catalysts from identical reactions were separated from the products via centrifugation, collected, and dried overnight to evaporate the acetone solvent. This spent catalyst was then combined to perform replicate reactions with a recycled catalyst. As shown in Figure S3, Ru/C could be recycled and reused, yielding similar liquid product distributions with minimal reduction in activity. We note that while acetone was used in the workup to quantify products, solvents are not necessary to recover the catalyst, as the catalyst can be separated directly from the liquid products and reused.

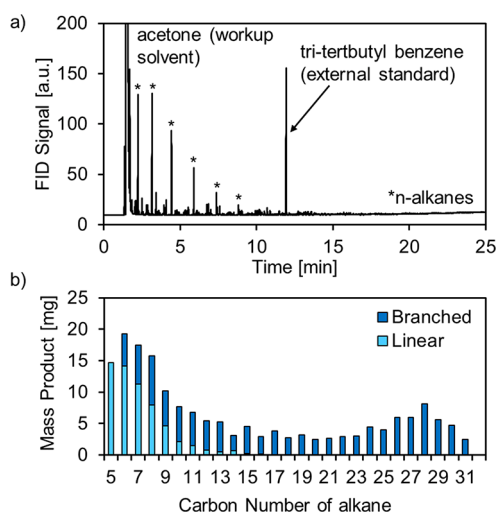
To demonstrate the proof of concept for the hydrogenolysis of realistic PP feedstocks, we used a plastic centrifuge tube as a waste PP substrate (Figure 4a). The clear sections of the tube



**Figure 4.** Hydrogenolysis of genuine postconsumer plastic substrate: (a) PP centrifuge tube, (b) clear plastic substrate sourced from centrifuge tube, (c) image of liquid product after hydrogenolysis, (d) product distribution for the liquid product over fresh catalyst, and (e) product distribution for hydrogenolysis of the plastic waste over recycled catalyst. Reaction conditions: 225 °C, 24 h, 50 bar H<sub>2</sub>, 600 rpm, 700 mg of PP, and 50 mg of 5 wt % Ru/C. Raw data are presented in the SI.

were cut into squares of approximately 3 mm by 3 mm and placed in the reactor with no pretreatment or solvent (Figure 4b). The resulting liquid products after performing hydrogenolysis over Ru/C (reaction conditions: 225 °C, 24 h, 50 bar H<sub>2</sub>, 600 rpm, 700 mg of PP, 50 mg of 5 wt % Ru/C) are shown in Figure 4c, with the quantified products shown in Figure 4d. As shown in Figure 4e, the catalyst could be recovered from the reaction and used again with minimal change in product distribution. A slight shift to higher molecular weight hydrocarbons over the spent catalyst is likely due to nanoparticle sintering during the reaction, as evidenced by transmission electron microscopy of the fresh and spent catalysts, which shows a shift in the average Ru particle diameter from 1.23 ± 0.61 to 1.78 ± 0.64 nm (Figure S4). The fact that the substrate could be used without any pretreatment or solvent, and that the catalyst could be recovered and recycled, is a promising step toward utilizing waste plastic streams.

To demonstrate the utilization of Ru/C for the hydrogenolysis of mixed plastic feeds, a mixture of PP (*M<sub>w</sub>* 340,000 Da) and HDPE was prepared and used as a model mixture for hydrogenolysis at 225 °C for 24 h under 40 bar H<sub>2</sub>. The resulting product was a clear liquid, which is characterized in Figure 5. From the raw chromatogram in Figure 5a, it is evident that the products contain a mixture of linear and branched alkanes. The linear *n*-alkanes are denoted by the asterisks and are centered around lower retention times, whereas the branched alkanes are more distributed throughout the chromatogram. Quantification of the linear and branched alkanes in Figure 5b reveals that the *n*-alkanes are centered around a carbon chain length of around 8 (*n*-octane), whereas



