

Application de la FT-ICR MS pour la caractérisation de bio-huile issue de la pyrolyse de bois de hêtre : évaluation des conditions de mode d'ionisation par électrospray (ESI)

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Résumé

Une analyse par spectrométrie de masse à résonance cyclotronique (FT-ICR MS) a été réalisée en utilisant l'ionisation par électrospray (ESI) dans les modes positifs et négatifs pour caractériser une bio-huile issue de la pyrolyse du bois de hêtre (PBO) produite dans un réacteur à lit fluidisé. L'analyse a révélé une composition moléculaire complexe de la bio-huile, avec une prédominance notable de composés oxygénés. La comparaison des modes d'ionisation positifs et négatifs a démontré des variations moléculaires, indiquant que le mode positif offre une caractérisation plus complète de la bio-huile. L'étude souligne l'importance de choisir la technique d'ionisation appropriée pour caractériser pleinement la diversité chimique des bio-huiles, ce qui permettra de mieux déterminer leur composition et d'optimiser leur application potentielle.

Application of FT-ICR MS for the characterization of beechwood pyrolysis bio-oil: evaluating ionization mode conditions by electrospray (ESI)

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Abstract

Analysis by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was conducted using electrospray ionization (ESI) in both positive and negative modes on beechwood pyrolysis bio-oil (PBO) produced in a fluidized bed reactor. The analysis revealed a complex molecular composition of the bio-oil, with a notable predominance of oxygenated compounds. The comparison of positive and negative ionization modes demonstrated molecular variations, indicating that positive mode offers a more comprehensive characterization of the bio-oil. The study highlights the importance of selecting appropriate ionization techniques to fully capture the chemical diversity of bio-oils, thereby advancing the determination of their composition and optimizing their potential applications.

Introduction

In recent years, European countries have increasingly sought independence from fossil fuels to meet the growing energy needs [1]. Among the alternative energy options, biomass has emerged as a particularly promising resource due to its widespread availability and renewable characteristics. Biomass, derived from agricultural residues, forestry by-products, and other organic materials, offers a sustainable solution that can be continuously replenished through natural processes, unlike finite fossil fuels. According to the Ministry of Ecological Transition, biomass currently represents the largest source of renewable energy in France, contributing 55% of total renewable energy production. This contribution spans a wide range of applications, including electricity generation, heating, biogas production, and creation of biofuels [2].

One promising method for converting readily available biomass into valuable products is pyrolysis. Pyrolysis is a thermochemical process in which biomass is subjected to high temperatures, usually between 400-600 °C, in the absence of oxygen. Under these conditions, the main components of lignocellulosic biomass: lignin, cellulose and hemicellulose, undergo depolymerization reactions, breaking down its complex organic structure and transforming it into three primary products: non-condensable pyrolysis gases, liquid pyrolysis bio-oil (PBO), and solid biochar [3,4]. Pyrolysis is particularly appealing due to its ability to produce a significant amount of liquid bio-oil, which can be further upgraded into biofuels, providing a renewable alternative to fossil fuels [5-8]. Additionally, PBO can be used as precursors in the synthesis of valuable industrial chemicals, pharmaceuticals, and specialty materials [9].

Understanding the composition of bio-oils is crucial for gaining deeper insights into the pyrolysis process and assessing the chemical potential of the liquid product. Variations in process conditions and feedstock types directly influence the complex chemical composition and physicochemical properties of pyrolysis oil. To achieve a comprehensive analysis, advanced techniques such as chromatography (both liquid and gas) [10], nuclear magnetic resonance (NMR), and high-resolution mass spectrometry (HRMS) are commonly employed [11].

The majority of studies characterizing pyrolysis bio-oils have utilized gas chromatography [12]. However, this technique is limited to the analysis of the volatile and semi-volatile fractions only, which together represent approximately 30% of the total composition of the bio-oil [4]. The non-volatile fraction of bio-oil, including sugars and lignin derivatives, can be effectively analyzed using HRMS. This capability has prompted researchers to adopt the petroleomics approach for a more comprehensive characterization of pyrolysis bio-oils [13]. Petroleomics utilizes HRMS techniques to study the

relationship between the chemical composition of petroleum fuels and biofuels, and their physical and chemical properties [14]. Among HRMS techniques, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has recently gained recognition for its exceptional mass accuracy and high-resolution capabilities [11,15–18]. The ionizing nature of this technique allows for a broader characterization of complex organic mixtures. For instance, this method has also been employed for the analysis of bio-oil derived from the pyrolysis of lignocellulosic biomass [19–21,21–26], plastic waste [27], and catalytic pyrolysis products [28–32], enabling the detection of “heavier” pyrolysis compounds, such as long-chain hydrocarbons and sugars, thereby demonstrating the versatility of this analytical approach.

FT-ICR MS relies on the efficient ionization of molecules within complex organic mixtures to enable accurate molecular formula assignment. Electrospray ionization (ESI) is the most commonly employed ionization source for the characterization of pyrolysis bio-oil. Notably, negative mode ESI has been extensively applied in such analyses [33]. Some chemical families are easily ionized in negative mode (i.e. acids) whereas for others (i.e. sugars), the positive mode favors their ionization. Studies utilizing both positive and negative ionization modes have revealed similar yet distinct chemical compositions [19,32,34–37]. These findings suggest that the combined use of both ionization modes is necessary to achieve a comprehensive characterization of the chemical complexity present in pyrolysis bio-oils.

