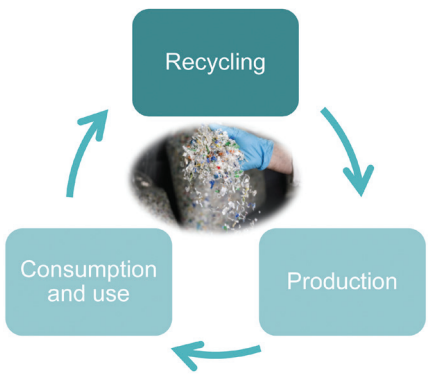
PLASTIC PYROLYSIS OIL CHARACTERIZATION FOR CIRCULAR ECONOMY APPLICATION

The large use of plastics in many sectors lead to the increase of global plastic production and consequently to the generation of plastic wastes inducing environmental concerns associated with non-renewable fossil resources and waste disposal. Sustainable plastics waste management remains therefore a major challenge nowadays [1]. Circular economy approaches are currently attracting a lot of interest by relying on plastic waste recycling and reuse [2]. Thermal treatments such as pyrolysis allow to degrade polymeric chains constituting plastics into lighter and high value-added oil derivatives. In particular, the pyrolysis oil produced is considered as an important source of fuels, chemicals and monomers, the basic unit of the plastic material that both circumvent the above-mentioned problems. However, to improve conversion and valorization processes, an advanced molecular description is essential.



Device:

Plastic pyrolysis oils are described as complex mixture composed of thousands of chemical species covering a wide range of masses and polarity [3]. For this purpose, several analytical methods can be applied depending on the desired information to characterize plastic pyrolysis oil. The targeted approach including infrared (IR), nuclear magnetic resonance (NMR) spectroscopies and gas (GC) and liquid chromatography (LC) allows identifying and quantifying known plastic pyrolysis oil components or their chemical functions but are limited to tackle such highly complex mixture [4-6]. Due to the complexity of the sample, ultra-high resolution mass spectrometry is required. Fourier transform ion cyclotron resonance (FTICR) mass spectrometry offers the best performances in terms of resolution, mass accuracy and dynamic range [7]. Indeed, it allows signals to be separated based on their mass-to-charge (m/z) ratio and then assigned to a unique molecular formula with an error less than 0.3 ppm (Figure 1). In our context and for an advanced molecular description of complex mixture, an untargeted approach, which ensures the detection and the assignment of thousands of species at the molecular level, has proven its efficiency [3, 8]. Typically, in this kind of approach, the sample is directly introduced into the mass spectrometer without an upstream separation step.

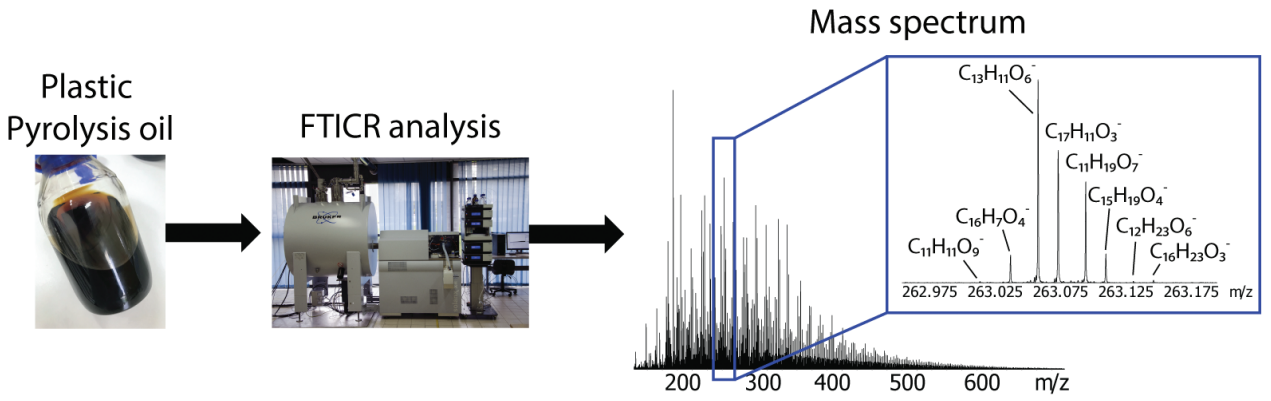


Figure 1. Analysis workflow with direct analysis by ESI-(−)-FTICR-MS and attribution of unique molecular formulas to each signal.