**Figure 5.** Hydrogenolysis of model mixture of polypropylene and polyethylene: (a) raw GC-FID signal of liquid products dissolved in acetone and (b) quantities of branched and linear liquid reaction products. Reaction conditions: 225 °C, 24 h, 40 bar H<sub>2</sub>, 600 rpm, 350 mg of PP (340,000 Da), 350 mg of HDPE (melt index 2.2), and 25 mg of 5 wt % Ru/C. Product quantities and additional reaction conditions are provided in the SI.

the branched alkanes range from C<sub>7</sub>–C<sub>32</sub>. This difference in product distribution suggests that the rate of hydrogenolysis was faster over the HDPE compared to the PP. The differences in reactivity of the substrates is an important consideration for developing product streams from mixed waste feedstocks with desired liquid properties. For example, for fuel applications, the ratio of branched alkanes will affect the cetane number.<sup>40</sup> This promising result highlights opportunities for producing tunable product streams by adjusting polyolefin feedstock composition, residence time, temperature, and additional reaction conditions.

## CONCLUSIONS AND OUTLOOK

In this study, ruthenium nanoparticles supported on carbon (5 wt % Ru/C) were shown to be effective heterogeneous catalysts for the depolymerization of PP plastic via hydrogenolysis under relatively low temperatures (225–250 °C) and hydrogen pressures (20–50 bar). Unlike PE hydrogenolysis, which produces linear *n*-alkanes, PP hydrogenolysis produces a range of iso-alkanes in both the liquid (C<sub>5</sub>–C<sub>32</sub>) and gas (C<sub>1</sub>–C<sub>5</sub>) ranges. Liquid iso-alkane yields of over 68% were achieved for the depolymerization of PP (*M<sub>w</sub>* 12,000 Da) under mild conditions (225 °C, 20 bar H<sub>2</sub>, 16 h) over 5 wt % Ru/C in the absence of solvent. Under slightly elevated conditions (225–250 °C, 50 bar H<sub>2</sub>, 6–24 h), higher molecular weight PP (*M<sub>w</sub>* 340,000 Da) could also be completely depolymerized into liquid and gaseous hydrocarbons. Through rigorous quantification of gaseous and liquid products, this study identified trade-offs between reaction time, temperature, and hydrogen pressure for PP depolymerization and demonstrated the feasibility and recyclability of Ru/C for the hydrogenolysis of genuine PP plastic waste and mixtures of PE and PP.

Challenges moving forward will include characterizing the mass transport of the system on both micro- and macro-molecular scales (e.g., diffusion of substrate to and from the active site, diffusion and activation of H<sub>2</sub>, solvation effects, viscosity, entanglement) and developing methods to increase

carbon selectivity toward central C–C bond cleavage to avoid loss of carbon and hydrogen to methane formation. Modification of nanoparticle size as well as investigation into acidic and confined supports (e.g., tandem hydrogenolysis/hydrocracking, shape selectivity) to suppress methane formation, improve liquid alkane yields, and lower hydrogen pressure requirements are currently underway. Ongoing work also includes conducting techno-economic analyses to compare hydrogenolysis to other methods of chemical recycling such as pyrolysis. Beyond ruthenium-based catalysts, investigation into earth-abundant alternatives to noble metals will be a critical step toward the economical chemical upcycling of waste polyolefins. By enabling targeted C–C bond cleavage of polyolefins, hydrogenolysis has the potential to give new value to waste plastics, producing tunable and high-quality liquid products that could replace fossil-derived resources to enable a circular plastic economy.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.1c03786>.

