2nd Advanced User School

EU FT-ICR MS

Pushing the capacity of the FT-ICR MS for the analysis of biooils to a higher level

Presented by : Anthony ABOU DIB

2nd year PhD student

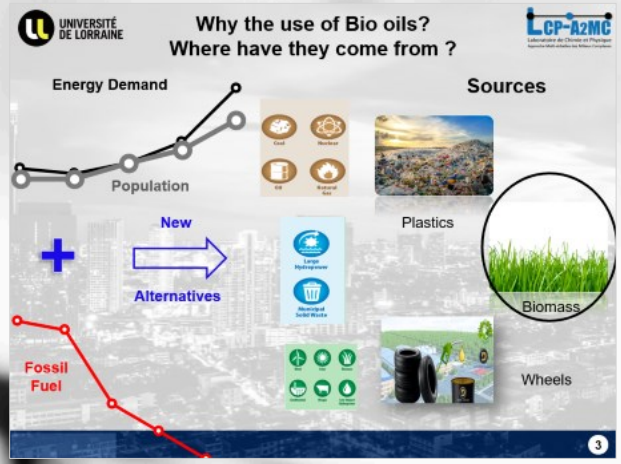
Supervisors : Frédéric AUBRIET

Vincent CARRE

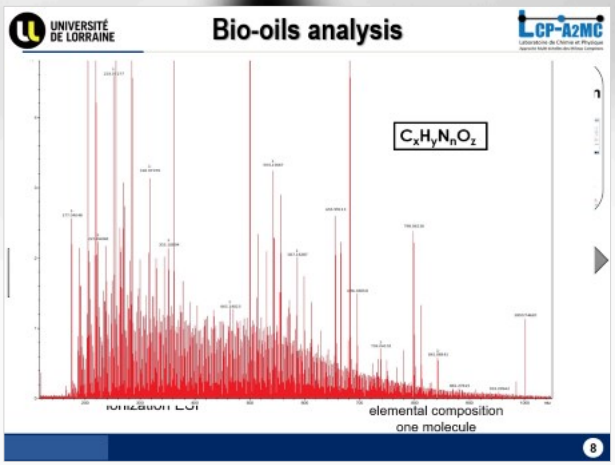
LCP-A2MC
Laboratoire de Chimie et Physique
Approche Multi-échelles des Milieux Complexes

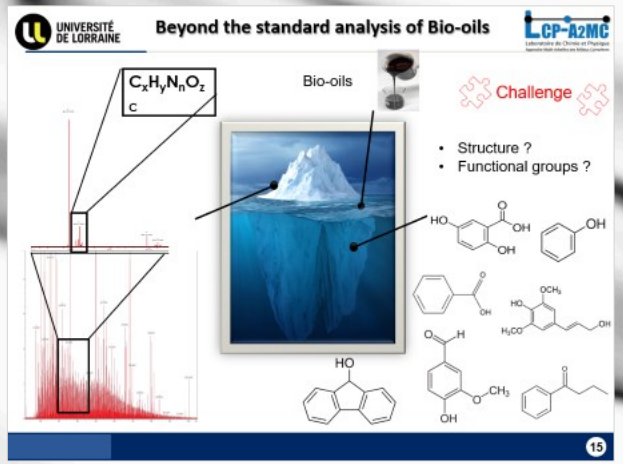
Presentation Plan

General context



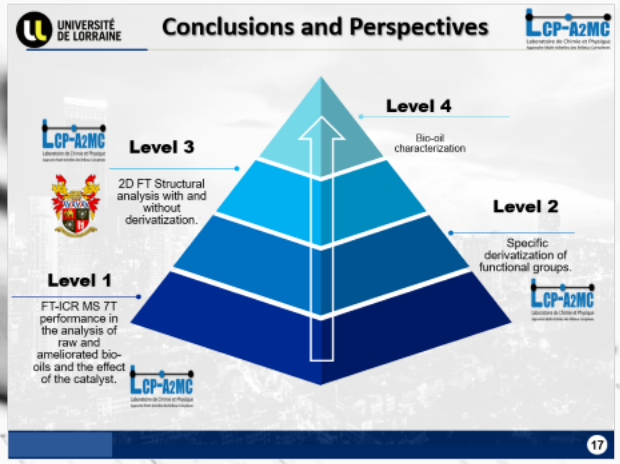
Experimental part





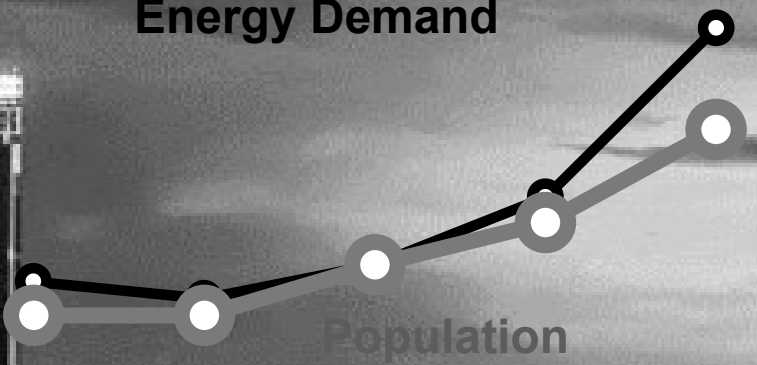
Experimental part

Conclusion and perspectives



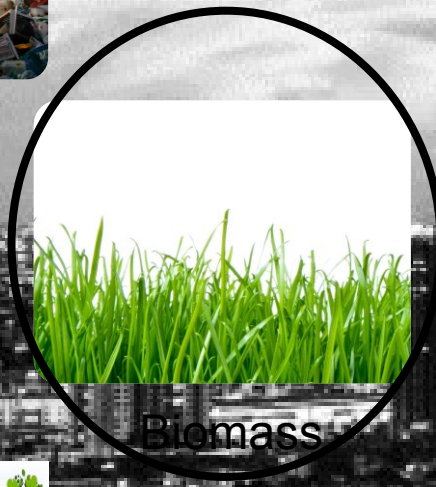
Why the use of Bio oils?
Where have they come from ?

