

Carbon-based biomass-derived catalyst for deoxygenation of fast pyrolysis bio-oil

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Introduction

Biomass is an interesting alternative for replacing conventional fossil sources with a highly available renewable feedstock while enabling zero net greenhouse gases emissions. Particularly, pyrolysis of biomass residues enables the production of bio-oil, a mixture of oxygenated hydrocarbons with a high calorific value, which can be upgraded to biofuels or value-added chemicals. This work studies the catalytic fast pyrolysis of olive stone using carbon-based catalysts with different acidic strengths, reporting its influence on the product yields, distribution, and composition of the different fractions.

Experimental

The pyrolysis of olive stone (OS), a biomass residue, with a particle size between 200 and 500 μm has been carried out by three different pyrolysis methods (conventional, fast and catalytic fast pyrolysis) using a fixed bed reactor under nitrogen flow, at a temperature of 500 $^{\circ}\text{C}$. For the conventional pyrolysis, nitrogen flow rate of 150 ml/min (STP) and heating ramp of 10 $^{\circ}\text{C}/\text{min}$ were used, whereas 700 ml/min (STP) and 200 $^{\circ}\text{C}/\text{s}$ were established for fast and catalytic fast pyrolysis, resulting in a gas residence time of 1 s.

For the catalytic fast pyrolysis experiments, three different catalysts were tested: i) commercial $\gamma\text{-Al}_2\text{O}_3$; ii) an activated carbon prepared by chemical activation of olive stone with phosphoric acid (AC), and iii) the same activated carbon loaded with Zr (ACZr). The total acidity and acid strength distribution of the three catalysts was determined by temperature programmed desorption of ammonia (NH_3 -TPD).

In every catalytic reaction, the selected ratio biomass/catalyst was 15. A condenser system was set at the reactor outlet to collect the condensable vapors, which were characterized by mass spectrometer gas chromatography (GC-MS) and by Karl Fischer to determine the water content, meanwhile the non-condensable gases were analyzed by a Siemens Ultramat 23 and Calomat systems.

Results

The activated carbon catalysts showed a well-developed BET surface area (value higher than 1100 m^2/g), a wide microporosity ($V_{\text{mic}} > V_{\text{DR}}$) and a large mesopore volume (V_{mes} of ca. 0.40 cm^3/g), as can be seen in Table 1. When Zr was loaded into the AC catalyst, the surface area and micropore volume decreased 10%, while mesopore volume dropped 20%. Differently, the $\gamma\text{-Al}_2\text{O}_3$ catalyst showed less developed porosity than those of the two carbon-based catalysts. XPS results revealed the presence of phosphorous groups on AC, which were preserved after the loading of zirconium on the ACZr sample. The Zr concentration determined by XPS in ACZr was lower than that of Zr in the bulk, pointing out the preferential location of the metal in the inner surface (porosity) of the carbon support. In terms of acidity, the alumina catalyst showed the highest total amount of desorbed ammonia (535 $\mu\text{mol}/\text{g}$), followed by ACZr and AC catalysts (175 and 128 $\mu\text{mol}/\text{g}$, respectively) [1]. These carbon-based catalysts desorbed most of the ammonia at 200 $^{\circ}\text{C}$, as a consequence of the weak acidic strength of their catalytic sites. The addition of Zr to the activated carbon catalyst (AC) increased the total weak acidity, which could be associated to the presence of zirconium phosphate groups that act as acid

sites. However, the alumina catalyst showed greater amount of sites with weak and moderate acid strength, with NH₃ desorption peaks at 200 and 300 °C.

Table 1. Textural parameters derived from N₂ ads-des at -196 °C, mass surface concentration obtained by X-ray photoelectron spectroscopy (XPS) and ammonia TPD.

Sample	N ₂ ads-des			XPS Mass Surface Concentration (%)					TPD-NH ₃
	A _{BET}	V _{mic}	V _{meso}	C	O	P	Zr	Al	NH ₃ (μmol/g)
	(m ² /g)	(cm ³ /g)	(cm ³ /g)						
γ-Al ₂ O ₃	180	<0.01	0.45	-	54.5	-	-	45.5	535
AC	1280	0.52	0.43	88.2	8.2	3.3	-	-	128
ACZr	1130	0.47	0.39	61.2	30.5	4.4	3.9	-	175

Bio-oil was identified as the most abundant fraction of pyrolysis of olive stone, no matter the heating rate used, as shown in Table 2. Specifically, the fast pyrolysis produced higher content of liquid fraction (68 wt.%) than that obtained during conventional pyrolysis, due to fast pyrolysis decreased the gas residence time, so that the volatile products leaved the isothermal zone quickly, with cracking and/or repolymerization reactions occurring to a lesser extent. In the catalytic fast pyrolysis, the acid character of the catalysts favored the cracking and deoxygenation reactions that reduced the production of the liquid fraction (55, 46 and 47 wt.% with γ-Al₂O₃, AC and ACZr, respectively).

Table 2. Yield (wt.%) values of the different fractions from pyrolysis of OS at 500 °C, using a ratio biomass/catalyst of 15.

Type of pyrolysis	Catalyst	Solid (wt.%)	Liquid (wt.%)	Gas (wt.%)
Conventional	-	26.7	57.5	15.86
Fast	-	19.3	67.6	13.1
Catalytic fast	γ-Al ₂ O ₃	19.6	55.1	25.3
	AC	21.0	45.7	33.3
	ACZr	18.6	46.7	34.7

The bio-oils produced showed an organic and an aqueous fraction well differentiated. The fast pyrolysis decreased the aqueous fraction yield compared to conventional one (9.3 and 17.7 %wt., respectively) and increases the pH (1.7 and 1.4, respectively), resulting in a less acid bio-oil. The catalyzed fast pyrolysis produced a further decrease of the aqueous fraction (6.7, 5.7 and 4.2 for γ-Al₂O₃, AC and ACZr catalyst, respectively). ACZr showed the best catalytic performance, achieving the lowest acid, a pH of 2, and water contents. The increase of pH is a favorable aspect, because acid compounds are responsible for a low stability of the bio-oil and also catalyzes dehydration and repolymerization reactions producing an increase of viscosity.

The main compounds identified in the bio-oil obtained from different pyrolysis (conventional, fast and catalytic fast pyrolysis) at 500 °C through GC/MS were acids and phenols. For the catalytic fast pyrolysis, the use of an acid catalyst in pyrolysis favored the deoxygenation of the bio-oil, resulting in an increase of the phenol content and a decrease of acid species. The extent of this trend was enlarged when the carbon-based

catalysts were used. On the other hand, in the non-condensable fraction, whose yield was increased with the use of catalyst (Table 2), the main gases obtained were CO, CO₂, CH₄ and H₂. A clear increment in the content of CO from 1 to 5 mmol_{gas}/g_{biomass} and a smaller increase in CH₄ content could be observed when the catalysts were used. Thus, the main oxygen removal from the bio-oil of CFP seemed to be promoted via decarbonylation reactions, which were favored in the presence of catalysts. The formation of CO and methane was greatly enhanced on the carbon-based catalysts, probably due to the higher surface area and the presence of wide mesopores, turning more accessible the active sites on micropores, which can promote aromatic condensation reactions, as reported for microporous zeolites [2].

Acknowledgements

This research has been funded by Spanish Ministry of Science and Innovation and NextGenerationEU/PRTR through RTI2018-097555-B-I00 and TED2021-131324B-C21 projects. M.C.R.R. gratefully acknowledges MCINN for FPI grant (PRE2019-089340).

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