

# Engineering biochar catalysts for plastic pyrolysis via a cold plasma treatment.

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## Highlights

- The concentration of Bronsted acid sites in biochar doubles after a 10 min plasma treatment.
- The plasma-modified catalysts showed an enhanced activity in polypropylene pyrolysis.
- After plasma treatment, the aromatic content in the liquid product increased by 4 times.
- The catalysts retained their textural properties, over multiple runs.

## 1. Introduction

The persistent accumulation of plastic waste poses a growing environmental concern, with millions of tons ending up in landfills, oceans, or being incinerated every year. Among different recycling methods, pyrolysis of polypropylene (PP)/ polyethylene (PE) mixed plastic waste has emerged as a promising thermochemical process for transforming waste plastics into valuable liquid fuels. However, pyrolysis of plastics like PP and PE often suffers from low product selectivity, formation of undesired heavy waxes, and the need for high operating temperatures. The use of catalysts can significantly enhance the process by promoting selective cracking reactions, lowering energy requirements, and improving product yield. Biomass-derived catalysts are considered as green catalysts, being inexpensive, sustainable, reusable, and environmentally benign. Biochar is a porous, carbon-rich material produced via the pyrolysis of biomass has gained considerable interest as a sustainable catalyst for acid catalyzed reactions. However, it is difficult to obtain a high efficiency of the pristine biochar in plastic pyrolysis because of the poor surface functionality pristine biochar and limited mesoporosity. While often effective in modification, wet chemistry approaches require harsh chemicals, generate hazardous waste, and consume large amounts of energy, limiting their sustainability. An emerging alternative is a cold plasma treatment with CO<sub>2</sub> gas which is a dry, reagent-free method that uses ionized gas to selectively introduce carboxylic groups. Non-thermal plasmas are effective for material processing because of the highly non-equilibrium characteristics of plasma with the coexistence of high energy electrons.

In this study, a CO<sub>2</sub> dielectric barrier discharge (DBD) plasma was used to process the biochar obtained by pyrolysis of wood before it was applied as a catalyst for the pyrolysis of plastic waste.

## 2. Methods

The catalyst pellets were prepared by blending biochar (60 wt%) and starch (40 wt%) as a binder, with the addition of water to facilitate mixing. The blend was then compressed into 2 mm extrudates. The extrudates were oven-dried at 100 °C for 12 hours to remove excess moisture. Then they were crashed and sieved to obtain 250–355 μm fraction. These pellets were placed in a glass DBD plasma reactor before introducing the discharge. The reactor comprises a central stainless steel rod serving as the high-voltage electrode, and an outer stainless steel sheet (100 mm long) that functions as the ground electrode. The CO<sub>2</sub> gas or CO<sub>2</sub>/Ar mixture was used as the working gas for the discharge. The pellets were treated with different treatment times (1, 2, 5, 10 and 20 min).

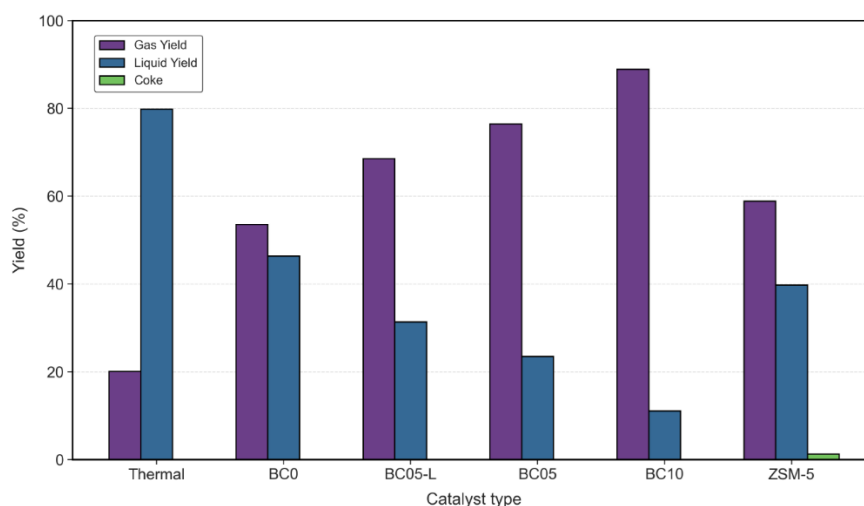
The plastic pyrolysis experiments were conducted in a stainless steel fixed-bed reactor (length: 200 mm and o.d. 27.7 mm) heated by an inductive coil connected to an inductive heating generator (EasyHeat, Ambrell UK). Volatile pyrolysis products were condensed in a condenser maintained at 2 °C. The non-condensable gases were collected in a separate vessel. The gas and liquid samples were characterized by a gas-chromatograph equipped with TCD and FID detectors. Further details about product analysis

are described in Ref [1]. The catalysts before and after pyrolysis reaction were characterized with N<sub>2</sub> chemisorption, FTIR analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy and <sup>13</sup>C-NMR spectroscopy. The concentration of acid sites was determined by Boehm titration.

### 3. Results and discussion

The gas composition in the DBD plasma system plays a crucial role in determining the nature and density of reactive species available for surface functionalization. The CO<sub>2</sub> plasma treatment successfully altered the biochar's surface chemistry, even at short treatment times. The highest concentration of carboxyl groups of 3.02 mmol/g was obtained after a plasma treatment for 10 min using an equimolar mixture of CO<sub>2</sub> and Ar. The intensity of band at 185 ppm, associated with carboxylic functional groups, considerably increased in the C-NMR spectra. This suggests surface oxidation and incorporation of oxygen-containing species to the biochar structure. The intensity of this band increases further at longer plasma processing times. The plasma treatment also improves mesoporosity with the mean pore size in the 25-30 nm region. This is consistent with literature data and can be explained by the formation of new mesopores due to partial collapse or shrinkage of larger mesopores and macropores. Plasma treatment tends to etch the biochar surface, opening smaller pores while simultaneously densifying or deforming the existing pore walls. The net result is a shift in the pore structure toward smaller, more numerous pores, contributing to a finer and more heterogeneous porous network [2].

The pyrolysis experiments demonstrate that plasma treatment enhances the formation of ethylene at the expense of liquid products (Figure 1). This shift in product distribution is attributed to the introduction of strong acid sites after the plasma treatment.



**Figure 1.** Gas, liquid and solid yields from PP pyrolysis using untreated biochar (BC0) and plasma-treated biochar catalysts BCx. The index x designates treatment time in minutes. ZSM-5 reference catalyst is shown for comparison.

### 4. Conclusions

CO<sub>2</sub> DBD plasma treatment was employed to directly modify the biochar surface without the use of chemicals. Compared with the pristine biochar, the plasma-treated sample exhibited an increase in oxygen content of more than 20%, mainly due to the enhanced presence of C=O and COOH functional groups on the biochar surface. The treated biochar showed a developed surface area and pore structure, which resulted in an enhanced catalytic activity in PP pyrolysis.

### References

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### Keywords

non-thermal plasma; surface functionalization; biochar modification; plastic pyrolysis.