Energy Demand



Sources

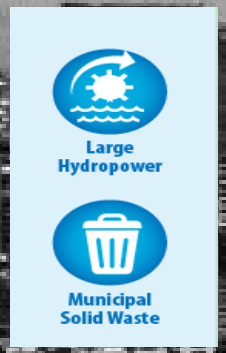
Plastics

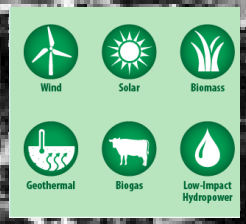


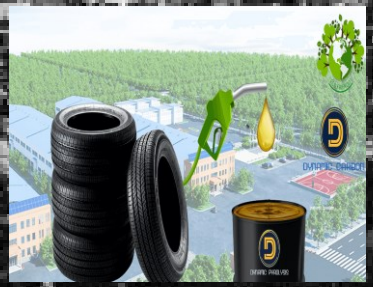
Biomass

New

Alternatives





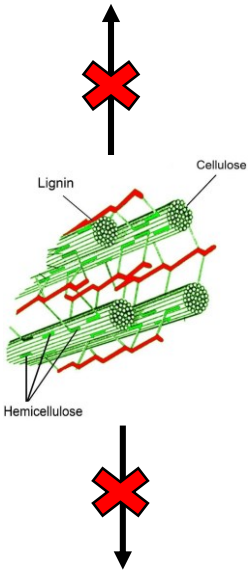


Wheels

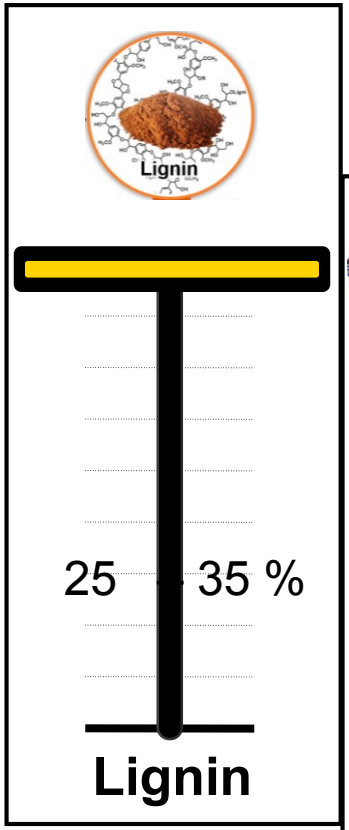
Fossil Fuel

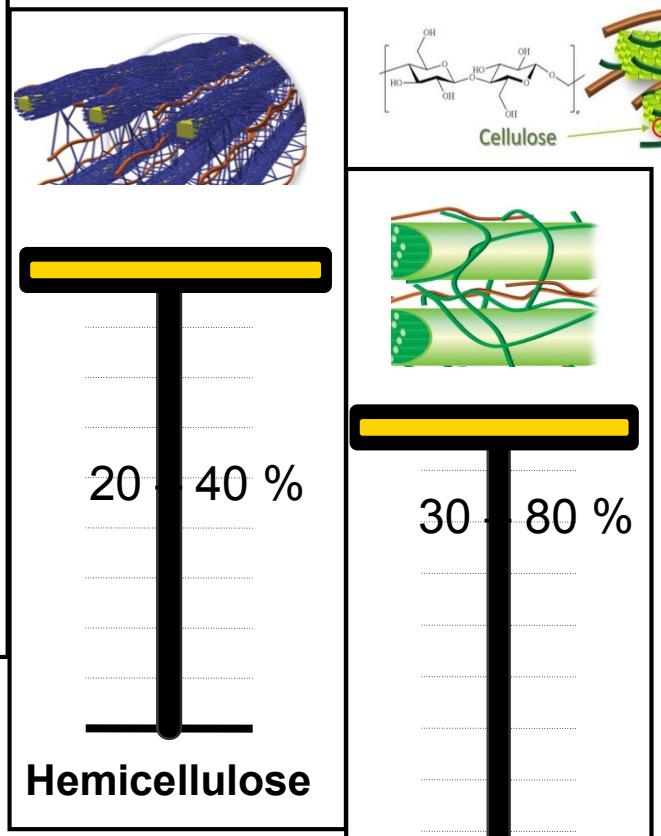
What is lignocellulosic biomass?

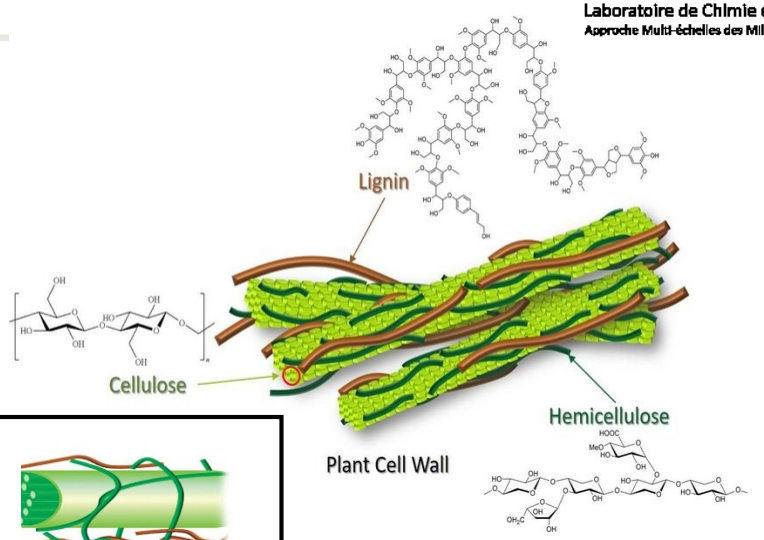
Animal Feed

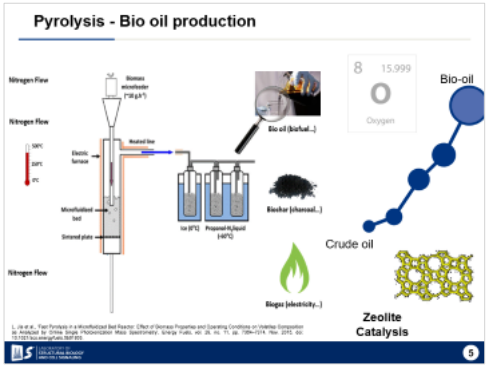


Human Feed

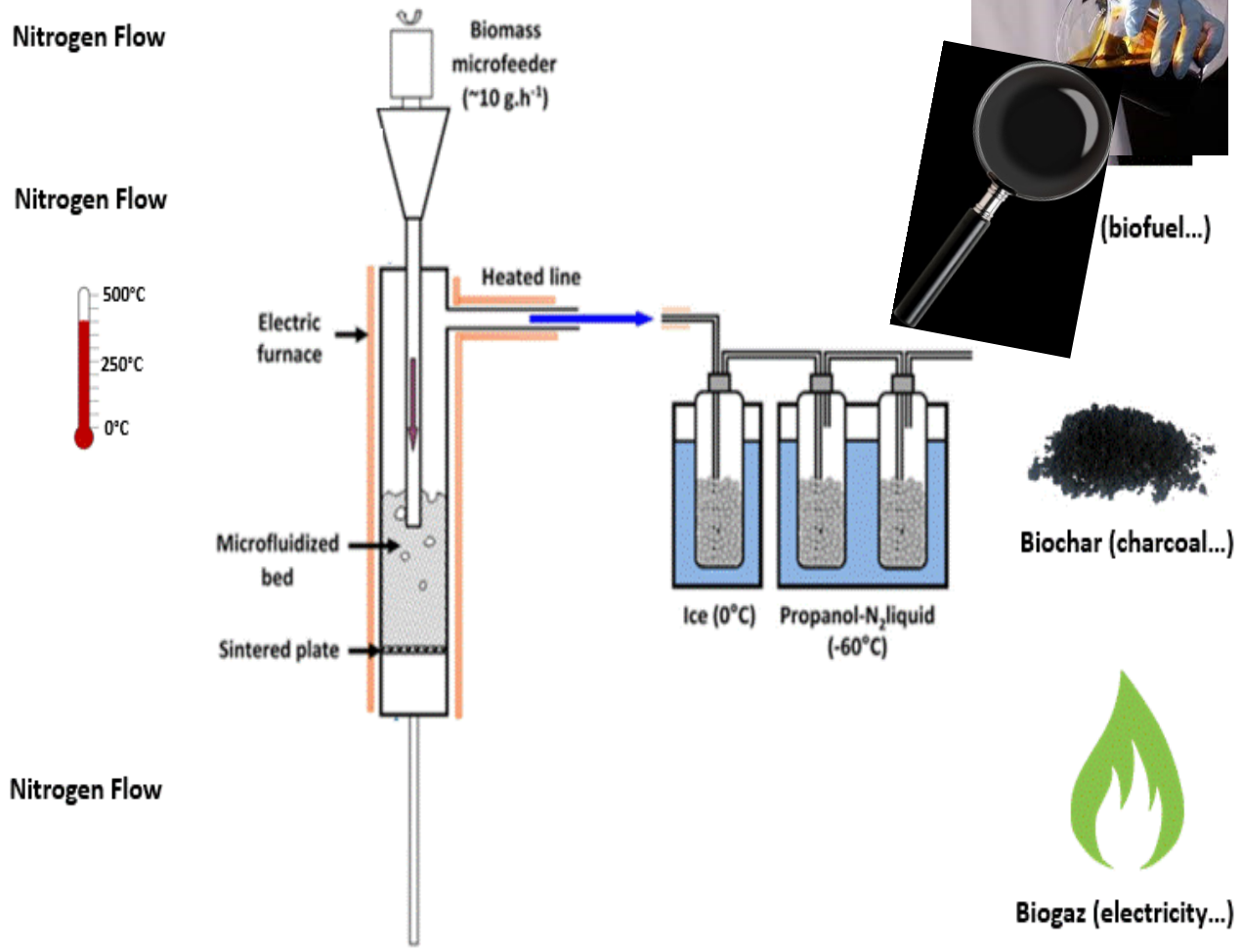








Pyrolysis - Bio oil production



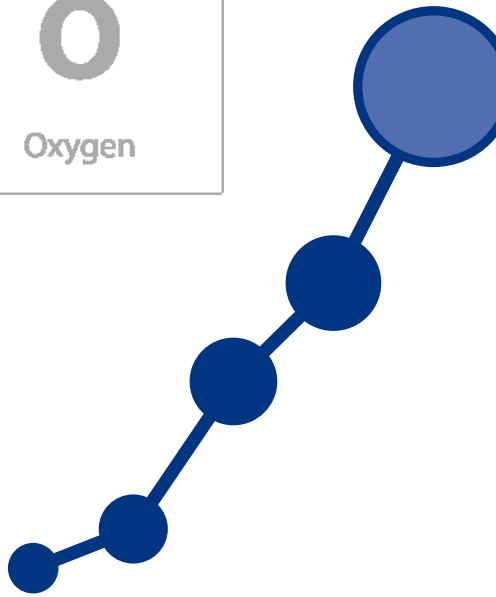
(biofuel...)

Biochar (charcoal...)

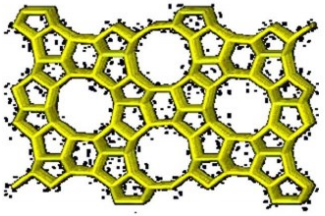
Biogaz (electricity...)