Materials and hydrogenolysis methods, quantification schemes and figures, supporting PP hydrogenolysis reactions, catalyst characterization, raw chromatograms, raw data, and additional screening of reaction conditions for PP and PP/PE hydrogenolyses (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

Yuriy Román-Leshkov – Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; [orcid.org/0000-0002-0025-4233](https://orcid.org/0000-0002-0025-4233); Email: [yroman@mit.edu](mailto:yroman@mit.edu)

### Authors

Julie E. Rorrer – Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; [orcid.org/0000-0003-4401-8520](https://orcid.org/0000-0003-4401-8520)

Clara Troyano-Valls – Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Gregg T. Beckham – Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory, Golden, Colorado 80401, United States; BOTTLE Consortium, Golden, Colorado 80401, United States; [orcid.org/0000-0002-3480-212X](https://orcid.org/0000-0002-3480-212X)

Complete contact information is available at: <https://pubs.acs.org/10.1021/acssuschemeng.1c03786>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Funding was provided by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office (AMO) and Bioenergy Technologies Office (BETO). This work was performed as part of the Bio-Optimized Technologies to keep Thermoplastics out of Landfills and the Environment (BOTTLE) Consortium and

was supported by AMO and BETO under Contract DE-AC36-08GO28308 with the National Renewable Energy Laboratory (NREL), operated by Alliance for Sustainable Energy, LLC. The BOTTLE Consortium includes members from MIT, funded under Contract DE-AC36-08GO28308 with NREL. J.E.R. is also supported by an Arnold O. Beckman Postdoctoral Fellowship. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

## ■ REFERENCES

- (1) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **2017**, *3* (7), No. e1700782.
- (2) Hong, M.; Chen, E. Y. X. Future Directions for Sustainable Polymers. *Trends Chem.* **2019**, *1* (2), 148–151.
- (3) Nicholson, S. R.; Rorrer, N. A.; Carpenter, A. C.; Beckham, G. T. Manufacturing energy and greenhouse gas emissions associated with plastics consumption. *Joule* **2021**, *5* (3), 673–686.
- (4) *The New Plastics Economy*; Ellen MacArthur Foundation, 2016; p 17.
- (5) *Chemical Economics Handbook (CEH): Plastics Recycling*; IHS Markit, 2020.
- (6) Al-Salem, S. M.; Lettieri, P.; Baeyens, J. Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Manage. (Oxford, U. K.)* **2009**, *29* (10), 2625–2643.
- (7) Mark, L. O.; Cendejas, M. C.; Hermans, I. The Use of Heterogeneous Catalysis in the Chemical Valorization of Plastic Waste. *ChemSusChem* **2020**, *13* (22), 5808–5836.
- (8) Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste Manage. (Oxford, U. K.)* **2017**, *69*, 24–58.
- (9) Chen, X.; Wang, Y.; Zhang, L. Recent Progresses in the Chemical Upcycling of Plastic Wastes. *ChemSusChem* **2021**, *1*, na DOI: [10.1002/cssc.202100868](https://doi.org/10.1002/cssc.202100868).
- (10) Rahimi, A.; García, J. M. Chemical recycling of waste plastics for new materials production. *Nat. Rev. Chem.* **2017**, *1* (0046), 1–11.
- (11) Ellis, L. D.; Rorrer, N. A.; Sullivan, K. P.; Otto, M.; McGeehan, J. E.; Román-Leshkov, Y.; Wierckx, N.; Beckham, G. T. Chemical and biological catalysts for plastics recycling and upcycling. *Nature Catalysis* **2021**, *4*, 539–556.
- (12) Serrano, D. P.; Aguado, J.; Escola, J. M. Developing Advanced Catalysts for the Conversion of Polyolefinic Waste Plastics into Fuels and Chemicals. *ACS Catal.* **2012**, *2* (9), 1924–1941.
- (13) Anuar Sharuddin, S. D.; Abnisa, F.; Wan Daud, W. M. A.; Aroua, M. K. A review on pyrolysis of plastic wastes. *Energy Convers. Manage.* **2016**, *115*, 308–326.
- (14) Kunwar, B.; Cheng, H. N.; Chandrashekar, S. R.; Sharma, B. K. Plastics to fuel: a review. *Renewable Sustainable Energy Rev.* **2016**, *54*, 421–428.
- (15) Yan, B.; Shi, C.; Beckham, G. T.; Chen, E. X.-Y.; Roman-Leshkov, Y. Breaking C-C Bonds via Electrochemically Mediated Hydrogen Atom Transfer Reactions. *ChemRxiv*, 2021. DOI: [10.26434/chemrxiv.14525619.v1](https://doi.org/10.26434/chemrxiv.14525619.v1).
- (16) Dogu, O.; Pelucchi, M.; Van de Vijver, R.; Van Steenberghe, 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 waste plastics via pyrolysis and gasification: State-of-the-art, challenges, and future directions. *Prog. Energy Combust. Sci.* **2021**, *84*, 100901.
- (17) Dufaud, V.; Basset, J.-M. Catalytic Hydrogenolysis at Low Temperature and Pressure of Polyethylene and Polypropylene to Diesels or Lower Alkanes by a Zirconium Hydride Supported on Silica-Alumina: A Step Toward Polyolefin Degradation by the Microscopic Reverse of Ziegler–Natta Polymerization. *Angew. Chem., Int. Ed.* **1998**, *37* (6), 806–810.
- (18) Rorrer, J. E.; Beckham, G. T.; Román-Leshkov, Y. Conversion of Polyolefin Waste to Liquid Alkanes with Ru-Based Catalysts under Mild Conditions. *JACS Au* **2021**, *1* (1), 8–12.