In this work, high-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with electrospray ionization (ESI) in both positive and negative modes, was employed to characterize the liquid product derived from the pyrolysis of beechwood pellets in a fluidized bed reactor. The results enabled us to determine the most effective ionization conditions for the accurate characterization of PBO produced from lignocellulosic biomass.

Materials and Methods

Pyrolysis bio-oil production

Beechwood pellets were supplied by ETS Lignex Company (Patornay, France). Ultimate and proximate analysis results as well as analysis conditions have been previously detailed elsewhere [38]. Pyrolysis of beechwood was performed in a fluidized bed reactor acquired by MTI Corporation (ref. OTF-1200X-S-FB). The reactor has been previously employed for gasification study [39,40] so it was adapted to carry out pyrolysis experiments. The reactor setup is depicted in Figure 1. The reactor is made of stainless steel. The reactional zone has a 42 mm inner diameter and 125 mm length. The top of the reactor is adapted for a continuous feed with a 20 mm tube that extends from the feed valve to the top of the reactional zone. After leaving the reactional zone, the pyrolysis vapor passes through a cyclone to retain any solid particles carried by the flow before passing through the condenser. Refrigerant temperature was set to -5 °C using a cooler. The non-condensable gases pass through a glass fiber filter and are then guided towards the gas exhaust. Prior to biomass feeding, 5 g of sand are placed inside the reactor and nitrogen gas is fed through the bottom of the reactor to ensure an oxygen-free atmosphere. Nitrogen flow was 1 L/min to guarantee the bed’s fluidization even after the feed. Under these conditions the residence time was calculated to 4-6 seconds. The pellets were crushed to facilitate the feed into the reactor. The biomass was fed at 0.5 g/min with a total of 40 g for each run. Pyrolysis was performed at 500 °C. The liquid product was directly collected in a glass flask by the end of the condenser.

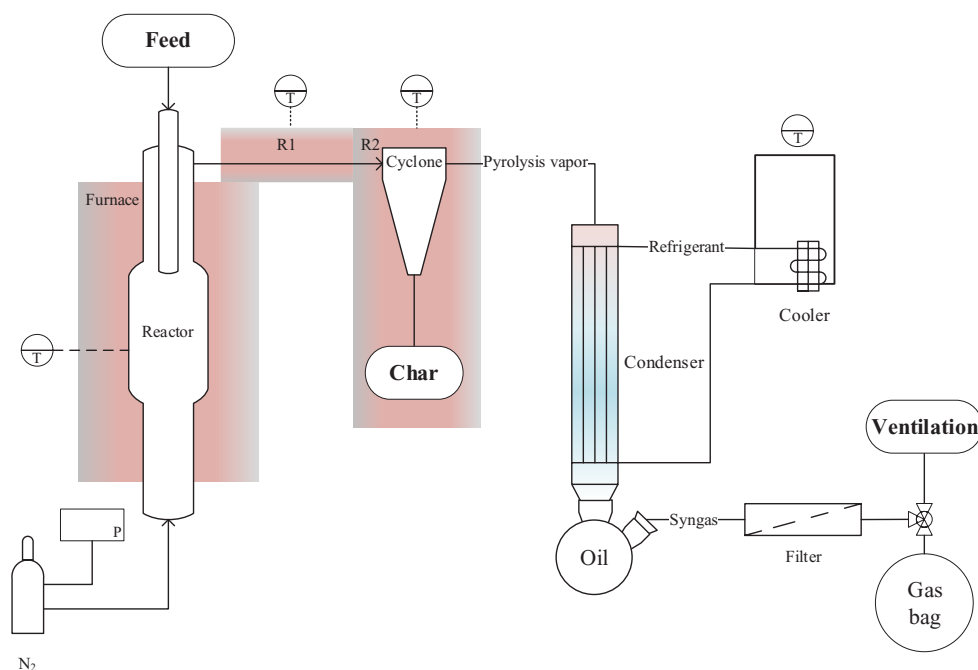


Figure 1. Pyrolysis reactor setup.

Analytical conditions

FT-ICR MS analyses were carried out on an FT-ICR solariX XR modified with 2XR technology (Bruker Daltonics, Bremen, Germany) and equipped with a 12 T superconducting magnet. The instrument was fitted with the commercially available electrospray ionization (ESI) source operating in positive and negative modes. Bio-oil was solubilized in methanol at 0.2 mg/mL for all experiments. The ionization and transmission parameters are reported in Table 1.

Table 1. Ionization and transmission parameters for FT-ICR MS.