8 15.999 O Oxygen

Bio-oil



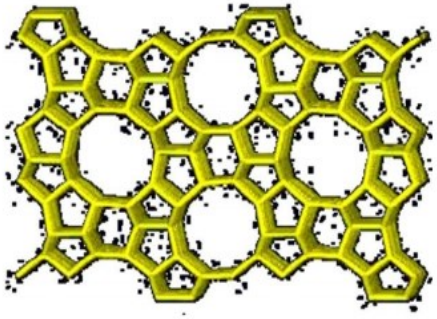
Crude oil



Zeolite Catalysis

L. Jia 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, vol. 29, no. 11, pp. 7364–7374, Nov. 2015, doi: 10.1021/acs.energyfuels.5b01803.

Type of bio-oils produced



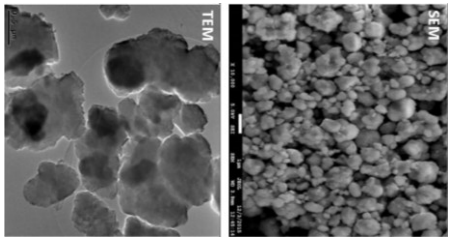
Raw bio-oil

Parental zeolite → Parental HZSM-5 bio-oil

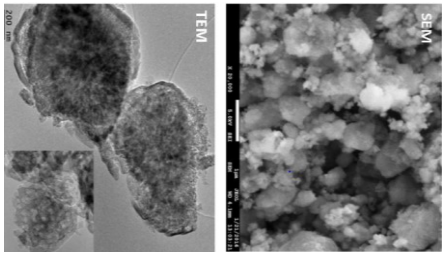
Hierarchical zeolite → Hierarchical HZSM-5 bio-oil

Zeolite Socony Mobil-5
ZSM-5

Parental



Hierarchical



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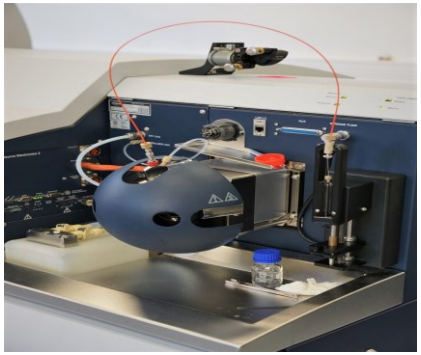
Structural (micropores and mesopores)

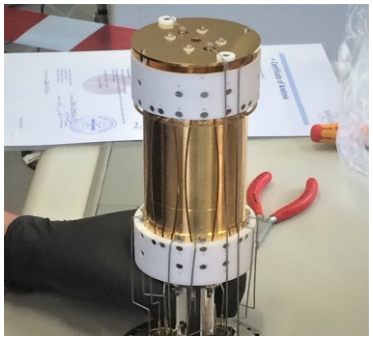
Jacobson, K., Maheria, K. C. & Kumar Dalai, A. Bio-oil valorization: A review. Renew. Sustain. Energy Rev. 23, 91–106 (2013).

