Mixed polyolefine recycling from a composting plant: Monomer recovery for circular economy by Pyrolytic process

Davide Sorino[1], Lorenzo Bartolucci[2], Stefano Cordiner[2], Alessia Falsetti[1], Francesco Lombardi[1], Vincenzo Mulone[2]

[1]Department of Civil Engineering and Computer Science Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1, 00133, Rome, Italy
[2]Department of Industrial Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1, 00133, Rome, Italy
Presenting author email: davide.sorino@uniroma2.it

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According to Plastic Europe, global plastics production in 2022 amounts to 400.7 Mt, of which about 362.3 Mt were fossil-based [1]. However, European statistical data [2] reveals that only 30% of plastics were recycled, 40% were incinerated, and 30% ended up in landfills, causing serious environmental problems, despite the loss of valuable chemical and highly energetic products [3]. Plastic materials are less recycled compared to other materials consumed in large quantities, such as glass, paper, ceramics, and aluminum [4].

The plastic recycling process can be classified into primary, secondary, tertiary, and quaternary stages, according to the ASTM Standard D5033. When primary and secondary recycling fail, tertiary recycling (chemical recycling) can be a complementary alternative, as it can generate chemical compounds with high added value.

Chemical recycling by pyrolysis can break the polymer chains, and starting monomers can be formed, resulting in the starting polymer. At present, most works show the results of a pyrolytic process that is fed with virgin plastic [3], [5]. However, in this way, the issues of a real process, where plastic waste is collected after its use, and this implies possible contamination, cannot be highlighted.

A little-discussed issue is the treatment of plastic waste in composting plants. In fact, plastics contribute to reduced compost quality due to contamination by microplastics, and therefore need to be discarded through incineration or landfills. A composting plant can discard more than 4% [6] of incoming wet-based waste, leading to high operating costs, especially when these plastic streams end up in landfills.

There are several works in the literature in which LDPE, HDPE, and PP are pyrolytically processed using virgin products before consumer use [5][3]. Many of these works show how it is possible from plastics to obtain oil and gas, which may contain precursors such as ethylene, propylene, butene, and fuels such as naphthalene, paraffins, etc. However, post-consumer use, plastic waste undergoes contamination by various impurities, prompting the need for research to ascertain the optimal conditions for its treatment [7].

In this work, characterization followed by modeling of a pyrolytic process of plastics from the waste stream of a real composting plant was done.

Specifically, a merceological analysis was performed on the sample (EER code 191912). which showed the following fractions: 72.18% of plastic, 26.79% of biomass, 0.38% of paper, and 0.65% of other. the plastic fraction was isolated and then dried at 40°C for three days. By chloroform testing, the percentage of bioplastic and traditional plastic was evaluated, and 100 percent traditional plastic was observed. Next, for polymer identification, a densimetric analysis was conducted. Two mixtures of distilled water and ethanol, one with a density of 915 kg/m^3 and one with a density of 940 kg/m^3, were prepared. Polymers (mainly plastic bags) were immersed within these solutions, and this allowed the identification of 3 polymers: LDPE, HDPE, and PP, with a mass percentage of 62.18%, 9.81%, and 28.07%, respectively.

These polymers were then characterized by: TGA, CHNS, FT-IR, ICP-OES. These analyses were used to find out the thermal behavior, the possible amount of oil/wax obtainable, and the type of contaminants present which could worsen the quality of the output products, and to define the feedstock properties into the Aspen Plus model.

The latter was implemented in order to identify the best processing strategy for polyolefins chemical recycling in order to maximize the amount of output precursors, namely olefins such as ethylene, propylene, and butene [8]. In addition, the developed model also simulates the production of oil/wax, which through a steam-cracking process can be converted into the precursors of the starting polymers, i.e., olefines. The developed layout mainly includes four zones, one for pretreatment (washing, drying, grinding, and pelletizing), one for pyrolysis, one for olefin distillation, and one for oil/wax steam cracking for olefin production. The preliminary layout of the model is shown in fig.1.