Parameter	ESI (+)	ESI (-)
Flow rate ($\mu\text{L/h}$)	120	120
Capillary (V)	-4500	3900
End plate offset (V)	-500	-500
Nebulizer (bar)	1	0.8
Dry gas flow rate (L/min)	3	3
Dry gas temperature ($^{\circ}\text{C}$)	180	180
Time of flight (ms)	0.7	0.7
Data point	4 M	4 M
m/z range	92-1000	92-1000
Accumulation time (s)	0.1	0.02
Transient length (s)	1.0486	1.0486
# scans	200	200

Data was processed with DataAnalysis (version 5.1, Bruker). Each mass spectrum was internally calibrated using confidently assigned ion signals present over the whole mass range resulting from an error standard deviation of < 0.3 ppm. m/z values were assigned with a signal to noise ratio (S/N threshold) greater than 6 considering only even electrons. Molecular formulas were attributed with a maximum 0.5 ppm error tolerance. Elemental boundaries were set to N_{0-2} and O_{0-15} for ESI (-) and N_{0-2} , O_{0-15} and Na_{0-1} , for ESI (+). The H/C and O/C ratios were limited to 3 and 1.2 respectively. Finally, DBE was limited to 30.

The python script, PyC₂MC viewer, developed by Sueur, M et al. in 2022, was used to visualize dataset [41]. Given the large number of molecular formula assignments resulting from the bio-oil's complexity, graphical representations were necessary to aid in interpretation and comparison. Different graphical representations were used in this study:

- The class distribution (C₀₋₁₀₀H₀₋₃₀₀, O₁₋₁₅, N₁₋₂O₁₋₁₅, N₁₋₂) represented in relative intensity. The relative intensity was calculated using equation (1) where I_i is the intensity of the compound class i and I the intensity of all compounds.

$$RI = \frac{I_i}{I} \times 100 \quad (1)$$

The DBE was calculated using equation (2) where n_C is the number of carbon atoms, n_H the number of hydrogen atoms and n_N the number of nitrogen atoms

$$DBE = n_C - \frac{n_H}{2} + \frac{n_N}{2} + 1 \quad (2)$$

- The Van Krevelen diagram, which plots molecular formulae based on their H/C and O/C ratios, and enables the differentiation of biochemical classes such as lipids, lignin derivatives, and carbohydrate or sugar derivatives.
- The Venn diagram uses the calculated *m/z* value of species present in two or more of the three replicates.

Results and Discussion

FT-ICR mass spectrometry coupled with electrospray ionization has shown to enable differentiation into saturated and very polar compounds with high mass (100 – 100 000 Da) such as lipids, pyrolytic sugars, and lignin derivatives [42]. It is the most used ionization source for characterization of bio-oil from lignocellulosic biomass, particularly in negative ion mode [33].

The pyrolysis bio-oil was analyzed via FT-ICR MS with electrospray ionization in positive and negative mode, ESI (+/–). Over 4000 molecular formulas were attributed in ESI positive mode, while close to 1000 were attributed with in ESI negative mode, evidencing the complexity of the chemical composition of pyrolysis bio-oils (Table 2). Stankovikj et al. also reported a higher number of molecular formula assignments in positive mode, suggesting that the alteration of the ionization mode can significantly improve the accessed molecules.

Independently of the ionization mode used, oxygenated species account for over 80% of the molecular assignments. Nitrogen classes were more abundant in positive mode. The basicity of nitrogen species allows for better ionization in positive mode since positive ESI produces mostly protonated species, [M+H]⁺, or cation adducts, [M+Na]⁺ [34]. The C_xH_yN_nO_z class was mostly absent in negative mode and no molecule in the C_xH_yN_n class was detected.

Table 2. Relative distribution of compound classes attributed to beechwood pyrolysis bio-oil by ESI (+/–) FT-ICR MS.

Source	No. of attributions	Classes			
		C _x H _y	C _x H _y O _z	C _x H _y N _n O _z	C _x H _y N _n
ESI (+)	4416	0.2 %	84 %	15 %	0.8 %
ESI (–)	973	0.04 %	99.64 %	0.32 %	-

The oxygenated compounds belong to the O₁ – O₁₅ class species (Figure 2a). Molecules with high content of oxygen (O₁₂ – O₁₅) were more or only detected when using ESI (+) mode. Contrary to its positive counterpart, ESI (–) did not allow the detection of O₁₃ – O₁₅ class species. For both modes, the species are dominated by the oxygenated compound classes O₅ – O₁₂ with the O₇ class showing the highest relative intensity.

The double bond equivalent (DBE) relative distribution can be seen in Figure 2b. DBE represents the “unsaturation degree” of detected compounds. Notably, ESI (+) favored the detection of compounds with low DBE (1-6), while ESI (-) improved the detection of more unsaturated molecules (DBE₅ – DBE₁₀) illustrating two different tendencies for each mode. Interestingly, no molecular formulas with DBE equal to 1 or 0 were attributed in positive mode.