FT-ICR MS – 7 Tesla 2w
Bruker SolariX

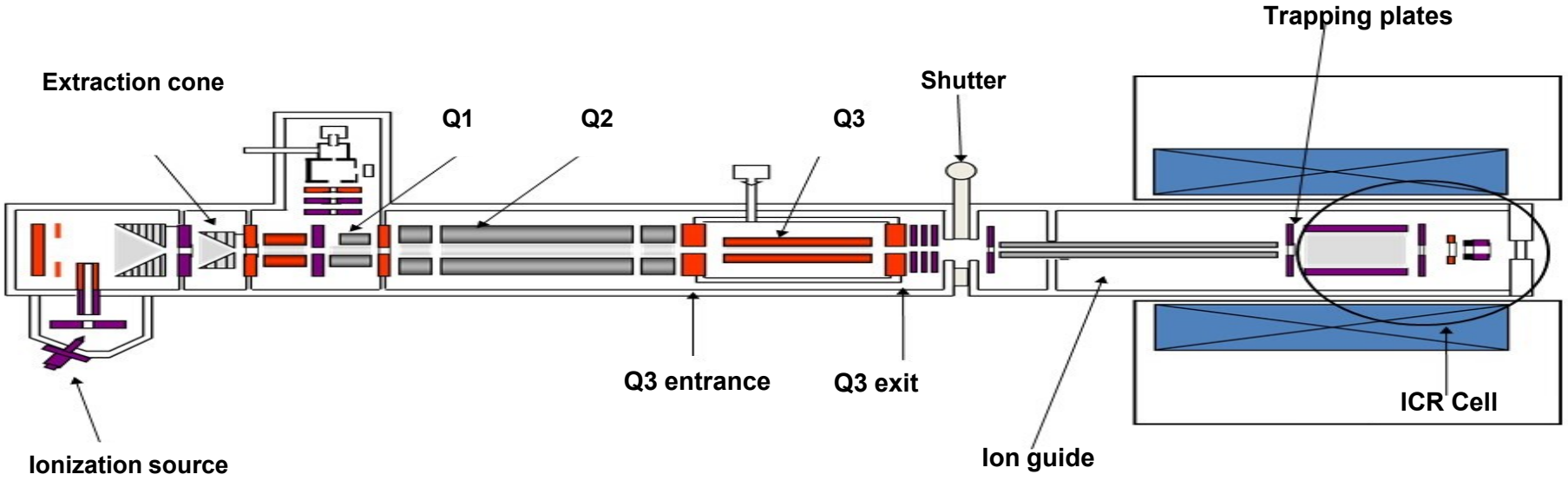


Ionization source

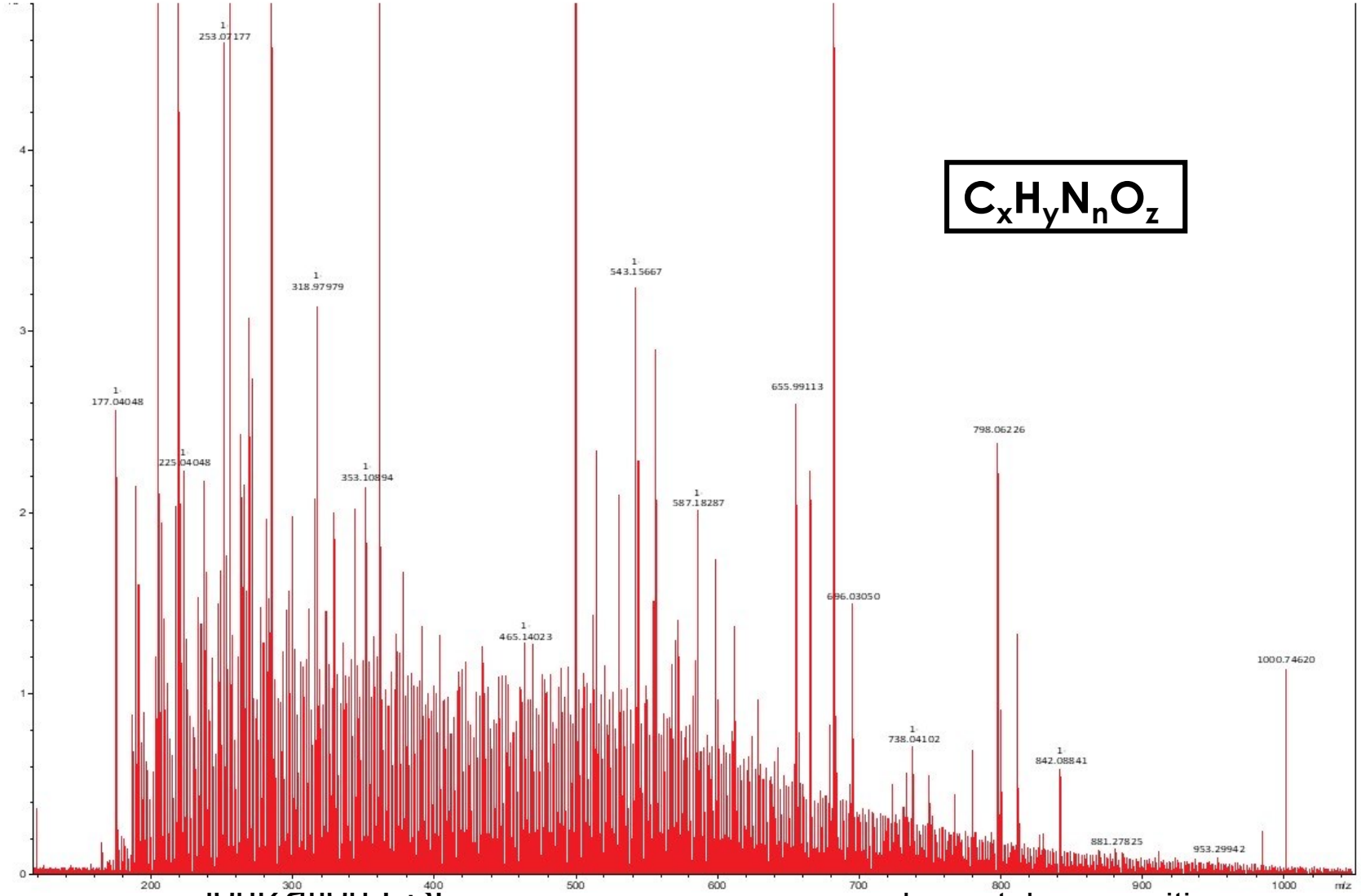
Ion guide



Paracell



Bio-oils analysis



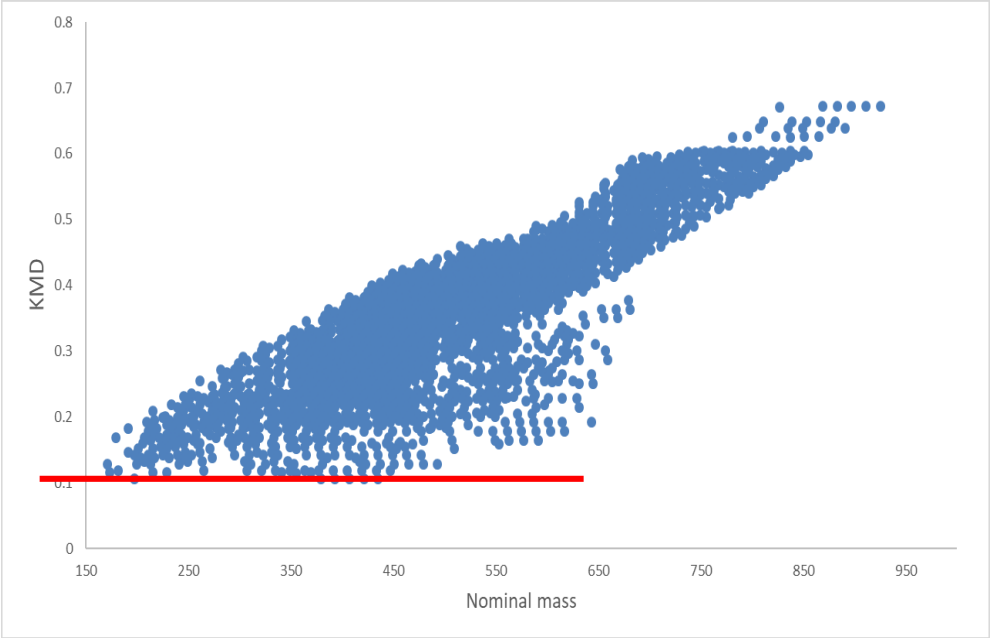
$C_xH_yN_nO_z$

ionization ESI

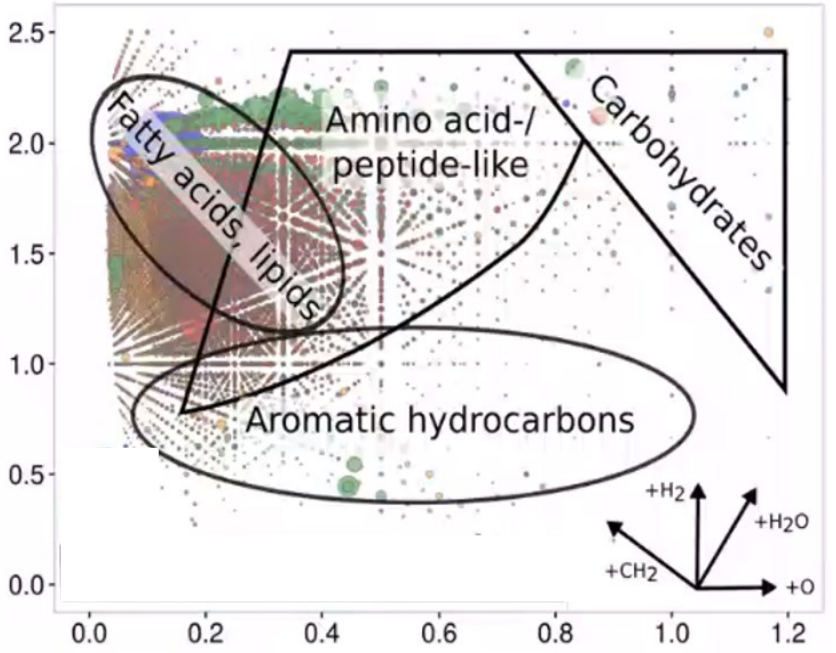
elemental composition
one molecule

Graphic representation of the results

Kendrick maps



Van Krevlen



A. Ruf, L. L. S. D'Hendecourt, and P. Schmitt-Kopplin, 'Data-Driven Astrochemistry: One Step Further within the Origin of Life Puzzle', Life, vol. 8, no. 2, Art. no. 2, Jun. 2018, doi: 10.3390/life8020018

KMD Kendrick's mass defect :

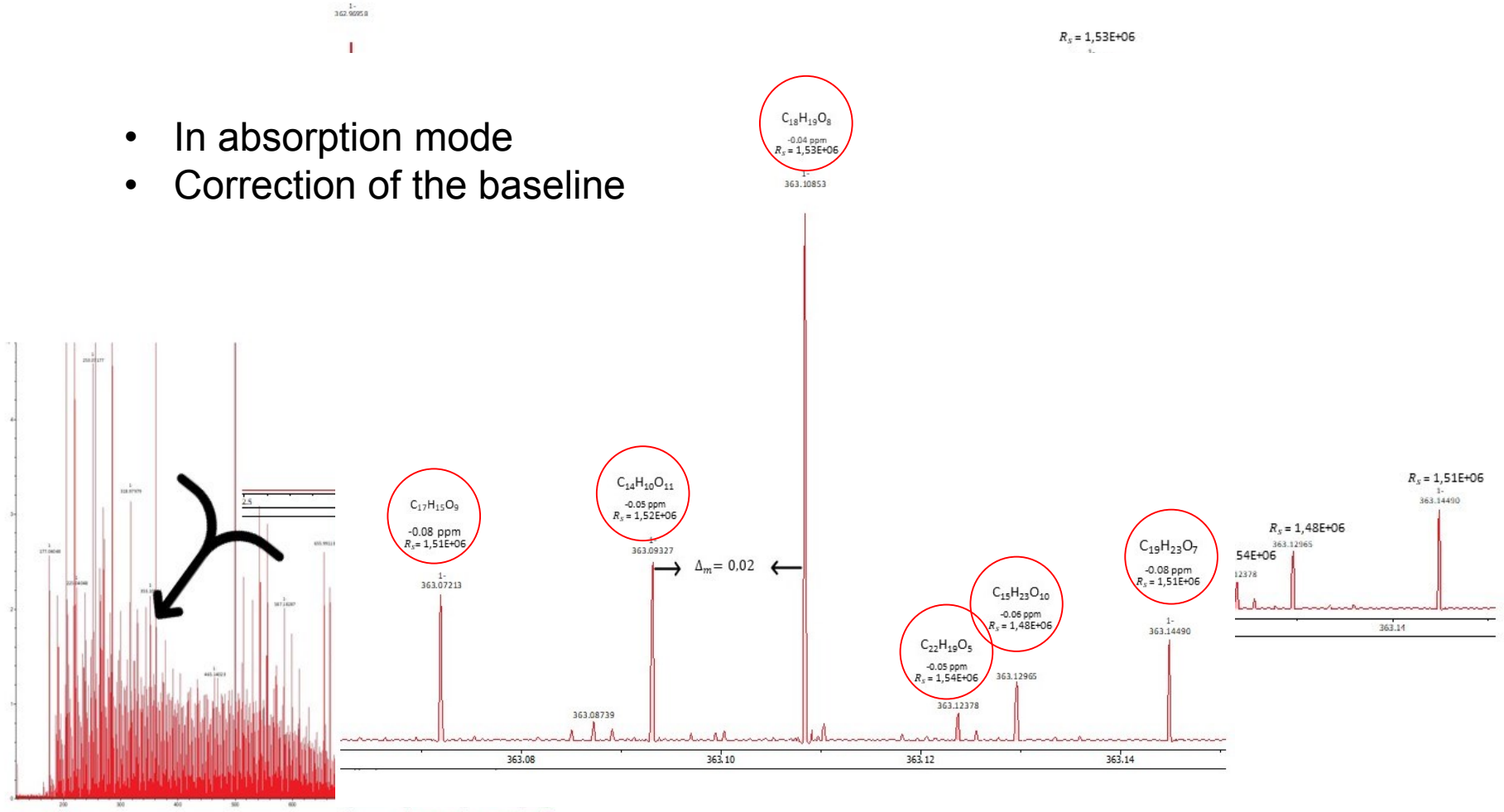
KMD = masse nominale – KM

KM Kendrick's Mass :

