**Chemical recycling of plastic marine litter using both commercial and coal ash zeolitic catalysts**

Maria Beatrice Falasconi1\*, Marco Cocchi1, Vincenzo Piemonte1, Lorenzo Cafiero2, Doina De Angelis2, Riccardo Tuffi2, Stefano Vecchio Ciprioti3

*1 Departmental faculty of engineering, Chemical-Physics Fundamentals in Chemical Engineering research unit, Campus Bio-Medico University, Via Alvaro del Portillo 21, 00128, Rome, Italy;*

*2 Department for Sustainability, ENEA, Casaccia Research Center, Via Anguillarese 301, 00123, S. Maria di Galeria, Rome, Italy;*

*3 Department SBAI, Sapienza University, Via del Castro Laurenziano 7, 00161, Rome, Italy;*

*\*Corresponding author E-Mail: maria.falasconi@unicampus.it*

**1.Introduction**

According to the principles of the Circular Economy, it is necessary to reduce the consumption of raw materials and increase the percentage of waste recycling. To this end, several decrees have been issued that encourage recycling, with strong focus on plastic waste [1]. In fact, the 350 Mt of plastics produced worldwide every year, with an ever increasing trend, are often disposed of inappropriately, causing serious environmental problems [2]. In particular, from 5 to 13 Mt of plastic end up in the sea, making up 40-80% of the so-called *Marine Litter* [3]. Marine plastic waste is a very heterogeneous mixture that is difficult to separate and mechanically recycle, but the European Union, in its "Action Plan for the Circular Economy", discourages landfills and incinerators [4]. Another particularly problematic waste is the *Coal Fly Ash* (CFA). About 6 Gt/y of coal is consumed and 1 Gt/y of CFA is generated from it [5]. This abundant industrial waste is considered by current legislation as a non-hazardous special waste, which is then stockpiled in open landfills, potentially causing water and soil pollution. This represents a material loss since CFA are rich in minerals, in particular metal oxides (such as SiO2 and Al2O3) which make them suitable for many applications, such as the production of concrete and bricks and in the ceramic industry. Catalysts obtained from CFA constitute a higher value-added product, but there are still no applications on the industrial scale. This is the background to the present work, which proposes a chemical recycling process, pyrolysis, of plastic marine waste combined with the synthesis of a low-cost zeolitic catalyst from CFA. Pyrolysis is a thermochemical decomposition process of organic materials, achieved by providing heat in an inert environment. In order to reduce the energy consumption and improve the quantity and quality of the liquid product compared to conventional thermal pyrolysis, various commercial and CFA-produced zeolitic catalysts are used. In particular, an attempt was made to understand how the acidity of the zeolites affects the pyrolysis products. This study is a development of previous works that tried to optimize the synthesis process of zeolites from CFA [6] and to apply these zeolites in the pyrolysis of homogeneous plastic waste [7]. The present work, therefore, aims to evaluate a possible recovery of material through chemical recycling from a heterogeneous plastic waste of marine origin, partly aged, thus avoiding an expensive selection (which would be indispensable in the case of mechanical recycling) and examining the effect of the acidity of the zeolitic catalyst used in the process. This work was carried out on a laboratory-scale at the ENEA Casaccia Research Center.

**2. Methods**

The five macro-phases, shown in *Figure 1*, outline the logical/temporal development of the present work:

**Figura 1.** Logical/temporal development of the present work.

**3. Results and discussion**

The product analysis of the marine waste sample showed that it is composed by almost 50% w/w of polypropylene (PP) and more than 50% w/w of polyethylene (PE). Subsequent characterization analysis showed that the sample is an ideal feed for the pyrolysis process. In fact, the proximate analysis obtained about 99% of volatile matter and low ash and humidity contents, which means that almost the entire mass can be converted into an oil or a gas. The ultimate analysis showed a high C and H content and a low content of heteroatoms, which makes the sample suitable for producing an interesting fuel, confirmed by the LHV of about 42 MJ/kg, which is comparable to that of conventional liquid fuels. Thermal analysis determined a sample decomposition temperature of 472°C and a total degradation heat required for the pyrolysis process of almost 2 MJ/kg which corresponds to 4.8% of the PCI of the feedstock. Thermal analysis also revealed the presence of both LDPE and HDPE within the sample, this distinction was not detected by infrared spectroscopy analysis. The use of catalysts has resulted in a more or less significant decrease in the degradation temperatures and thus in the required degradation heat. This was more significant for acidic zeolites, especially those with large pore structures such as HY and HX.