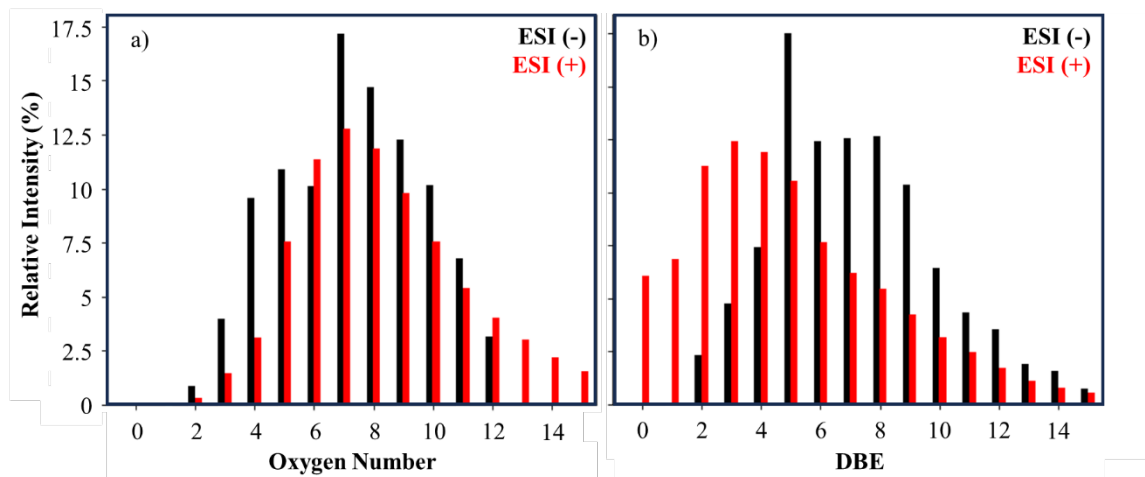


Figure 2. Distribution of relative intensity as a function of (a) oxygen number and (b) DBE class species for the bio-oil analysis in FT-ICR MS with ESI (+ in red, – in dark)

The molecular H/C ratio can be plotted as a function of the O/C ratio, known as the Van Krevelen diagram, and shown in Figure 3. Each dot corresponds to one $C_xH_yO_z$ attribution. A color scale is used to highlight its respective normalized intensity. Different regions in the diagram refer to a specific class of compounds, such as amino-sugars, carbohydrates, lignin-derivatives, lipids, condensed and unsaturated hydrocarbons and proteins as reported by Mase et al, in 2023 and illustrated in Figure 4. The patterns observed in the data distribution of these diagrams can be explained by considering that the oligomeric primary products from the depolymerization of cellulose, hemicellulose, and lignin undergo further modification through possible secondary reactions. Based on the line patterns observed, the pyrolysis products are primarily formed through dehydration, the loss of glycolaldehyde, and decarboxylation. Regardless of the ionization mode, both plots primarily show the presence of lignin-derived compounds. The molecules ionized by ESI (+) were predominantly unsaturated hydrocarbons, amino sugars and carbohydrates.

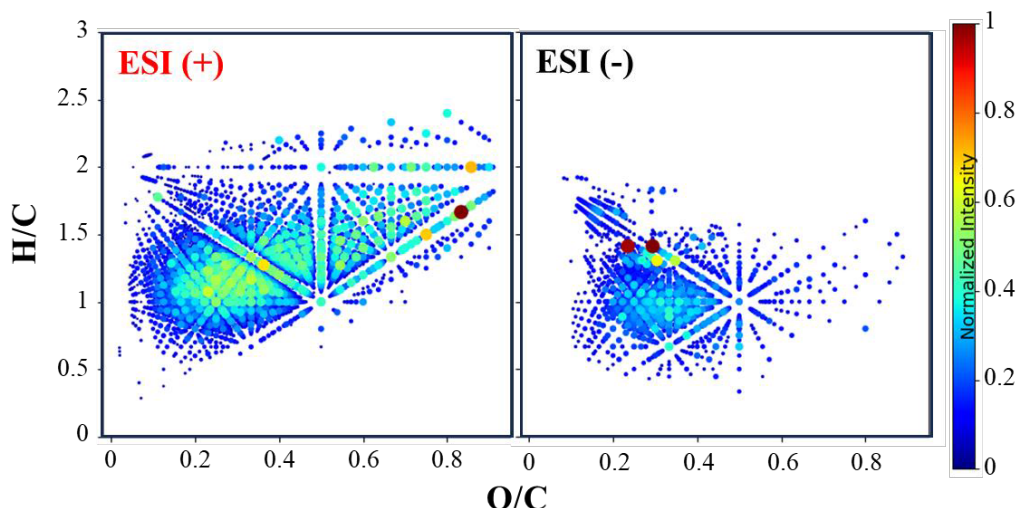


Figure 3. Van Krevelen diagram for $C_xH_yO_z$ class derived from FT-ICR MS analysis of beechwood pyrolysis bio-oil ionized by ESI (+) and ESI (-). Represented in square root scale for better visualization.