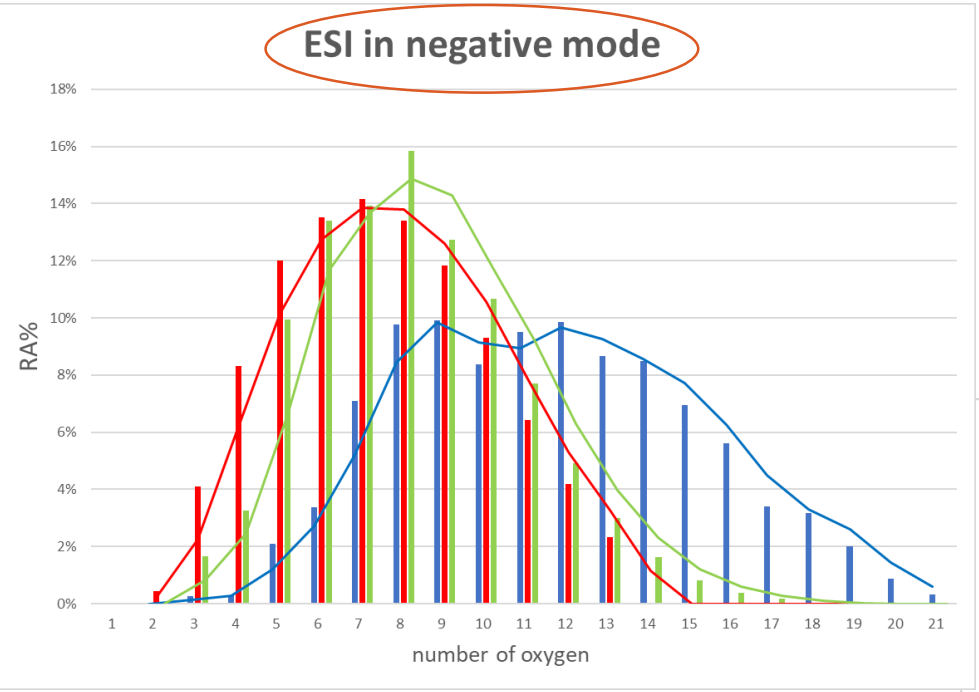
$$KM = \text{masse exacte mesurée} \times \frac{14.00000}{14.01565}$$

