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Review on evolved gas analysis mass spectrometry with soft photoionization for the chemical description of petroleum, petroleum-derived materials and alternative feedstocks

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Review Article

Review on evolved gas analysis mass spectrometry with soft photoionization for the chemical description of petroleum, petroleum-derived materials and alternative feedstocks

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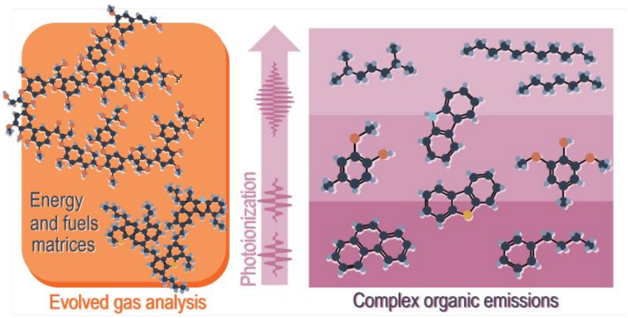

Abstract

Modern industry strongly relies on the molecular analysis of fossil petroleum and petroleum-derived materials. In the context of a circular economy and carbon neutrality, the chemical description of alternative feedstock materials, such as waste plastic and biomass pyrolysis oils, increases in importance. Moreover, online monitoring of the thermochemical and catalytic conversion processes have gained rising attention. In this framework, evolved gas analysis (EGA) concepts with soft photoionization mass spectrometry (PIMS) were successfully deployed for numerous challenges. On the one hand, photoionization is a highly versatile technique and allows to "softly" ionize the analyte molecule, preserving the molecular information. On the other hand, multiple evolved gas analysis concepts exist with unique benefits, such as the mass loss information in thermogravimetry coupling, high-throughput in direct inlet probe concepts, or straightforward reactor monitoring, allowing direct online insights into pyrolytic transformation processes. Hence, this review aims to summarize the recent work in the field of EGA-PIMS. After technical description of the multiple photoionization and thermal analysis concepts, applied studies are summarized, discussed, and evaluated. Besides fossil fuels, studies on alternatives from renewable materials such as biomass pyrolysis, plastic pyrolysis oils, and recycling processes, are reviewed. Finally, future perspectives on this field are given, highlighting the importance of those soft ionization schemes together with state-of-the-art detection by high-resolution mass spectrometry in the field of energy and fuels research.

Introduction

Molecular-level analysis of complex organic mixtures remains to be one of the most challenging tasks in analytical chemistry. Considering the world's energy demand and the wide variety of products made from petroleum, its chemical characterization continues to be an essential part of the 21st century. Nonetheless, considering the movement to a carbon-neutral society and circular economy, the in-depth analysis of alternative feedstocks, such as waste pyrolysis oils and bio-oils, becomes more and more decisive. Alternative energy sources are heavily investigated, involving solid fuels, such as biomass, coal and organic polymers from municipal solid waste (MSW). Together with heavier crude oils containing higher levels of asphaltenes and the utilization of "the bottom of the barrel", such as bitumen and vacuum residues, new challenges for chemical analysis arise.

From an analytical perspective, spectroscopic approaches, such as nuclear magnetic resonance spectroscopy, or electrochemical methods, such as polarography or electrophoresis, are limited in terms of peak capacity and separation power. Given the complexity of petroleum, bio-oils and pyrolysis products, mass spectrometry is most often utilized as one of the most versatile analytical techniques. In fact, mass spectrometry should not be regarded as a single analysis method but more as a repository of analytical techniques. The modular variation possibilities, given by the combination of sample introduction, ionization scheme, and mass analyzer, lead to high popularity in almost every domain of analytical chemistry and, thus, also in energy and fuels research.

In the last two decades, tremendous effort was made in the further development of mass spectrometric techniques. Particularly, soft ionization schemes, preserving the molecular identity of the analyte, became frequent. Besides the classical spray- and desorption-based techniques, such as electrospray ionization (ESI) or direct analysis in real-time (DART), photon-based approaches are commonly used. The ability to conduct photoionization at vacuum conditions or atmospheric pressure as well as variation of the wavelength changing the nature of ionization makes it a versatile concept. Excellent reviews discussing ionization techniques in general or atmospheric pressure ionization schemes have been published.[1,2] The review article of Li et al. from 2015 reporting on the field of gas chromatography coupled to atmospheric pressure ionization nicely points out the individual properties of a wide variety of ionization schemes.[3] However, this review article will especially focus on soft photoionization schemes. Due to overlapping similarities in ionization nature, atmospheric pressure chemical ionization (APCI) is discussed together with classical discharge lamp-based atmospheric pressure photoionization (APPI).