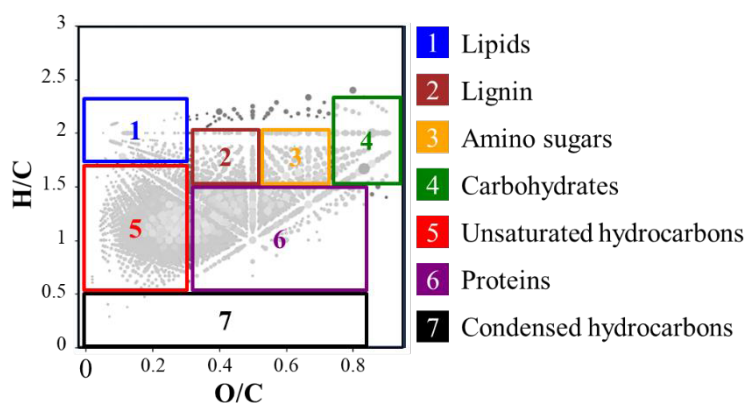


Figure 4. Van Krevelen diagram and corresponding common areas. Plotted with PyC2MC.

When comparing positive and negative ESI; the primary distinction is the quantity of molecular attributions, where 3612 molecular formulas are exclusive to positive mode and 142 are exclusive to negative mode, thus evidencing the complementary nature of ionization modes. Moreover, as illustrated in the Venn diagram in Figure 5, 85% of the molecular formulas assigned in negative mode were also assigned in positive mode. These findings suggest that for pyrolysis bio-oil produced from lignocellulosic biomass, the positive ion mode is the most suitable analytical condition for ESI. This outcome aligns with the findings reported by Buss et al. in 2021. They characterized pyrolysis liquids obtained from biochar production from wheat straw and softwood using ESI (+/-) FT-ICR MS, reporting a broader range of molecular attributions in positive mode, including the detection of $C_xH_yN_n$ species that were absent in ESI (-) analysis.

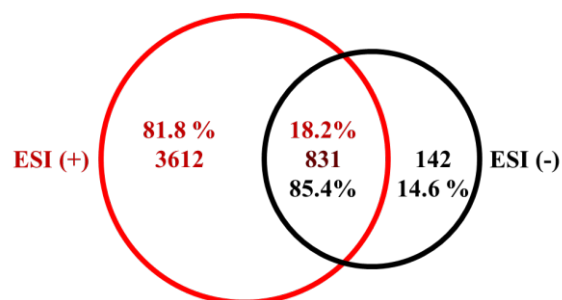


Figure 5. Venn diagram for molecular formulas assigned to beechwood pyrolysis bio-oil with FT-ICR MS by ESI (+) and ESI (-)

Conclusions

The application of FT-ICR mass spectrometry coupled with electrospray ionization has proven to be highly effective for differentiating and characterizing a wide range of compounds in beechwood pyrolysis bio-oil, including saturated and highly polar molecules such as lipids, pyrolytic sugars, and lignin derivatives. This study demonstrated the significant impact of ionization mode on the characterization of bio-oil derived from lignocellulosic biomass. Specifically, ESI in positive mode provided a broader range of molecular formula assignments—over 4000—compared to close to 1000 in negative ion mode, highlighting the complexity of the bio-oil's chemical composition.

The double bond equivalent (DBE) class distribution offered valuable insights into the aromatic nature of the pyrolysis bio-oil, with ESI (-) allowing the detection of molecules with higher DBE values (DBE₅ – DBE₁₀). Both ionization modes exhibited a similar trend in the distribution of oxygenated species, yet it was noted that molecules with a higher oxygen content were only ionized in positive mode.

Furthermore, the Van Krevelen diagram provided a detailed overview of the chemical composition, revealing that the pyrolysis products were primarily formed through key reactions such as dehydration, the loss of glycolaldehyde, and decarboxylation. This analysis underscores the complex interplay of chemical reactions that occur during pyrolysis, leading to the formation of a wide range of oxygenated compounds.

Regardless of the ionization mode employed, all plots consistently indicated a significant presence of lignin-derived compounds in the bio-oil. This finding aligns with the understanding that lignin, being the most complex and aromatic-rich component of lignocellulosic biomass, contributes heavily to the composition of pyrolysis bio-oils.

Overall, the results suggest that positive ion mode is more suitable for analyzing complex organic mixtures such as pyrolysis bio-oil, aligning with previous research that also reported a more extensive range of molecular attributions and the detection of additional species in positive mode. Indeed, 3612 molecular formulas were exclusively assigned by ESI (+), 142 by ESI (-); and 831 in both positive and negative modes. These findings confirm that both ionization modes are complementary and should be combined for a more comprehensive characterization of the organic mixture. Furthermore, integrating ESI with other commercially available ionization sources could further expand the detectable chemical composition [42–44]. The results shared in this work enhance the understanding of pyrolysis bio-oil's chemical complexity and emphasize the value of FT-ICR MS for its detailed characterization, which is essential for optimizing its potential applications.

