Characterization of the water-insoluble fraction isolated from the slow steam pyrolysis of biomasses

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Researches on renewable energy are of increasing importance due to the gradually decreasing reserves of fossil fuels and the growing concern about environmental issues. Renewable energy is obtained from biomasses which are expected to be a primary energy source within the next 20 years.
Pyrolysis, a zero-waste process, is one of the most thermally efficient processes to obtain liquid products from biomass and typically generates three products: a mixture of gasses (CO, CO_2, H_2, CH_4), a liquid phase, and solid (char), all of which are potential sources of energy, fuel, and chemicals [1].
The liquid phase, a dark brown/yellow and viscous liquid, is a complex mixture of organic molecules (more than 200 compounds), mainly oxygen-rich, deriving from the rapid condensation of vapors released during the pyrolysis process.
The increasing interest in the research and application of biomass-derived pyrolysis liquids derives from their possible use as fuel in diesel engines and boilers and as source of chemicals [2].
As a result of their heterogeneous composition and their high oxygen content, biomass-derived pyrolysis liquids are instable mixture and many reactions can occur while the liquid is being stored. For combustion and other applications, these aging processes are undesirable. The fraction that contributes significantly to the viscosity, reactivity and instability of pyrolysis liquids is named "pyrolytic lignin" and consists of a water-insoluble material formed by the polymerization of lignin-derived components of the biomass [3].
The characterization of pyrolytic lignin in terms of composition and structure may be helpful to understand aging processes during pyrolysis liquids storage and may help in the identification of ways to reduce the efficiency problems related to the use of biomass-related pyrolysis product.
Literature reporting data about the pyrolytic lignin characterization is still limited [3-6]. The mechanism of the formation of these polymeric compounds is still under debate.
This work reports data on the composition of pyrolytic lignin samples isolated form the pyrolysis liquids obtained from the slow steam-assisted pyrolysis of *Arundo donax* canes [7] and *Eucalyptus occidentalis*. Steam has been chosen as pyrolysing agent as with respect to nitrogen it enhances the yield of the liquid phase and affects positively its composition determining an increase of its carbon content [8]. The data are compared to those of the pyrolitic lignin fraction isolated from the pyrolysis liquid of a reference biomass (alkali lignin).
Pyrolitic lignin samples were analyzed by thermogravimetry, infrared spectroscopy (FTIR) and mass spectrometry (atmospheric pressure photoionization source coupled with ion trap mass analyzer, APPI-IT). Results allowed to define the structure of the most abundant components of the samples and to relate the composition to the thermal behaviour of the samples.
The APPI-IT mass spectrum of the pyrolitic lignin fraction isolated from the pyrolysis liquid of alkali lignin is reported in the Figure 1. Multiple fragmentation spectra were also

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obtained on selected peaks to elucidate the structure of the compounds. The analysis of the mass spectrum indicates that the pyrolytic lignin fraction is composed by four classes of phenolic compounds: monomers, dimers, trimers and tetramers.

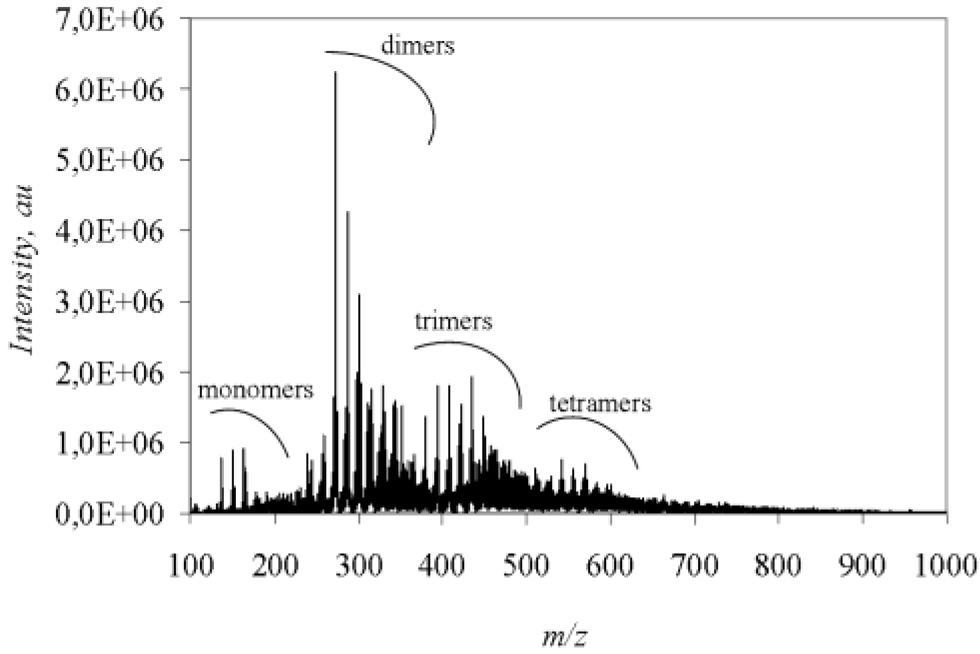

Figure 1. *APPI-IT mass spectrum of the pyrolitic lignin fraction isolated from the pyrolysis liquid of alkali lignin*

Since pyrolytic lignin derives from the condensation of lignin-derived components of the biomass, a monomeric structures contains a phenolic ring with a variable number of aliphatic or olefinic side chains (i.e. molecules as guaiacols, syringol eugenol, iso-eugenol, vinyl guaiacol, vinyl-syringol) while dimeric, trimeric and tetrameric structures contain phenylcoumaran, biphenyl, stilbene and resinol moities.

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