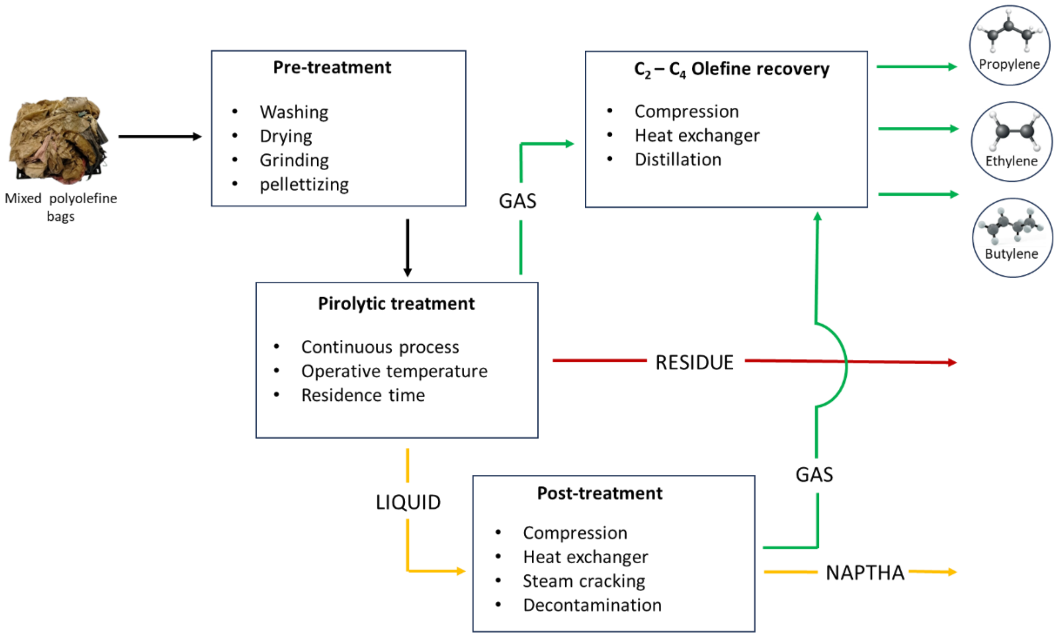

Figure 1 - Preliminary layout of chemical recycling plant model

Some of the results obtained from conducted TGA analysis are shown in Table 1.

Table 1 - Plastics thermogravimetric results

Polymer	Moisture (wt%)	Volatile (wt%)	Fixed carbon (wt%)	Ash (wt%)
PP	1.796 ± 0.635	94.520 ± 0.938	0.698 ± 0.119	2.982 ± 0.328
LDPE	0.356 ± 0.028	95.588 ± 0.1496	0.910 ± 0.028	3.128 ± 0.328
HDPE	0.725 ± 0.037	94.822 ± 0.327	1.507 ± 0.136	2.945 ± 0.175

The results shown by thermogravimetric analysis show that these polymers lend themselves very well to a pyrolytic process. In fact, the high amount of volatile matter, allows for high recovery of high value-added gaseous and liquid compounds, including olefins, which allow for closing the circle of circular economy.

[1] “Plasticsthefastfacts2023-1 (1).” Accessed: Jan. 15, 2024. [Online]. Available: https://plasticseurope.org/knowledge-hub/plastics-the-fast-facts-2023/

[2] “Plastics Europe.”

[3] Y. Jaafar, L. Abdelouahed, R. El Hage, A. El Samrani, and B. Taouk, “Pyrolysis of common plastics and their mixtures to produce valuable petroleum-like products,” *Polym Degrad Stab*, vol. 195, Jan. 2022, doi: 10.1016/j.polymdegradstab.2021.109770.

[4] E. Naderi Kalali, S. Lotfian, M. Entezar Shabestari, S. Khayatzadeh, C. Zhao, and H. Yazdani Nezhad, “A critical review of the current progress of plastic waste recycling technology in structural materials,” *Current Opinion in Green and Sustainable Chemistry*, vol. 40. Elsevier B.V., Apr. 01, 2023. doi: 10.1016/j.cogsc.2023.100763.

[5] A. F. Anene, S. B. Fredriksen, K. A. Sætre, and L. A. Tokheim, “Experimental study of thermal and catalytic pyrolysis of plastic waste components,” *Sustainability (Switzerland)*, vol. 10, no. 11, Oct. 2018, doi: 10.3390/su10113979.

[6] S. Bottausci, C. Magrini, G. A. Tuci, and A. Bonoli, “Plastic impurities in biowaste treatment: environmental and economic life cycle assessment of a composting plant,” *Environmental Science and Pollution Research*, 2023, doi: 10.1007/s11356-023-28353-8.

[7] M. Kusenberg *et al.*, “A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition,” *Fuel Processing Technology*, vol. 227, Mar. 2022, doi: 10.1016/j.fuproc.2021.107090.

[8] G. Yadav *et al.*, “Techno-economic analysis and life cycle assessment for catalytic fast pyrolysis of mixed plastic waste,” *Energy Environ Sci*, vol. 16, no. 9, pp. 3638–3653, Jun. 2023, doi: 10.1039/d3ee00749a.