# Valorization of municipal solid waste through pyrolysis and applications of its products

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## Introduction

Thermochemical valorization offers an alternative management to traditional landfill disposal, promoting material recycling, circular economy, reducing greenhouse gas emissions, and decreasing costs. Among all thermochemical technologies, pyrolysis has gained considerable attention in recent years due to its flexibility in generating a combination of solid, liquid, and gaseous products, depending on the operational parameters. Pyrolysis can produce high value-added products, such as precursors for bioplastics, biopolymers, adsorbents, fertilizing substrates, or biofuels, from solid wastes. Thus, pyrolysis is seen as a promising route for waste valorization (Hasan *et al*, 2021).

CIEMAT (Center for Energy, Environmental and Technological Research) is analyzing the potential of pyrolysis to transform residues into intermediate products for further applications, such as biofuel, activated carbon for $CO_2$ adsorption, or synthesis of bio-plastics, among others. This work is part of the RETOPROSOST-2-CM Program aimed at sustainable production and industrial symbiosis relations between companies in the productive sector of the Community of Madrid (Spain). One of the main objectives of the project is the reduction of the environmental impact related to the management and treatment of solid waste generated.

In the present work, municipal solid waste (MSW) from ECONWARD treatment plant was selected to be subsequently subjected to a pyrolysis process. Studies are carried out at laboratory scale and the bio-oil, biochar, and non-condensable gases obtained during pyrolysis are analysed and their potential applications are studied.

## Material and Methods

MSW generated from ECONWARD treatment plant, a company associated with the program was selected for thermochemical valorization via pyrolysis. Firstly, the MSW physicochemical characterization, including proximate and ultimate analysis, was performed according to European standards. TGA was performed in a Mettler Toledo TGA 2 STAR SYSTEM, about 15 mg of the sample were subjected to different heating rates (5, 10, and 20ºC/min) in a temperature range from 30ºC to 900ºC using nitrogen at 50 ml/min.

Pyrolysis tests were subsequently carried out at laboratory scale in a fixed bed reactor of 21,8 mm O.D, 385 mm L, providing a 143 ml capacity. The sample, 30 g, was subjected to a heating rate of 63ºC/min, in nitrogen atmosphere with a flow rate of 343 ml/min, until a final temperature of 500ºC was reached and then maintained for 15 minutes. Condensable gases were collected in two gas washing bottles, introduced in a thermostatic bath at -10ºC. An Agilent Model 7890A chromatograph coupled to an Agilent 5975C mass spectrometer was used for chromatographic analysis of the bio-oil, and the gas was analyzed online in a HP-5890 series II coupled to a TCD.

In the next stage, the solid biochar fraction has been subjected to a physicochemical characterization, including proximate and ultimate analysis, determination of BET Surface Area and its ability for $CO_2$ uptake is being studied. To that goal, the performance of raw and activated biochar will be compared. The activation of biochar is conducted by two techniques, chemical and physical activation. $CO_2$ capture study is carried out on Mettler Toledo TGA 2 STAR SYSTEM thermobalance. The sample is subjected through three stages, first is heated in $N_2$ atmosphere up to 120ºC to remove moisture. Then it is cooled to room temperature and afterwards the $N_2$ flow rate is changed to $CO_2$. The sample adsorbs $CO_2$ until constant mass is achieved. By difference the amount of $CO_2$ adsorbed per unit mass of biochar sample is calculated.

## Results and discussion

From the proximate and ultimate analysis of MSW a high presence of ashes is observed, reducing the bio-oil yield, and increasing the char during the pyrolysis process, and it also reduces the calorific value of the sample. Despite that fact, the high availability and low price of MSW is a major feature for it to be considered as a good feedstock for pyrolysis.

According to the TGA and DTGs curves, four different steps of thermal degradations are determined. Regarding pyrolysis process, bio-oil, char, and gases yield obtained were 37%, 43%, 20%, respectively. Chromatogram of the most predominant compounds in the bio-oil are shown in Figure 1. Some valuable compounds are obtained, for instance, styrene monomer is obtained in high proportions, which may be upgraded and isolated to be used in an industrial symbiosis approach. Other aromatic compounds like Benzene, Toluene and Ethylbenzene are present in the liquid fraction obtained.

Subsequently the physicochemical characterization of the biochar shown in Table 1, studies will focus on their activation and assessment of performance as an adsorbent. As shown in Table 1, the low BET surface area obtained in the raw biochar sample provides a low $CO_2$ adsorption capacity.

Consequently, the activation studies will be focused on improving the $CO_2$ uptake, via chemical and physical activation. Chemical activation consists of doping the char with a chemical agent, in this case a 1M KOH solution is used. Then, the sample is submitted to high temperatures (800ºC) for 1 hour under a $N_2$ flow. Finally, the activated biochar is washed with deionized water up to neutral pH and leaving it to dry. On the other hand, physical activation consists of a single step method, the biochar is heated to temperatures higher than 700ºC to an activating gas ($CO_2$) for 2 hours (Cha *et al*, 2016). A comparison of the physicochemical characteristics obtained for both methods will be undertaken.

Table 1. Physicochemical analysis of raw MSW and Biochar.

| Parameters | MSW | Biochar |
|---|---|---|
| Chemical Composition | - | - |
| Carbon (%) | 41 | 41 |
| Hydrogen (%) | 5,5 | 2,7 |
| Nitrogen (%) | 1,8 | 2,1 |
| Oxygen (%) | 28 | 8,3 |
| Sulfur (%) | 0,44 | 0,80 |
| Ash (%) | 23 | 45 |
| BET ($m^2/g$) | Nd | 3,19 |
| Porosity (%) | Nd | 64,74 |
| Adsorption Capacity (%) | Nd | 1,12 |

n.d. not determined

## Conclusions

Despite the high amounts of ashes in the MSW, a significant bio-oil yield, 37%, is obtained in the pyrolysis process. The chromatographic analysis of the bio-oil shows a high presence of organic compounds, but also the presence of significant value products, like Styrene monomer and BTEX. Next studies will focus on the upgrading and transformation of the bio-oil fraction.

From the characterization of biochar, a large decrease in oxygen content compared to MSW is observed and a low BET surface area is obtained. Due to the variable composition of MSW and the possible presence of pollutants, the application of biochar as a fertilizer is rejected. For that reason, higher added value applications are investigated, and studies will look into its activation to increase the BET surface area and its application as a $CO_2$ adsorbent. Other residues, such as beer bagasse, from companies associated with the project will be selected to enhance synergies of the pyrolysis products.

## References

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