Bibliographical references

1. Directorate-General for Communication (European Commission) *Circular Economy Action Plan: For a Cleaner and More Competitive Europe*; Publications Office of the European Union, 2020; ISBN 978-92-76-19070-7.
2. Biomasse énergie | Ministère du Partenariat avec les territoires et de la Décentralisation Ministère de la Transition écologique, de l'Énergie, du Climat et de la Prévention des risques Ministère du Logement et de la Rénovation urbaine Available online: <https://www.ecologie.gouv.fr/politiques-publiques/biomasse-energie> (accessed on 14 January 2025).
3. Vuppaladadiyam, A.K.; Vuppaladadiyam, S.S.V.; Awasthi, A.; Sahoo, A.; Rehman, S.; Pant, K.K.; Murugavelh, S.; Huang, Q.; Anthony, E.; Fennel, P.; et al. Biomass Pyrolysis: A Review on Recent Advancements and Green Hydrogen Production. *Bioresource Technology* **2022**, *364*, 128087, doi:10.1016/j.biortech.2022.128087.
4. Mohan, D.; Pittman, C.U.Jr.; Steele, P.H. Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. *Energy Fuels* **2006**, *20*, 848–889, doi:10.1021/ef0502397.
5. Feroso, J.; Pizarro, P.; Coronado, J.M.; Serrano, D.P. Advanced Biofuels Production by Upgrading of Pyrolysis Bio-Oil. *WIREs Energy and Environment* **2017**, *6*, e245, doi:10.1002/wene.245.
6. Mohabeer, C.; Reyes, L.; Abdelouahed, L.; Marcotte, S.; Buvat, J.-C.; Tidahy, L.; Abi-Aad, E.; Taouk, B. Production of Liquid Bio-Fuel from Catalytic de-Oxygenation: Pyrolysis of Beech Wood and Flax Shives. *Journal of Fuel Chemistry and Technology* **2019**, *47*, 153–166, doi:10.1016/S1872-5813(19)30008-8.
7. Mohabeer, C.; Reyes, L.; Abdelouahed, L.; Marcotte, S.; Taouk, B. Investigating Catalytic De-Oxygenation of Cellulose, Xylan and Lignin Bio-Oils Using HZSM-5 and Fe-HZSM-5. *Journal of Analytical and Applied Pyrolysis* **2019**, *137*, 118–127, doi:10.1016/j.jaap.2018.11.016.
8. Wang, J.; Jabbour, M.; Abdelouahed, L.; Mezghich, S.; Estel, L.; Thomas, K.; Taouk, B. Catalytic Upgrading of Bio-Oil: Hydrodeoxygenation Study of Acetone as Molecule Model of Ketones. *The Canadian Journal of Chemical Engineering* **2021**, *99*, 1082–1093, doi:10.1002/cjce.23909.
9. Machado, H.; Cristino, A.F.; Orišková, S.; Galhano dos Santos, R. Bio-Oil: The Next-Generation Source of Chemicals. *Reactions* **2022**, *3*, 118–137, doi:10.3390/reactions3010009.
10. Hung, N.V.; Mohabeer, C.; Vaccaro, M.; Marcotte, S.; Agasse-Peulon, V.; Abdelouahed, L.; Taouk, B.; Cardinael, P. Development of Two-dimensional Gas Chromatography (GC×GC) Coupled with Orbitrap-technology-based Mass Spectrometry: Interest in the Identification of Biofuel Composition. *Journal of Mass Spectrometry* **2020**, *55*, doi:10.1002/jms.4495.
11. Michailof, C.M.; Kalogiannis, K.G.; Sfetsas, T.; Patiaka, D.T.; Lappas, A.A. Advanced Analytical Techniques for Bio-Oil Characterization. *WIREs Energy and Environment* **2016**, *5*, 614–639, doi:10.1002/wene.208.
12. Staš, M.; Kubička, D.; Chudoba, J.; Pospíšil, M. Overview of Analytical Methods Used for Chemical Characterization of Pyrolysis Bio-Oil. *Energy Fuels* **2014**, *28*, 385–402, doi:10.1021/ef402047y.
13. Staš, M.; Chudoba, J.; Kubička, D.; Blažek, J.; Pospíšil, M. Petroleomic Characterization of Pyrolysis Bio-Oils: A Review. *Energy Fuels* **2017**, *31*, 10283–10299, doi:10.1021/acs.energyfuels.7b00826.
14. Marshall, A.G.; Rodgers, R.P. Petroleomics: The next Grand Challenge for Chemical Analysis. *Accounts of Chemical Research* **2004**, *37*, 53–59, doi:10.1021/ar020177t.
15. Katano, K.; Suzuki, T.; Matsumoto, K.; Kato, H.; Norinaga, K. New Data Processing Method for Heavy Oil Components Analyzed by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Journal of the Japan Petroleum Institute* **2023**, *66*, 101–108, doi:10.1627/jpi.66.101.
16. Smith, D.F.; Podgorski, D.C.; Rodgers, R.P.; Blakney, G.T.; Hendrickson, C.L. 21 Tesla FT-ICR Mass Spectrometer for Ultrahigh-Resolution Analysis of Complex Organic Mixtures. *Analytical Chemistry* **2018**, *90*, 2041–2047, doi:10.1021/acs.analchem.7b04159.
17. Jiang, S.-F.; Sheng, G.-P.; Jiang, H. Advances in the Characterization Methods of Biomass Pyrolysis Products. *ACS Sustainable Chemistry & Engineering* **2019**, *7*, 12639–12655, doi:10.1021/acssuschemeng.9b00868.