Results : Resolution and precision

- In absorption mode
- Correction of the baseline



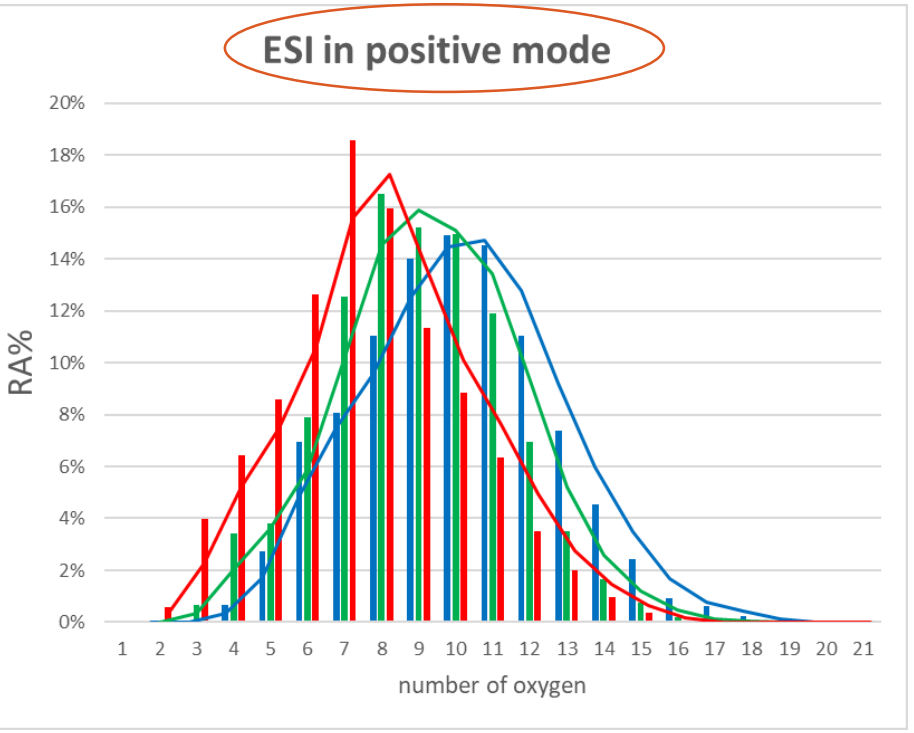
Results : graphic representation

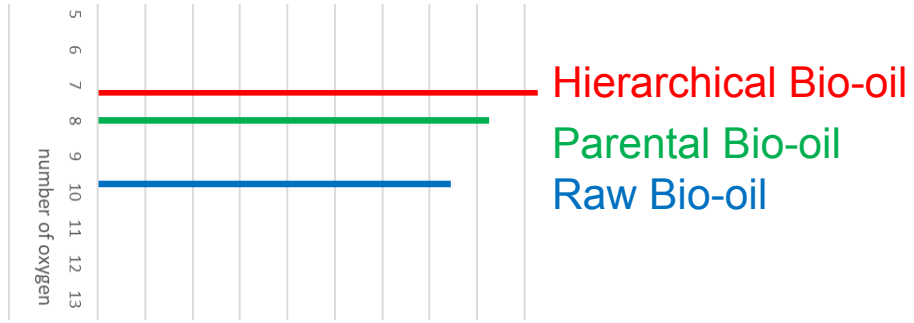


Intensity

Ameliorated BO

Raw BO



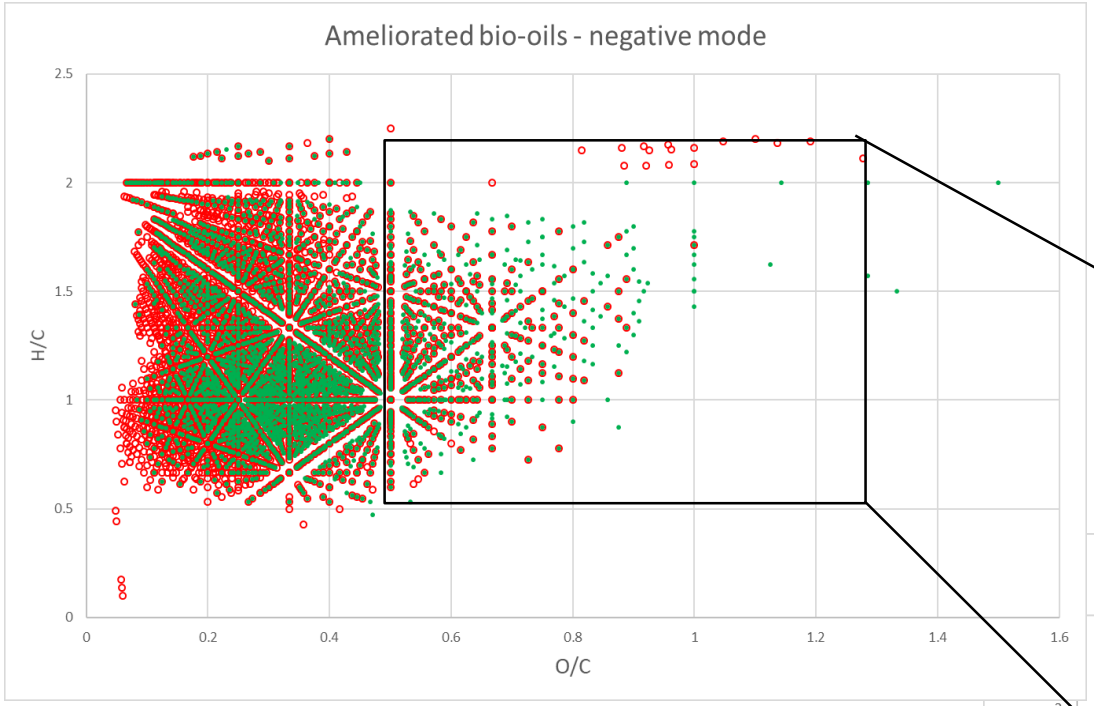


Hierarchical Bio-oil

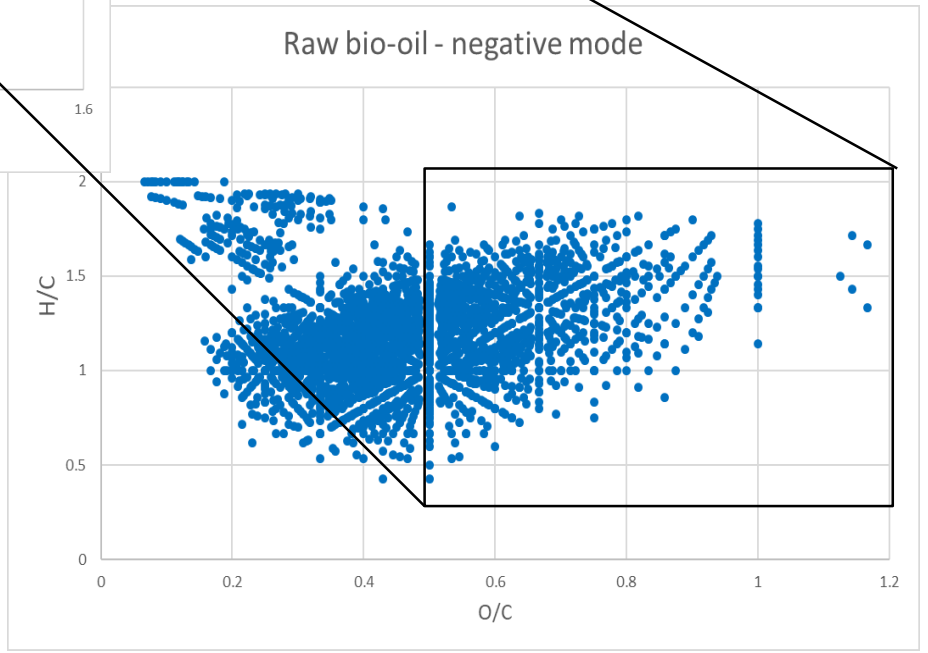
Parental Bio-oil

Raw Bio-oil

Results : graphic representation

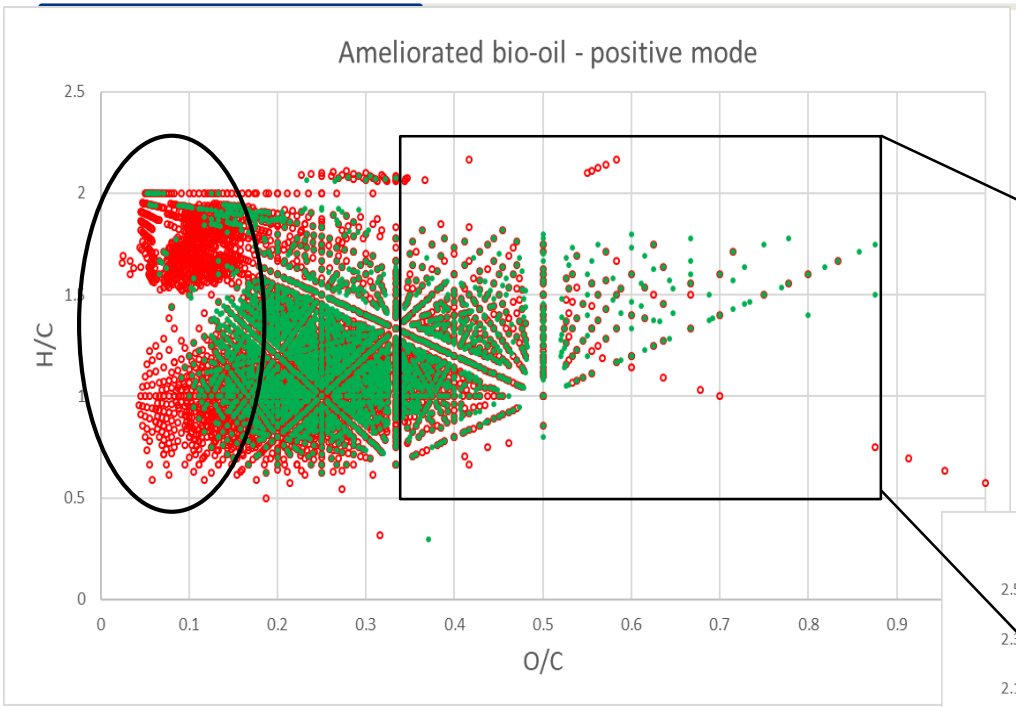


Cellulose and Hemicellulose

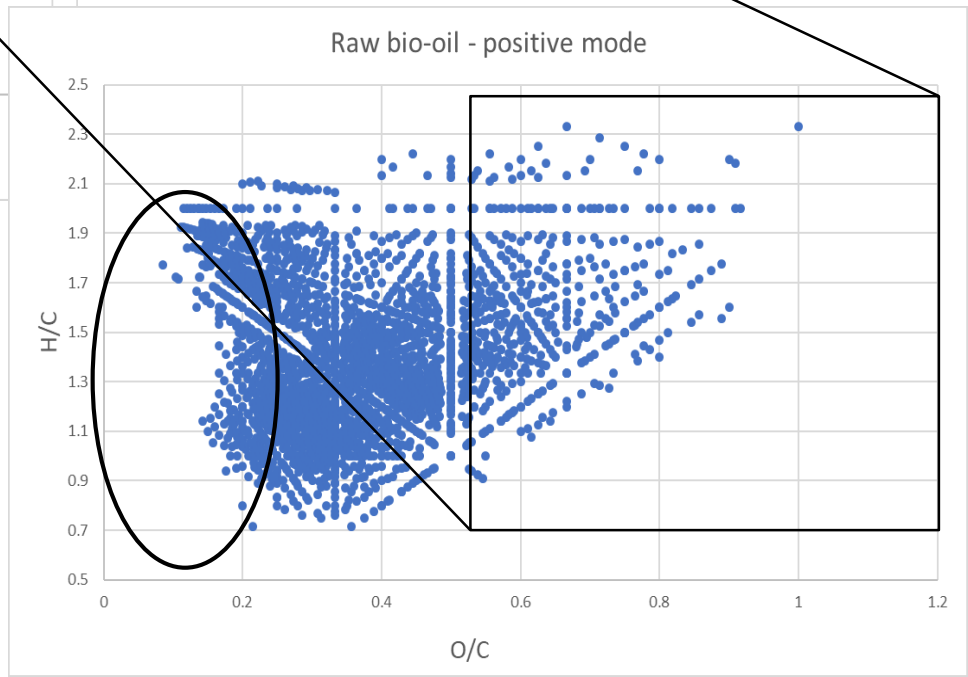


- Hierarchical Bio-oil
- Parental Bio-oil
- Raw Bio-oil

Results : graphic representation



Cellulose and Hemicellulose



Hierarchical Bio-oil

Parental Bio-oil

Raw Bio-oil

Polyaromatic compounds

ULTRA-HIGH RESOLUTION

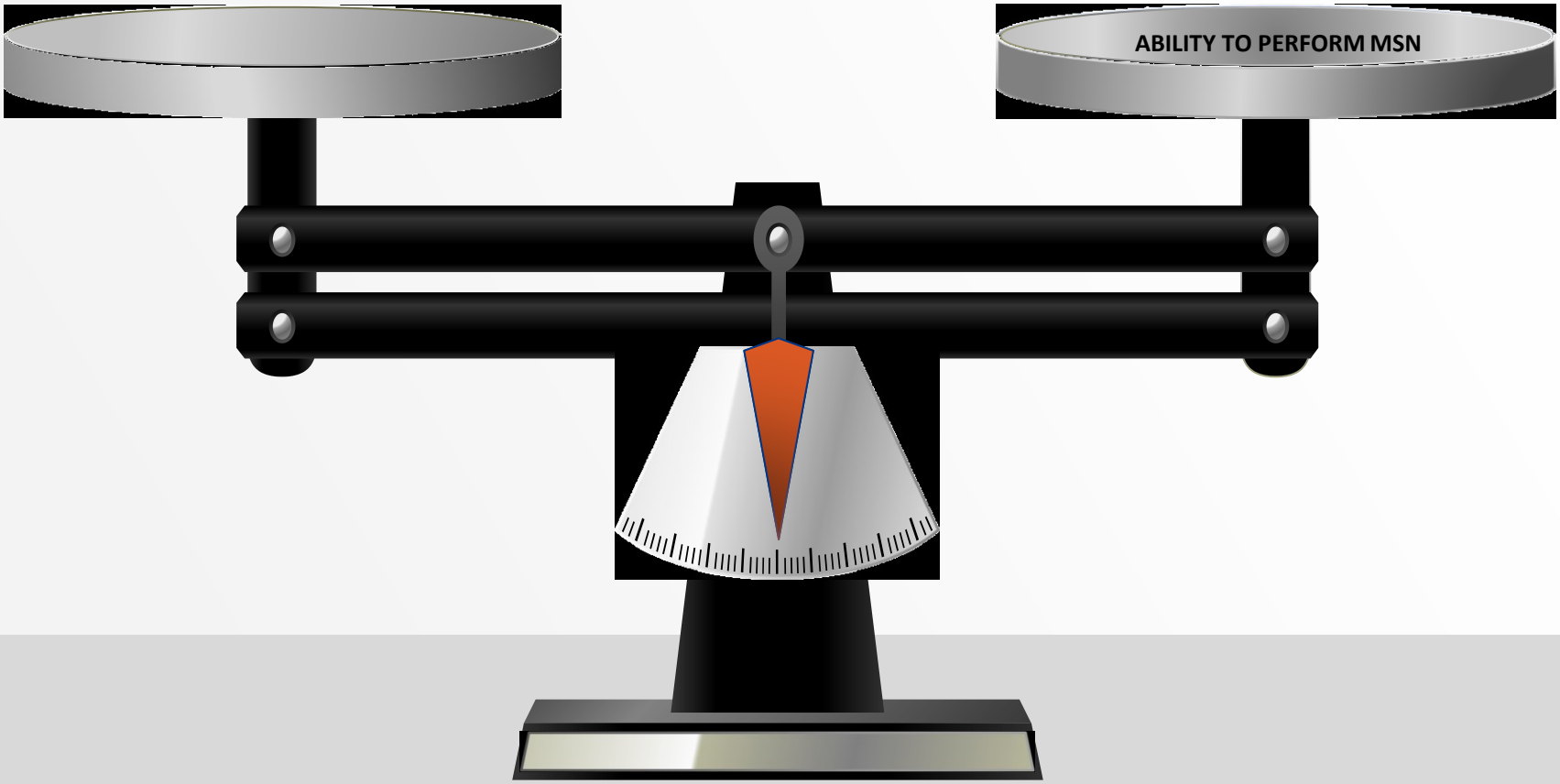
HIGH ACCURACY OF MASS MEASUREMENT AND SENSIBILITY