Aside from the ionization technique, sample introduction and hyphenation strategies remain one core research field in mass spectrometry, particularly for the analysis of complex mixtures. Despite the progress in liquid chromatography and ion mobility spectrometry, heavily accelerated by biochemical and medical research, evolved gas techniques remain one of the most widely used concepts. For volatile and semi-volatile constituents, the analysis is primarily encountered by gas chromatography mass spectrometry (GCMS), while in polymer science, the analysis is faced by pyrolysis gas chromatography mass spectrometry (Pyr-GCMS). Evolved gas analysis techniques encompass a wide variety of methods, from which all rely on a thermal desorption and degradation of the sample material with subsequent chemical analysis by ionization and mass selective detection. One of the first reviews on evolved gas analysis mass spectrometry (EGA-MS) was published almost 40 years ago in 1984 by Holdiness, already exhaustively describing on over 40 figures and almost 40 pages the current advances in evolved gas analysis mass spectrometry.[4] Since the late 1990s, the group of Materazzi et al. is frequently reviewing the publication landscape of evolved gas analysis with no particular focus towards an applicative area or ionization technique.[5–11] Benhammada et al. reviewed thermogravimetric coupling for the specific application towards the decomposition of energetic materials.[12] Pyr-GCMS is almost exclusively conducted with hard electron ionization and will not be reviewed extensively within this article. Instead, the reader is directed to a very detailed and recent overview on Pyr-GCMS with special emphasis towards organic matter and microplastics by Picó et al.[13] or to the work of Ma et al.[14,15] and Alkalin et al.[16]. Nonetheless, the general concept of Pyr-GCMS and the existing studies deploying soft photoionization are given below.

From the applicative perspective, this review article will cover work on classical fossil petroleum and petroleum-derived materials but also on alternative feedstocks, such as bio-oils and plastic pyrolysis oils. In this respect, the terminology “Petroleomics” is often used, describing the molecular-level analysis of petroleum and petroleum-derived materials, most often conducted by high-resolution mass spectrometry. Very recently, the Barrow-group presented an exhaustive review on “Petroleomics: Tools, Challenges, and Developments”.[17] Here, the authors discuss in detail the technical development of ultra-high resolution mass spectrometric instrumentation but also focus towards experimental protocols and data analysis procedures. Furthermore, in the context of bio-oil analysis, a review article on the comprehensive gas chromatographic investigation of those materials was recently presented.[18] Other review articles covering the mass spectrometric analysis of fossil petroleum[19,20], solid fuels[21], and alternative sources feature ultra-high resolution mass spectrometry, ion mobility coupling, or spray-based ionization concepts[22].

Evolved gas analysis mass spectrometry with soft ionization is increasingly used for the chemical description of petroleum, petroleum-derived materials, solid fuels, bio oils, and pyrolysis oils. This trend can be clearly depicted from Figure 1 (descriptive details can be found in the supporting information), visualizing the annual publications featuring selected keywords from 2005 to today. Wang et al. considered this aspect and excellently reviewed 2016 the pyrolysis studies on solid fuels focusing on photoionization mass spectrometry[21]. One of the reasons for this popularity in energy and fuels research is certainly the ability to mimic pyrolysis processes and thermochemical conversion reactions, a promising approach for direct industrial applications. However, this review aims to summarize a broader range of recent instrumental developments and application fields of EGA-PIMS, including, besides fossil fuels, also alternatives from renewable materials such as biomass pyrolysis, plastic pyrolysis oils, and recycling processes. Herein, the terminology evolved gas analysis is covering classical gas chromatography (GC) and thermal analysis, such as thermogravimetric coupling, separating sample introduction and ionization volume but also combined approaches, such as direct inlet probe at reduced and atmospheric pressure conditions. Neither other ionization concepts, such as laser desorption/ionization or field desorption/ionization, or other separation techniques, such as supercritical fluid chromatography (SFC), liquid chromatography (LC) and ion mobility spectrometry (IMS), will be covered within this article. After briefly summarizing the instrumental fundamentals of soft photoionization concepts and evolved gas analysis approaches, an applicative overview on the analysis of classical fossil petroleum, residues and solid fuels, bio-oils, and waste pyrolysis oils is given. The material contained in this report primarily represents advances and studies that have been published in the last ten years, since 2011.