18. Smith, E.A.; Thompson, C.; Lee, Y.J. Petroleomic Characterization of Bio-Oil Aging Using Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry. *Bulletin of the Korean Chemical Society* **2014**, *35*, 811–814, doi:10.5012/bkcs.2014.35.3.811.
19. He, Z.; Guo, M.; Sleighter, R.L.; Zhang, H.; Chanel, F.; Hatcher, P.G. Characterization of Defatted Cottonseed Meal-Derived Pyrolysis Bio-Oil by Ultrahigh Resolution Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Journal of Analytical and Applied Pyrolysis* **2018**, *136*, 96–106, doi:10.1016/j.jaap.2018.10.018.
20. Kekäläinen, T.; Venäläinen, T.; Jänis, J. Characterization of Birch Wood Pyrolysis Oils by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Insights into Thermochemical Conversion. *Energy Fuels* **2014**, *28*, 4596–4602, doi:10.1021/ef500849z.
21. Stankovikj, F.; McDonald, A.G.; Helms, G.L.; Olarte, M.V.; Garcia-Perez, M. Characterization of the Water-Soluble Fraction of Woody Biomass Pyrolysis Oils. *Energy Fuels* **2017**, *31*, 1650–1664, doi:10.1021/acs.energyfuels.6b02950.
22. Jarvis, J.M.; McKenna, A.M.; Hilten, R.N.; Das, K.C.; Rodgers, R.P.; Marshall, A.G. Characterization of Pine Pellet and Peanut Hull Pyrolysis Bio-Oils by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2012**, *26*, 3810–3815, doi:10.1021/ef300385f.
23. Liu, Y.; Shi, Q.; Zhang, Y.; He, Y.; Chung, K.H.; Zhao, S.; Xu, C. Characterization of Red Pine Pyrolysis Bio-Oil by Gas Chromatography–Mass Spectrometry and Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2012**, *26*, 4532–4539, doi:10.1021/ef300501t.
24. Buss, W.; Hertzog, J.; Pietrzyk, J.; Carré, V.; Mackay, C.L.; Aubriet, F.; Mašek, O. Comparison of Pyrolysis Liquids from Continuous and Batch Biochar Production—Influence of Feedstock Evidenced by FTICR MS. *Energies* **2020**, *14*, 9, doi:10.3390/en14010009.
25. Miettinen, I.; Mäkinen, M.; Vilppo, T.; Jänis, J. Compositional Characterization of Phase-Separated Pine Wood Slow Pyrolysis Oil by Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. *Energy Fuels* **2015**, *29*, 1758–1765, doi:10.1021/ef5025966.
26. Mase, C.; Moulian, R.; Lazzari, E.; Garnier, C.; Piparo, M.; Hubert-Roux, M.; Afonso, C.; Dayton, D.C.; Barrère-Mangote, C.; Giusti, P. Comparison of Lignocellulosic-Based Biomass Pyrolysis Processes by Multi-Scale Molecular Characterization. *Journal of Analytical and Applied Pyrolysis* **2024**, *177*, 106354, doi:10.1016/j.jaap.2024.106354.
27. Ware, R.L.; Rowland, S.M.; Rodgers, R.P.; Marshall, A.G. Advanced Chemical Characterization of Pyrolysis Oils from Landfill Waste, Recycled Plastics, and Forestry Residue. *Energy Fuels* **2017**, *31*, 8210–8216, doi:10.1021/acs.energyfuels.7b00865.
28. Chacón-Patiño, M.L.; Mase, C.; Maillard, J.F.; Barrère-Mangote, C.; Dayton, D.C.; Afonso, C.; Giusti, P.; Rodgers, R.P. Petroleomics Approach to Investigate the Composition of Upgrading Products from Pyrolysis Bio-Oils as Determined by High-Field FT-ICR MS. *Energy Fuels* **2023**, *37*, 16612–16628, doi:10.1021/acs.energyfuels.3c02599.
29. Olcese, R.; Carré, V.; Aubriet, F.; Dufour, A. Selectivity of Bio-Oils Catalytic Hydrotreatment Assessed by Petroleomic and GC*GC/MS-FID Analysis. *Energy Fuels* **2013**, *27*, 2135–2145, doi:10.1021/ef302145g.
30. Koike, N.; Hosokai, S.; Takagaki, A.; Nishimura, S.; Kikuchi, R.; Ebitani, K.; Suzuki, Y.; Oyama, S.T. Upgrading of Pyrolysis Bio-Oil Using Nickel Phosphide Catalysts. *Journal of Catalysis* **2016**, *333*, 115–126, doi:10.1016/j.jcat.2015.10.022.
31. Tessarolo, N.S.; Silva, R.V.S.; Vanini, G.; Casilli, A.; Ximenes, V.L.; Mendes, F.L.; de Rezende Pinho, A.; Romão, W.; de Castro, E.V.R.; Kaiser, C.R.; et al. Characterization of Thermal and Catalytic Pyrolysis Bio-Oils by High-Resolution Techniques: ¹H NMR, GC×GC-TOFMS and FT-ICR MS. *Journal of Analytical and Applied Pyrolysis* **2016**, *117*, 257–267, doi:10.1016/j.jaap.2015.11.007.
32. Hertzog, J.; Carré, V.; Jia, L.; Mackay, C.L.; Pinard, L.; Dufour, A.; Mašek, O.; Aubriet, F. Catalytic Fast Pyrolysis of Biomass over Microporous and Hierarchical Zeolites: Characterization of Heavy Products. *ACS Sustainable Chemistry & Engineering* **2018**, *6*, 4717–4728, doi:10.1021/acssuschemeng.7b03837.

