PYRANA : Analytical characterization of fast pyrolysis oilse

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PROJECT 2007

Title of the project	**Analytical characterization of fast pyrolysis oilse.**
Acronym	PYRANA
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Duration	2 years Final report : December 2010

Summary

Fast pyrolysis is a thermochemical pathway that enables the liquefaction of lignocellulosic material (wood, straw,…) into bio-oils which might be potentially upgraded into biofuels by further processing. Thus, developing knowledge about the chemical composition of pyrolysis oils is essential. However, since these liquids are very complex chemical samples, their detailed analysis is not directly available.
This project aims at developing analytical methods for the characterization of the fast pyrolysis oils of lignocellulosic biomass. The work programme is structured into four parts :

Identification and selection of representative bio-oil samples produced by the CIRAD and BFH (or by other laboratories) fast pyrolysis experimental tool,
Fractionation of the bio-oils by a special precipitation technique operated by BFH to separate the oligomeric pyrolytic lignin (water-insoluble fraction of bio-oil). A solid-phase extraction technique can be performed by CIRAD to separate compounds according to the chemical families they belong to,
Analysis of fractions resulted from part 2. Fractions can be analysed by gas chromatographic techniques using different detectors and liquid chromatography. The results obtained by the partners can be compared,
A final report will discuss the results obtained from the fractionation and analysis of fractions of the pyrolysis oils.

Results

The aim of this study was to develop a multi-technique analytical approach to describe as completely as possible the chemical composition of fast pyrolysis oils. To achieve this goal, six bio-oils were produced using the fluidized bed fast pyrolysis CIRAD and vTI units and using the same lignocellulosic materials. The four hardwood and softwood pyrolysis oils were single phase liquids while bio-oils produced from wheat straw were heterogeneous. This phase separation is a typical phenomenon of annual plants.
Gas chromatographic methods enable a very detailed molecular description of the composition of the samples, providing quantitative information about more than 90 compounds belonging to several chemical families

(carboxylic acids, alcohols, aldehydes, ketones, furans, pyrans, sugars, benzene, catechols and phenolics). The part of bio-oils that can be characterized by this GC approach represents between 29 to 39 wt% (based on dry basis) of the pyrolysis liquids. A high resolution Fourier Transform-Ion Cyclotron Resonance mass spectrometry technique (FT-ICR/MS) was performed to analyse the whole bio-oils, the water-soluble fraction and the pyrolytic lignin. Results show that aqueous phases contain molecules detected by ionization mode having molecular weights up to 900 Da and owing 3 to 20 oxygen atoms. This observation indicates that not all the compounds present in such matrices are described by the GC methods used in this work.
Pyrolytic lignin, defined as the water-insoluble fraction of a fast pyrolysis oil, represents from 15 to 21 wt% (based on dry basis) of the investigated oils. No molecular information is available for this fraction since the present compounds in pyrolytic lignin cannot be eluted by the GC methods used in this project. Size exclusion chromatography linked with an UV or a RI detector was performed to determine the MW distribution of the pyrolytic lignin. The results are greatly dependant of the type of detector used. Mean molecular weights are ranging from 1000 to 1600 g/mole for RI detection. Thanks to its high resolution power, FT-ICR mass spectrometry provides information about chemical formulae of the detected ions. Results show that these water-insoluble fractions contain molecules with a large range of composition, having from 3 to 15 oxygen atoms and from 9 to 55 carbon atoms.

Results obtained in this study show that up to 40 wt% of the bio-oils can be analysed by GC at a molecular level. Around 15 to 21 wt% of the oils are high molecular weight water-insoluble oligomeric compounds. The molecular weight distribution of the pyrolytic lignin fraction can be determined by Size Exclusion Chromatography and the chemical composition of the detected ions can be provided using FT-ICR/MS technique. The part of the bio-oils that cannot be quantitatively described by GC or analysed as pyrolytic lignin is relatively low but still significant since it represents around 10 to 17 wt% (dry basis) of the oils.

Deliverables

Final report IFP Energies nouvelles, Report 61640 : December 2010 : Analytical characterization of fast pyrolysis oils

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