

## ON-LINE PHOTOIONISATION MASS SPECTROMETRY: AN INTERESTING TECHNIQUE TO STUDY BIOMASS PYROLYSIS

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It is essential to analyse the composition of volatiles in order to understand pyrolysis mechanisms and to design reactors. In this context, the on-line analysis of volatiles appears to be a powerful approach, because it has the ability to analyse the volatiles directly at the gas-phase avoiding their condensation and re-vaporisation of the liquid bio-oils (e.g. for their GC analysis). On-line analysis of volatiles by direct mass spectrometry requires a soft ionisation method in order to reduce the fragmentation of fragile volatiles during their ionisation (fragmentation inside the mass spectrometer). Indeed, the common mass spectrometers using electron impact are not suitable for the on-line analysis of biomass primary volatiles [1]. For this purpose, soft photoionization (PI) mass spectrometry (MS) is a relevant technique to analyse on-line the volatiles. In this talk, we will present the development conducted in our groups on PI-MS analysis of biomass pyrolysis volatiles by (1) synchrotron light PI-MS [2] and (2) custom PI-MS techniques [3–6]. We will give an overview of some studies performed by means of this PI-MS technique, namely:

- 1) the formation profiles of volatiles as a function of temperature during the slow pyrolysis of different biomasses [3];
- 2) the effect of biomass composition [6,7] and of fast pyrolysis conditions [7] on primary volatiles produced in a micro-fluidized bed;
- 3) the kinetic modeling of biomass fast pyrolysis [5];
- 4) the effect of zeolites structure on aromatics formation during catalytic fast pyrolysis [8].

[1] Brown AL, Dayton DC, Nimlos MR, Daily JW. Characterization of biomass pyrolysis vapors with molecular beam, single photon ionization time-of-flight mass spectrometry. *Chemosphere* 2001;42:663–9. [https://doi.org/10.1016/S0045-6535\(00\)00240-X](https://doi.org/10.1016/S0045-6535(00)00240-X).

[2] Dufour A, Weng J, Jia L, Tang X, Sirjean B, Fournet R, et al. Revealing the chemistry of biomass pyrolysis by means of tunable synchrotron photoionisation-mass spectrometry. *RSC Adv* 2013;3:4786–92. <https://doi.org/10.1039/C3RA40486B>.

[3] Le Brech Y, Jia L, Cissé S, Mauviel G, Brosse N, Dufour A. Mechanisms of biomass pyrolysis studied by combining a fixed bed reactor with advanced gas analysis. *Journal of Analytical and Applied Pyrolysis* 2016;117:334–46. <https://doi.org/10.1016/j.jaap.2015.10.013>.

[4] Jia L, Le Brech Y, Mauviel G, Qi F, Bente-von Frowein M, Ehlert S, et al. Online Analysis of Biomass Pyrolysis Tar by Photoionization Mass Spectrometry. *Energy Fuels* 2016;30:1555–63. <https://doi.org/10.1021/acs.energyfuels.5b02274>.

[5] Jia L, Dufour A, Le Brech Y, Authier O, Mauviel G. On-line analysis of primary tars from biomass pyrolysis by single photoionization mass spectrometry: Experiments and detailed modelling. *Chemical Engineering Journal* 2017;313:270–82. <https://doi.org/10.1016/j.cej.2016.12.021>.

[6] Jia L, Buendia-Kandia F, Dumarcay S, Poirot H, Mauviel G, Gérardin P, et al. Fast Pyrolysis of Heartwood, Sapwood, and Bark: A Complementary Application of Online Photoionization Mass Spectrometry and Conventional Pyrolysis Gas Chromatography/Mass Spectrometry. *Energy Fuels* 2017;31:4078–89. <https://doi.org/10.1021/acs.energyfuels.7b00110>.

[7] Jia L, Le-Brech Y, Shrestha B, Frowein MB, Ehlert S, Mauviel G, et al. Fast Pyrolysis in a Microfluidized Bed Reactor: Effect of Biomass Properties and Operating Conditions on Volatiles Composition as Analyzed by Online Single Photoionization Mass Spectrometry. *Energy Fuels* 2015;29:7364–74. <https://doi.org/10.1021/acs.energyfuels.5b01803>.

[8] Jia LY, Raad M, Hamieh S, Toufaily J, Hamieh T, Bettahar MM, et al. Catalytic fast pyrolysis of biomass: superior selectivity of hierarchical zeolites to aromatics. *Green Chem* 2017;19:5442–59. <https://doi.org/10.1039/C7GC02309J>.