33. Hertzog, J.; Mase, C.; Hubert-Roux, M.; Afonso, C.; Giusti, P.; Barrère-Mangote, C. Characterization of Heavy Products from Lignocellulosic Biomass Pyrolysis by Chromatography and Fourier Transform Mass Spectrometry: A Review. *Energy Fuels* **2021**, *35*, 17979–18007, doi:10.1021/acs.energyfuels.1c02098.
34. Cole, D.P.; Smith, E.A.; Dalluge, D.; Wilson, D.M.; Heaton, E.A.; Brown, R.C.; Lee, Y.J. Molecular Characterization of Nitrogen-Containing Species in Switchgrass Bio-Oils at Various Harvest Times. *Fuel* **2013**, *111*, 718–726, doi:10.1016/j.fuel.2013.04.064.
35. Santos, J.; Santos, L.; Silva, F.; Eberlin, M.; Wisniewski Jr, A. Comprehensive Characterization of Second-Generation Biofuel from Invasive Freshwater Plants by FT-ICR MS. *BioEnergy Research* **2015**, *8*, 1–8, doi:10.1007/s12155-015-9650-x.
36. Hertzog, J.; Carré, V.; Le Brech, Y.; Mackay, C.L.; Dufour, A.; Mašek, O.; Aubriet, F. Combination of Electrospray Ionization, Atmospheric Pressure Photoionization and Laser Desorption Ionization Fourier Transform Ion Cyclotronic Resonance Mass Spectrometry for the Investigation of Complex Mixtures – Application to the Petroleomic Analysis of Bio-Oils. *Analytica Chimica Acta* **2017**, *969*, 26–34, doi:10.1016/j.aca.2017.03.022.
37. Hertzog, J.; Tews, I.; Mood, S.H.; Aubriet, F.; Carré, V.; Garcia-Perez, M. Performance of Catalytic Wet Oxidation on Thermochemical Aqueous Effluents Assessed by FT-ICR MS. *Journal of Environmental Chemical Engineering* **2024**, *12*, 113721, doi:10.1016/j.jece.2024.113721.
38. Jaafar, Y.; Arias, G.; Abdelouahed, L.; El Samrani, A.; El hage, R.; Taouk, B. Upgrading Pyrolytic Oil via Catalytic Co-Pyrolysis of Beechwood and Polystyrene. *Molecules* **2023**, *28*, 5758, doi:10.3390/molecules28155758.
39. Reyes, L.; Abdelouahed, L.; Campusano, B.; Buvat, J.-C.; Taouk, B. Exergetic Study of Beech Wood Gasification in Fluidized Bed Reactor Using CO₂ or Steam as Gasification Agents. *Fuel Processing Technology* **2021**, *213*, 106664, doi:10.1016/j.fuproc.2020.106664.
40. Reyes, L.; Abdelouahed, L.; Mohabeer, C.; Buvat, J.-C.; Taouk, B. Energetic and Exergetic Study of the Pyrolysis of Lignocellulosic Biomasses, Cellulose, Hemicellulose and Lignin. *Energy Conversion and Management* **2021**, *244*, 114459, doi:10.1016/j.enconman.2021.114459.
41. Sueur, M.; Maillard, J.F.; Lacroix-Andrivet, O.; Rüger, C.P.; Giusti, P.; Lavanant, H.; Afonso, C. PyC2MC: An Open-Source Software Solution for Visualization and Treatment of High-Resolution Mass Spectrometry Data. *Journal of the American Society for Mass Spectrometry* **2023**, *34*, 617–626, doi:10.1021/jasms.2c00323.
42. Mase, C.; Maillard, J.F.; Marcuz, S.; Hubert-Roux, M.; Afonso, C.; Giusti, P. Contribution of LDI and MALDI for the Characterization of a Lignocellulosic-Based Pyrolysis Bio-Oil. *Journal of the American Society for Mass Spectrometry* **2023**, *34*, 1789–1797, doi:10.1021/jasms.3c00197.
43. Ghislain, T.; Faure, P.; Michels, R. Detection and Monitoring of PAH and Oxy-PAHs by High Resolution Mass Spectrometry: Comparison of ESI, APCI and APPI Source Detection. *Journal of The American Society for Mass Spectrometry* **2012**, doi:10.1007/s13361-011-0304-8.
44. Sanguineti, M.M.; Hourani, N.; Witt, M.; Sarathy, S.M.; Thomsen, L.; Kuhnert, N. Analysis of Impact of Temperature and Saltwater on Nannochloropsis Salina Bio-Oil Production by Ultra High Resolution APCI FT-ICR MS. *Algal Research* **2015**, *9*, 227–235, doi:10.1016/j.algal.2015.02.026.