With FTICR analyzer, different sources of ionization could be used. The choice of ionization method is significant and depends on the type of information required [9]. Indeed, all ionization sources present some specificities in term of ionization efficiency, which allows their complementarity in the description of a mixture. In this study, three atmospheric pressure ionization sources were used. Electrospray ionization (ESI) is specific to polar and mid-polar species. Typically, in negative mode ESI acid species ionization is favored whereas in positive mode, the ionization of basic species is dominant. Atmospheric pressure photoionisation (APPI) and atmospheric pressure chemical ionization (APCI) are less selective and allow the detection of low-polarity species (Figure 2). Especially, with APCI, alkanes ionization could be obtained by the use of hydrocarbon solvents such as heptane [10].

How to represent the data set?

Many representations exist in literature to represent the observed molecular information [11]. The heteroatoms class distribution represents the relative abundance of the achieved molecular species such as pure hydrocarbons (CH), oxygen-containing species (O_x), nitrogen-containing species (N_y) and nitrogen- and oxygen-containing species (O_xN_y). To have more detailed about the unsaturation degree of the detected species, their double bond equivalent (DBE) can be calculated and represented versus the number of carbon atoms. The DBE represents the number of rings and unsaturated bonds and therefore its aromatic or aliphatic character. In Figure 3, each point correspond to an ion with its DBE and number of carbon atom. By choice, a color scale is used to represent the relative intensity of each ion.

Results:

A pyrolysis oil was produced from municipal waste without prior separation and was analyzed by FTICR analysis. The nitrogen-containing species were detected using both positive and negative modes ESI-FTICR. The other classes, such as hydrocarbons and oxygenated species were detected using

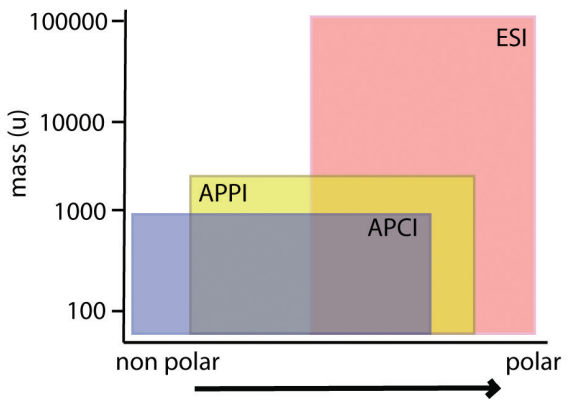


Figure 2. Ionization source selectivity

positive mode ESI, APPI and APCI and negative mode ESI-FTICR.

Hydrocarbon compounds are described using both APPI and APCI sources in positive ion mode. Both aliphatic and aromatic distributions were observed which is consistent with the fact that plastic pyrolysis waste was composed of aliphatic and aromatic polymers. Moreover, the presence of aromatic species could result to the elimination of small molecules in place in the pyrolysis process inducing the formation of unsaturation. As expected, APCI affords the detection of alkanes (DBE 0 value) by a hydride transfer gas mechanism. Species at DBE 3 were also observed that could be assigned to triolefins, cyclopentadiene or three naphtenic cycles. The main class observed was species at DBE 2, which could be attributed to diolefins. This class is important because it can cause undesirable polymerization during refining processes, when the diolefins are conjugated.

Basic and neutral nitrogen-containing species were highlighted by ESI in both positive and negative ion modes respectively. Nitrogen-containing species are important because they are poison in refining processes [12]. They could come from polymers constituting the plastic waste such as polyamide. They could also come from different additives such as UV-stabilizers and colorants [13, 14]. Interestingly, structures observed (quinoline, pyridine, quinoxaline or naphtyridine) for nitrogen-containing species are consistent with the similar molecule classes typically detected in petroleum fractions [15, 16]. This observation was interesting because the elimination of these types of species is already known and will be performed in the same manner.