Once the optimal chemical-physical properties of the sample were ascertained, thermal (at 450 and 600°C) and catalytic (at 450°C) pyrolysis tests were carried out. It is found that the use of catalysts generally prevents the production of heavy oils/tar, in favor of lighter fractions. In particular, the use of acid catalysts, such as HX, HY and HZ, compared to the basic ones, such as CFA as it is and NaX, also prevent the production of wax which is an annoying by-product that can lead to problems of clogging in plants and in pipes. The yields of the various pyrolysis products were then compared and a particular focus was made on the composition of the oils, as it is the product of greatest interest.

It is important to emphasize the effectiveness of HX synthesized by CFA, which gave excellent results both in terms of yield (almost 90%) and light oil composition, on a par with the widely used but expensive commercial HY. HZ on the other hand, compared to thermal pyrolysis, did not improve the aliphatic composition, but results in the production of moderate amounts of monoaromatic compounds, such as benzene, toluene, xylene and cumene.

**4. Conclusions**

This study represents a first step for the exploitation of mixed plastic marine litter into valuable fuels and chemicals.

In fact, the physico-chemical characterization of the sample shows optimal properties, such as a high LHV, a high content of volatile substances and a very low concentration of heteroatoms, making the sample an ideal feed for the pyrolysis process. It was calculated that the process would require a total degradation heat of almost 2 MJ/kg, which corresponds to 4.8% of the exploitable energy of the input material.

These results are confirmed by pyrolysis tests carried out in a laboratory-scale set-up. In thermal pyrolysis, a greater amount of light oil (which is the most valuable product) is produced at the operating temperature of 450°C in comparison to the tests conducted at 600°C. Consequently, all the catalytic tests were carried out at 450°C. All catalysts inhibited heavy oil production, but the use of acid catalysts also prevented wax production, showing the best results. In particular, HX/CFA, the catalyst synthesized from CFA in the ENEA Laboratory, produced a light oil with a yield of about 90% by weight and with a high content of short-chain aliphatic hydrocarbons, obtaining results very similar to those obtained with commercial HY, which is renowned as being effective, but expensive, in cracking processes. The HZ, on the other hand, converted about half of the plastic sample into a gaseous mixture and the related oils are also rich in aromatic hydrocarbons. There were some problems with the gas analysis due to a partial loss of gases during several tests, resulting in not comparable replicates although yields and compositions of the oils always are.

A possible future outcome of this work is a technical-economic analysis for a pilot and industrial-scale implementation, including assessments of the regeneration of the zeolitic catalyst.

The application of the model to study the acidity of zeolites requires further tests on zeolites with different acidities.

**References**

[1] ISPRA, “Rapporto Rifiuti Urbani ISPRA 2020.”

[2] P. Europe, “Plastics – the Facts 2020,” *PlasticEurope*, p. 16, 2020.

[3] M. E. Iñiguez, J. A. Conesa, and A. Fullana, “Marine debris occurrence and treatment: A review,” *Renew. Sustain. Energy Rev.*, vol. 64, pp. 394–402, 2016, doi: 10.1016/j.rser.2016.06.031.

[4] C. Europea, “L’anello mancante - Piano di azione dell’Unione Europea per l’economia circolare,” pp. 1–23, 2015, [Online]. Available: https://eur-lex.europa.eu/resource.html?uri=cellar:8a8ef5e8-99a0-11e5-b3b7-01aa75ed71a1.0009.02/DOC\_1&format=PDF.

[5] IEA, “IEA 2018.” https://www.iea.org/data-and-statistics/?country=WORLD&fuel=Coal&indicator=CoalConsBySector.

[6] G. Verrecchia *et al.*, “Study of the parameters of zeolites synthesis from coal fly ash in order to optimize their CO2 adsorption,” *Fuel*, vol. 276, no. March, 2020, doi: 10.1016/j.fuel.2020.118041.

[7] P. Nardozzi, “Utilizzo di catalizzatori a basso costo in processi di pirolisi sul residuo di un impianto di riciclo plastica da imballaggio,” Università Campus Biomedico di Roma.