REQUIREMENT FOR A HIGH-FIELD SUPERCONDUCTING MAGNET

SHORT ANALYSIS TIME FOR HIGHLY COMPLEXE MIXTURES

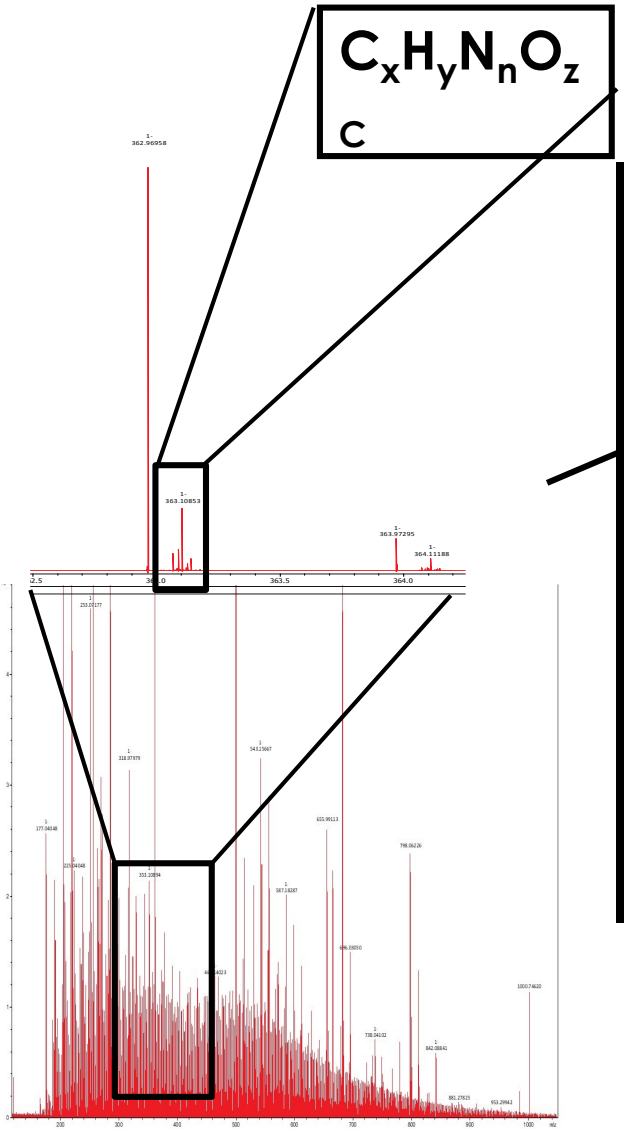
HIGH COSTS OF OPERATION AND MAINTENANCE

HIGH CAPACITY OF THE NEW 2W TECHNOLOGY



Advantage and disadvantage of FT ICR-MS 7T

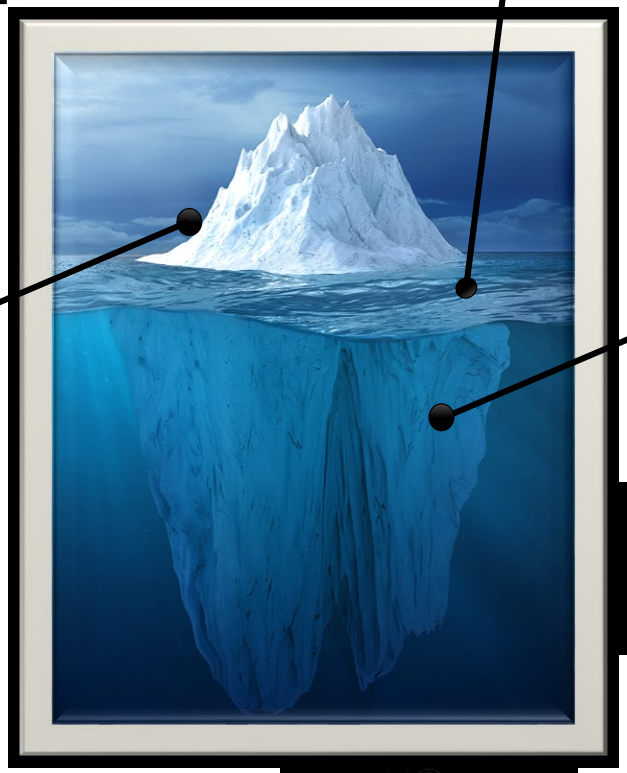
Beyond the standard analysis of Bio-oils

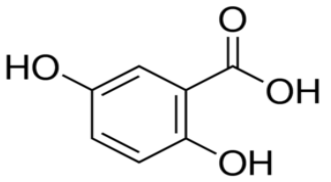


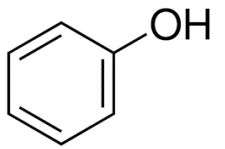
Bio-oils

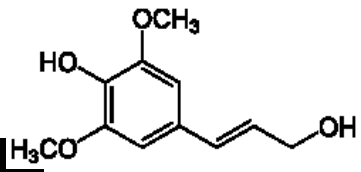
Challenge

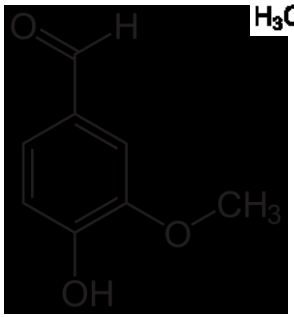
- Structure ?
- Functional groups ?

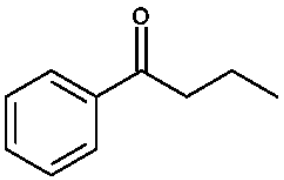






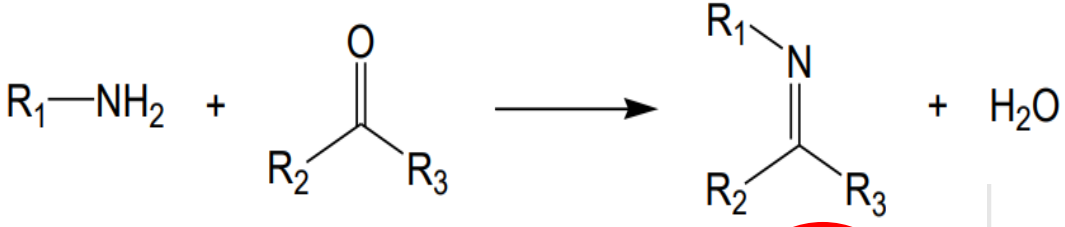


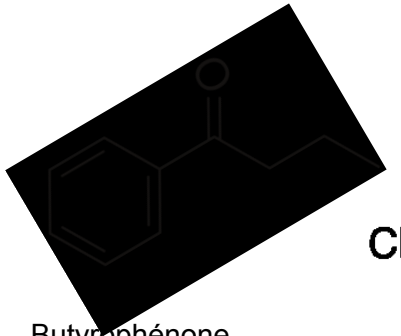




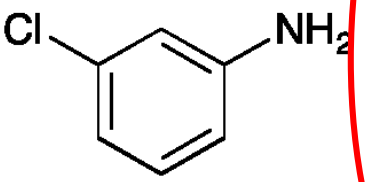
Beyond the standard analysis of Bio-oils