The oxygen-containing species was revealed in ESI in negative ion mode, APPI in positive ion mode, and APCI in positive ion mode. In the same way as hydrocarbon compounds, both aliphatic and aromatic contributions were observed. Especially, an aromatic contribution at DBE 4 was observed in O_1 class. These species could be attributed to phenol that are marker of paper label stuck on the plastic packaging. The aromatic species could be obtained from the pyrolysis of aromatic plastics such as polyethylene terephthalate (PET) [17] or from the degradation of different additives and colorants.

Conclusion:

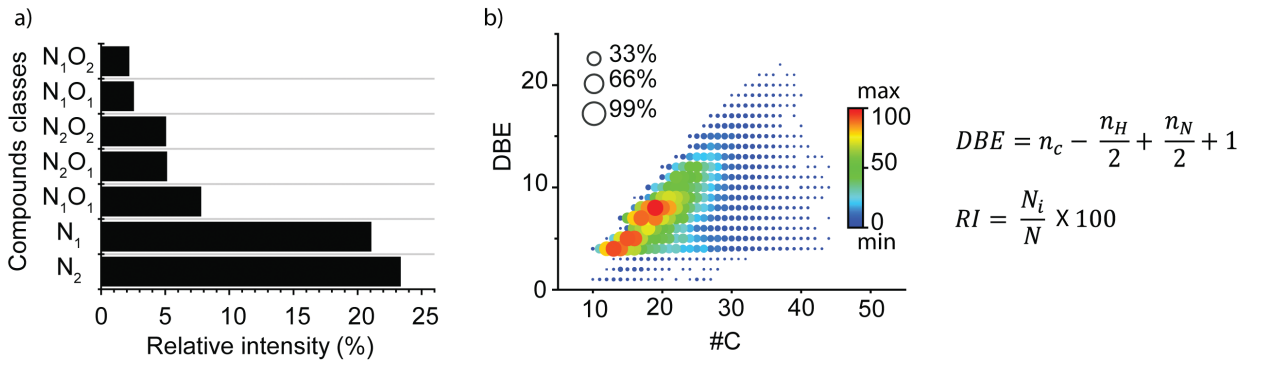
Ultra-high resolution FTICR mass spectrometry has proven to be useful for the characterization of molecular fingerprint of plastic pyrolysis oil. The combination of atmospheric pressure ionization sources has shown to be effective for the highlight of different molecular classes. The molecular based information on heteroatoms-containing compounds in a mixed plastic pyrolysis oil by this untargeted method will enable to adapt the recycling/ refining process of plastics.

Additional information:

Mase, C., et al. (2021). "Molecular Characterization of a Mixed Plastic Pyrolysis Oil from Municipal Wastes by Direct Infusion Fourier Transform Ion Cyclotron Resonance Mass Spectrometry." Energy & Fuels.

References :

