



WCCE11 - 11th WORLD CONGRESS OF CHEMICAL ENGINEERING

IACCHE - XXX INTERAMERICAN CONGRESS OF CHEMICAL ENGINEERING
CAIQ2023 - XI ARGENTINIAN CONGRESS OF CHEMICAL ENGINEERING
CIBIQ2023 - II IBEROAMERICAN CONGRESS OF CHEMICAL ENGINEERING

Buenos Aires - Argentina - June 4-8, 2023

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Catalytic fast pyrolysis of olive stone for bio-oil deoxygenation.

María del Carmen Recio-Ruiz, Ramiro Ruiz-Rosas, Juana María Rosas,
José Rodríguez-Mirasol, Tomás Cordero.

Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Andalucía Tech., Campus de Teatinos s/n, 29010 Málaga, España email: jmrosas@uma.es

Producing energy and chemicals from biomass is an interesting alternative by substitution of conventional fossil sources with a renewable feedstock while enabling zero net greenhouse gases emissions. Pyrolysis is a well-known process, which can produce fuels and chemicals from biomass.

In this work, conventional, fast and catalytic fast pyrolysis of olive stone residues were studied. The objective is to deoxygenate the liquid fraction with the use of catalysts with different acidic strengths, and thus study their influence on the yields, products distribution and composition of the different fractions.

The reactions were carried out in a fixed bed reactor under nitrogen flow, at 500 °C. Three catalysts were selected for the catalytic fast pyrolysis, a commercial catalyst with mild acidity, $\gamma\text{-Al}_2\text{O}_3$, an activated carbon from olive stones (AC) prepared by chemical activation with phosphoric acid and the same activated carbon loaded with Zr as active phase (ACZr). In every catalytic reaction, the selected ratio biomass/catalyst was 15. In the catalytic fast pyrolysis, the catalyst was placed inside the reactor. A condenser system was set at the reactor outlet to collect the condensable gases, which were characterized by mass spectrometer gas chromatography (GC-MS), meanwhile the non-condensable gases were analyzed by a Siemens Ultramat 23 and Calomat systems.

The results showed that fast pyrolysis has a higher content of liquid fraction (64 %wt) than that obtained in conventional pyrolysis (52 %wt), due to cracking reactions occur at a lesser extent. In the catalytic fast pyrolysis, the acid character of the catalysts favors the cracking and deoxygenation reactions that reduce the production of the liquid fraction (53, 41 and 43 %wt with $\gamma\text{-Al}_2\text{O}_3$, AC and ACZr, respectively). Regarding the liquid composition, an increase in the phenols species and a decrease in the acid species can be highlighted, due to deoxygenation reactions, which are favored by the acid catalysts. On the other hand, in the non-condensable fraction, whose yield is increased, the main gases obtained were CO, CO₂, CH₄ and H₂. A clear increment in the content of CO from 4 to 14 %wt can be observed (conventional and catalytic fast pyrolysis, respectively), due to decarbonylation reactions, which are favored in the presence of catalysts.

Conclusions

The fast pyrolysis of olive stone promoted the formation of the liquid fraction compared to conventional pyrolysis. The use of an acid catalyst in the fast pyrolysis of olive stone decreased and increased the liquid and the gases yields, respectively. The highest H₂ yield was obtained by ACZr. The yield to aromatic monomers was considerably higher in the catalytic fast pyrolysis. These results show the feasibility of using olive stones for the catalyst preparation and as feedstock for catalytic fast pyrolysis.

Acknowledgements

The authors thank MCINN (RTI2018-097555-BI00 and TED2021-131324B-C21) and Junta de Andalucía (UMA18-FEDERJA-110) for financial support. M.C.R.R. gratefully acknowledges MCINN for FPI grant (PRE2019-089340).

References

1. Dhyani, V., Bhaskar, T.(2017). A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew Energy*, 129,695-716.