- (19) Zhang, F.; Zeng, M.; Yappert, R. D.; Sun, J.; Lee, Y.-H.; LaPointe, A. M.; Peters, B.; Abu-Omar, M. M.; Scott, S. L. Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* **2020**, *370*, 437–441.
- (20) Tennakoon, A.; Wu, X.; Paterson, A. L.; Patnaik, S.; Pei, Y.; LaPointe, A. M.; Ammal, S. C.; Hackler, R. A.; Heyden, A.; Slowing, I. I.; Coates, G. W.; Delferro, M.; Peters, B.; Huang, W.; Sadow, A. D.; Perras, F. A. Catalytic upcycling of high-density polyethylene via a processive mechanism. *Nat. Catal.* **2020**, *3* (11), 893–901.
- (21) Liu, S.; Kots, P. A.; Vance, B. C.; Danielson, A.; Vlachos, D. G. Plastic waste to fuels by hydrocracking at mild conditions. *Sci. Adv.* **2021**, *7*, No. eabf8283.
- (22) Ellis, L. D.; Orski, S. V.; Kenlaw, G. A.; Norman, A. G.; Beers, K. L.; Román-Leshkov, Y.; Beckham, G. T. Tandem Heterogeneous Catalysis for Polyethylene Depolymerization via an Olefin-Intermediate Process. *ACS Sustainable Chem. Eng.* **2021**, *9* (2), 623–628.
- (23) Jing, Y.; Wang, Y.; Furukawa, S.; Xia, J.; Sun, C.; Hulse, M. J.; Wang, H.; Guo, Y.; Liu, X.; Yan, N. Towards the Circular Economy: Converting Aromatic Plastic Waste Back to Arenes over a Ru/Nb<sub>2</sub>O<sub>5</sub> Catalyst. *Angew. Chem., Int. Ed.* **2021**, *60*, 5527–5535.
- (24) Jia, C.; Xie, S.; Zhang, W.; Intan, N. N.; Sampath, J.; Pfaendner, J.; Lin, H. Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants by hydrogenolysis over Ru catalyst. *Chem. Catalysis* **2021**, *1*, 437.
- (25) Sanchez-Rivera, K. L.; Huber, G. W. Catalytic Hydrogenolysis of Polyolefins into Alkanes. *ACS Cent. Sci.* **2021**, *7* (1), 17–19.
- (26) 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. *Appl. Catal., B* **2021**, *285*, 119805.
- (27) Lee, W.-T.; Bobbink, F. D.; van Muyden, A. P.; Lin, K.-H.; Corminboeuf, C.; Zamani, R. R.; Dyson, P. J. Catalytic hydrocracking of synthetic polymers into grid-compatible gas streams. *Cell Rep. Phys. Sci.* **2021**, *2* (2), 100332.
- (28) Nakagawa, Y.; Oya, S. I.; Kanno, D.; Nakaji, Y.; Tamura, M.; Tomishige, K. Regioselectivity and Reaction Mechanism of Ru-Catalyzed Hydrogenolysis of Squalane and Model Alkanes. *ChemSusChem* **2017**, *10* (1), 189–198.
- (29) Su, F.; Lv, L.; Lee, F. Y.; Liu, T.; Cooper, A. I.; Zhao, X. S. Thermally Reduced Ruthenium Nanoparticles as a Highly Active Heterogeneous Catalyst for Hydrogenation of Monoaromatics. *J. Am. Chem. Soc.* **2007**, *129*, 14213–14223.