1. Qureshi, M.S., et al., Pyrolysis of plastic waste: Opportunities and challenges. Journal of Analytical and Applied Pyrolysis, 2020. 152.
2. Ilyas, M., et al., Plastic waste as a significant threat to environment - a systematic literature review. Rev Environ Health, 2018. 33(4): p. 383-406.
3. Ware, R.L., et al., Advanced Chemical Characterization of Pyrolysis Oils from Landfill Waste, Recycled Plastics, and Forestry Residue. Energy & Fuels, 2017. 31(8): p. 8210-8216.
4. Toraman, H.E., et al., Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors. J Chromatogr A, 2014. 1359: p. 237-46.
5. Siddiqui, M.N. and H.H. Redhwi, Pyrolysis of mixed plastics for the recovery of useful products. Fuel Processing Technology, 2009. 90(4): p. 545-552.
6. Dunkle, M.N., et al., Method development and evaluation of pyrolysis oils from mixed waste plastic by GC-VUV. J Chromatogr A, 2021. 1637: p. 461837.
7. Marshall, A.G., C.L. Hendrickson, and G.S. Jackson, Fourier transform ion cyclotron resonance mass spectrometry: a primer. Mass Spectrom Rev, 1998. 17(1).
8. Dhahak, A., et al., Analysis of Products Obtained from Slow Pyrolysis of Poly(ethylene terephthalate) by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Coupled to Electrospray Ionization (ESI) and Laser Desorption Ionization (LDI). Industrial & Engineering Chemistry Research, 2020. 59(4): p. 1495-1504.
9. Farenc, M., et al., Comparison of Atmospheric Pressure Ionization for the Analysis of Heavy Petroleum Fractions with Ion Mobility-Mass Spectrometry. Energy & Fuels, 2016. 30(11): p. 8896-8903.
10. Tose, L.V., et al., Analyzes of hydrocarbons by atmosphere pressure chemical ionization FT-ICR mass spectrometry using isooctane as ionizing reagent. Fuel, 2015. 153: p. 346-354.
11. Staš, M., et al., Petroleomic Characterization of Pyrolysis Bio-oils: A Review. Energy & Fuels, 2017. 31(10): p. 10283-10299.
12. Prado, G.H.C., Y. Rao, and A. de Klerk, Nitrogen Removal from Oil: A Review. Energy & Fuels, 2016. 31(1): p. 14-36.
13. Kim, S., N. Lee, and J. Lee, Pyrolysis for Nylon 6 Monomer Recovery from Teabag Waste. Polymers (Basel), 2020. 12(11).
14. Gijsman, P., J. Hennekens, and D. Tummers, The mechanism of action of hindered amine light stabilizers. Polymer Degradation and Stability, 1993. 39(2): p. 225-233.
15. Purcell, J.M., et al., Speciation of nitrogen containing aromatics by atmospheric pressure photoionization or electrospray ionization fourier transform ion cyclotron resonance mass spectrometry. J Am Soc Mass Spectrom, 2007. 18(7): p. 1265-73.
16. Zhang, Y., et al., Tracking Neutral Nitrogen Compounds in Subfractions of Crude Oil Obtained by Liquid Chromatography Separation Using Negative-Ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Energy & Fuels, 2010. 24(12): p. 6321-6326.
17. Dimitrov, N., et al., Analysis of recycled PET bottles products by pyrolysis-gas chromatography. Polymer Degradation and Stability, 2013. 98(5): p. 972-979.



$$DBE = n_c - \frac{n_H}{2} + \frac{n_N}{2} + 1$$

$$RI = \frac{N_i}{N} \times 100$$

Figure 3. Data representations: (a) bar plot showing the element content and (b) DBE vs C# plot of the N_2 class

About the authors:

Charlotte Mase is currently conducting a PhD in analytical chemistry at COBRA laboratory in collaboration with TotalEnergies. She works on the molecular characterization of pyrolysis oils (plastic or biomass) and new sources of energies by ultra-high-resolution mass spectrometry

After receiving his PhD in analytical chemistry in 2000, at Paris VI University, **Carlos Afonso** joined the group of Prof. Catherine Fenselau, at Maryland University. In 2002, he obtained a CNRS researcher position in Paris. Since 2011, he is professor at Rouen University where he leads the mass spectrometry group of COBRA laboratory. His research interests are the development of new methodologies for the characterization of complex organic mixtures by FTICR MS and IM-MS.

Pierre Giusti obtained his PhD in analytical chemistry, from the University of Pau and Pays de l'Adour, in 2006. He is currently the manager of the Molecular Separation and Identification Service in R&D department of TotalEnergies Refining & Chemicals. Co-founder of the iC2MC laboratory, he also obtained the position of CNRS Research Director in January 2021. His research interests are the elemental and molecular analyses of complex matrices in the field of energy.

Author Contact Details

Carlos Afonso • University of Rouen, UMR 6014 COBRA / IRCOF, Rue Lucien Tesnière,
76130 Mont Saint Aignan, France • Tel: +33 2 35 52 29 40 • Email: carlos.afonso@univ-rouen.fr • **Web: www.lab-cobra.fr**

Charlotte Mase *Carlos Afonso* *Pierre Giusti*