Derivatization

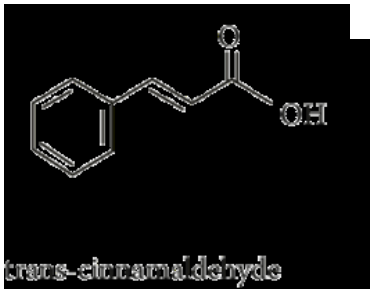


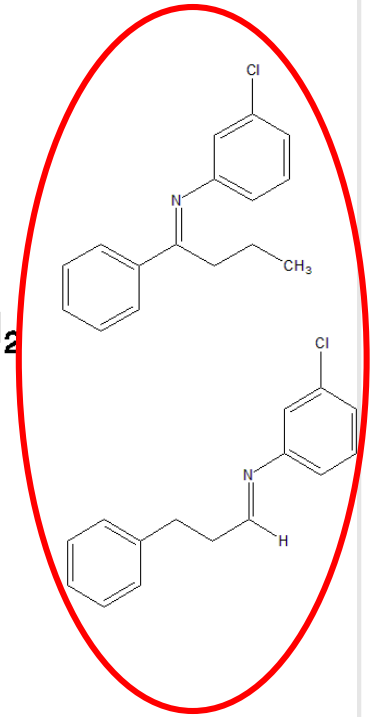


Butyrophénone



3-chloroaniline





Iminiums

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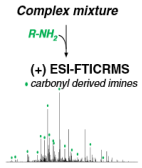
J. Am. Soc. Mass Spectrom. (2018) 29:543–557
DOI: 10.1007/s13361-017-1865-y

RESEARCH ARTICLE

Semi-Targeted Analysis of Complex Matrices by ESI FT-ICR MS or How an Experimental Bias may be Used as an Analytical Tool

Jasmine Hertzog,[1] Vincent Carré,[1] Anthony Dufour,[2] Frédéric Aubriet[1]

[1]LCP-A2MC, FR 2843 Institut Jean Barriol de Chimie et Physique Moléculaires et Biomoléculaires, FR 3624 Réseau National de Spectrométrie de Masse FT-ICR à très haut champ, Université de Lorraine, ICPM, 1 boulevard Arago, 57078, Metz Cedex 03, France
[2]LRGP, CNRS, Université de Lorraine, ENSIC, 1, Rue Grandville, 54000, Nancy, France

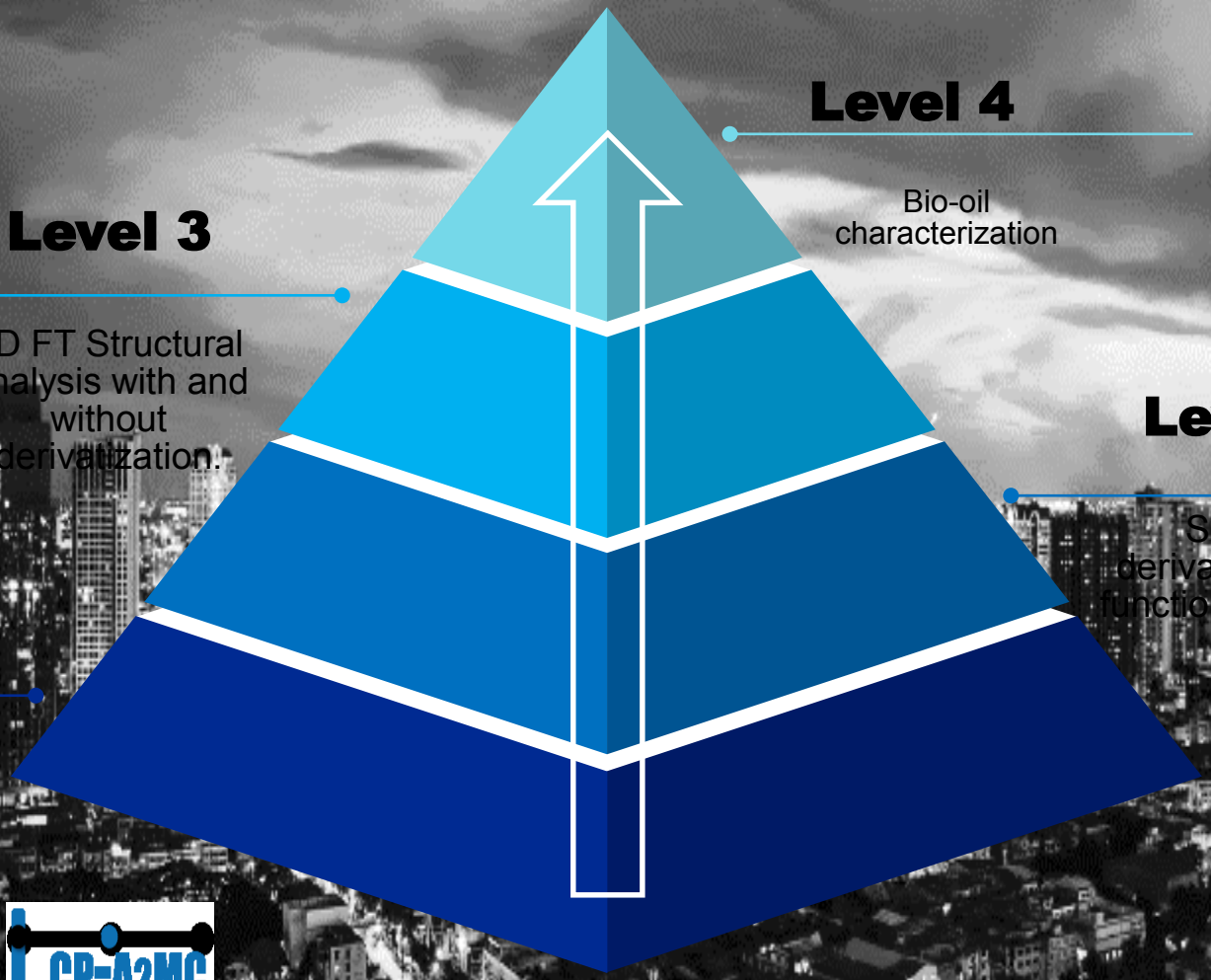


Abstract. Ammonia is well suited to favor deprotonation process in electrospray ionization mass spectrometry (ESI-MS) to increase the formation of $[M-H]^-$. Nevertheless, NH_3 may react with carbonyl compounds (aldehyde, ketone) and bias the composition description of the investigated sample. This is of significant importance in the study of complex mixture such as oil or bio-oil. To assess the ability of primary amines to form imines with carbonyl compounds during the ESI-MS process, two aldehydes (vanillin and cinnamaldehyde) and two ketones (butyrophenone and trihydroxyacetophenone) have been infused in an ESI source with ammonia and two different amines (aniline and 3-chloronaniline). The (+) ESI-MS analyses have demonstrated the formation of imine whatever the considered carbonyl compound and the used primary amine, the structure of which was extensively studied by tandem mass spectrometry. Thus, it has been established that the addition of ammonia, in the solution infused in an ESI source, may alter the composition description of a complex mixture and leads to misinterpretations due to the formation of imines. Nevertheless, this experimental bias can be used to identify the carbonyl compounds in a pyrolysis bio-oil. As we demonstrated, infusion of the bio-oil with 3-chloroaniline in ESI source leads to specifically derivatized carbonyl compounds. Thanks to their chlorine isotopic pattern and the high mass measurement accuracy, (+) ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) unambiguously highlighted them from the numerous $C_xH_yO_z$ bio-oil components. These results offer a new perspective into the detailed molecular structure of complex mixtures such as bio-oils.

Keywords: Negative ESI, Imine formation, Analytical biases, Petroleomic

Received: 11 October 2017/Revised: 29 November 2017/Accepted: 29 November 2017/Published Online: 16 January 2018

Conclusions and Perspectives



Level 4

Bio-oil characterization

Level 3

2D FT Structural analysis with and without derivatization.

Level 2

Specific derivatization of functional groups.

Level 1

FT-ICR MS 7T performance in the analysis of raw and ameliorated bio-oils and the effect of the catalyst

Thank you for your attention!

EU FT-ICR MS

LAB COLLEAGUES:

FRÉDÉRIC AUBRIET

VINCENT CARRE

SÉBASTIEN SCHRAMM

PATRICK CHAIMBAULT

LIONEL VERNEX-LOSSET

JULIEN COMEL

CLARISSE GOSSET-ERRAD

THEO VOELLINGER

PIERRE PACHOLSKI

Sponsors of the Project: ResEx Program

- Feder (Europe)
- Metz Métropole
- Conseil Général 57 (Moselle)
- Région Grand EST

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731077.