- (30) Chandra, D.; Inoue, Y.; Sasase, M.; Kitano, M.; Bhaumik, A.; Kamata, K.; Hosono, H.; Hara, M. A high performance catalyst of shape-specific ruthenium nanoparticles for production of primary amines by reductive amination of carbonyl compounds. *Chem. Sci.* **2018**, *9* (27), 5949–5956.
- (31) Carrillo, A. I.; Schmidt, L. C.; Marín, M. L.; Scaiano, J. C. Mild synthesis of mesoporous silica supported ruthenium nanoparticles as heterogeneous catalysts in oxidative Wittig coupling reactions. *Catal. Sci. Technol.* **2014**, *4* (2), 435–440.
- (32) Bazargan, A.; McKay, G. A review - Synthesis of carbon nanotubes from plastic wastes. *Chem. Eng. J.* **2012**, *195–196*, 377–391.
- (33) Larrain, M.; Van Passel, S.; Thomassen, G.; Van Gorp, B.; Nhu, T. T.; Huysveld, S.; Van Geem, K. M.; De Meester, S.; Billen, P. Techno-economic assessment of mechanical recycling of challenging post-consumer plastic packaging waste. *Resour. Conserv. Recy.* **2021**, *170*, 105607.
- (34) Eagan, J. M.; Xu, J.; Di Girolamo, R.; Thurber, C. M.; Macosko, C. W.; LaPointe, A. M.; Bates, F. S.; Coates, G. W. Combining polyethylene and polypropylene: Enhanced performance with Pe/iPP multiblock polymers. *Science* **2017**, *355*, 814–816.
- (35) Teh, J. W.; Rudin, A.; Keung, J. C. A Review of Polyethylene-Polypropylene Blends and Their Compatibilization. *Adv. Polym. Technol.* **1994**, *13* (1), 1–23.
- (36) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRS Press: Boca Raton, FL, 2003.
- (37) Knyazev, V. D. Effects of Chain Length on the Rates of C-C Bond Dissociation in Linear Alkanes and Polyethylene. *J. Phys. Chem. A* **2007**, *111*, 3875–3883.
- (38) Gómez-Elvira, J. M.; Benavente, R.; Martínez, M. C. Correlation between chain microstructure and activation energy in the pyrolysis of a high molecular weight isotactic polypropylene. *Polym. Degrad. Stab.* **2015**, *117*, 46–57.
- (39) Hibbitts, D. D.; Flaherty, D. W.; Iglesia, E. Effects of Chain Length on the Mechanism and Rates of Metal-Catalyzed Hydrogenolysis of n-Alkanes. *J. Phys. Chem. C* **2016**, *120* (15), 8125–8138.
- (40) Lapuerta, M.; Hernández, J. J.; Sarathy, S. M. Effects of methyl substitution on the auto-ignition of C16 alkanes. *Combust. Flame* **2016**, *164*, 259–269.