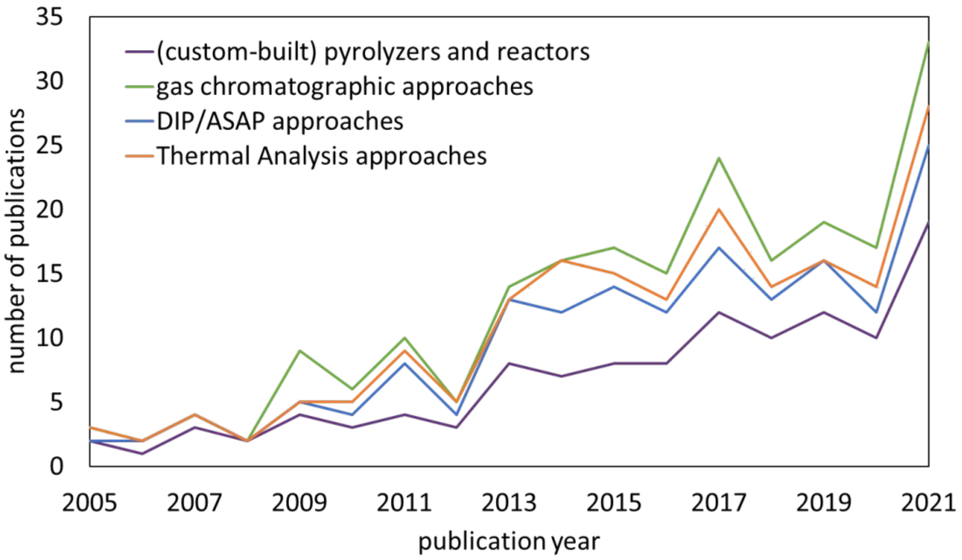

Figure 1: Time-trend covering 2005-2021 for the number of publications featuring the keywords related to the field of evolved gas analysis photoionization mass spectrometry in energy and fuels research grouped to: custom-built pyrolyzers and reactors, thermal analysis (TA) and gravimetry approaches, gas chromatography (GC) and pyrolysis gas chromatography concepts and direct inlet probe techniques (DIP/ASAP). A substantial increase in the scientific output over the last one and a half decades can be seen. Please note: The trend is given as a stacked line plot, summing up the publications per category per year.

Soft ionization concepts with focus towards photoionization (PI)

Ionization techniques in mass spectrometry can be divided into hard concepts, causing strong fragmentation of the ionized molecule, and soft schemes, mostly preserving the molecular ion and, as thus, the chemical information. Photoionization attempts to ionize a given analyte by one or multiple photons, preferably without fragmentation. Generally, photoionization mass spectrometric approaches can be classified according to the deployed wavelength and light source. Direct ionization of a molecule by absorption of one photon with the energy equal or larger to the ionization potential of the analyte is referred to as single-photon ionization (SPI). Ionization cross-section of an analyte can be used for direct quantification.[23–26] In contrast, resonance-enhance multiphoton ionization (REMPI) requires the absorption of at least two photons for ionization. Here, it is taken advantage of the absorption properties and a resonant intermediate state. Various REMPI schemes exist with one-color, two-photon (1+1 REMPI) being the most popular technique.

The ultraviolet (UV) and vacuum ultraviolet (VUV) radiation required for photoionization is commonly be generated by various laser types, different concepts of discharge lamps, or even by utilizing a beamline at a synchrotron. In the following, the general concepts of vacuum and atmospheric pressure photo and laser ionization are given briefly, schematically summarized in Figure 2. The evolved gas analysis instrumentation used as sample introduction and respective reaction pathways are schematically summarized in Figure 4. Atmospheric pressure chemical ionization (APCI) is included in this review for completeness. Compared with classical APPI, they share certain similarities in the ionization process.

For detailed aspects of photoionization and photo-induced ionization schemes in mass spectrometry, the reader is directed to a very recent book edited by Zimmermann and Hanley[27] and to multiple review articles[28–30]. More specifically, the review of Ryan et al. summarizing laser desorption/ionization mass spectrometry attempts in petroleum research should be mentioned here.[31] Table 1 provides a brief comparison of VUV light sources utilized in EGA-MS.

Laser-based photoionization

Lasers emit coherent, collimated monochromatic light with high photon density, highly preferable characteristics for their utilization in analytical chemistry in general and mass spectrometry specifically. Most aromatic organic species in the context of energy and fuels research exhibit a distinct absorption band in the UV region (200-300 nm). This wavelength region is easily accessible by various commercial laser systems, such as solid-state laser, *e.g.*, fourth harmonic of a Nd:YAG (266 nm), or excimer laser, *e.g.*, Krypton fluoride excimer (248 nm). Consequently, photoionization through an optical resonant absorption step (REMPI) was also largely conducted for evolved gas analysis mass spectrometry. In the last decade, energy and fuels applications utilizing 266 nm for thermogravimetric[32,33] and gas chromatographic[34] coupling need to be mentioned. REMPI is also conducted at atmospheric pressure conditions for mass spectrometric usage, firstly reported by Benter and co-workers in 1999 and referred to as atmospheric pressure laser ionization (APLI).[35] Schiewek et al. introduced evolved gas analysis APLI, in terms of GC-APLI-MS, in 2007 and reported detection limits in the nanogram range for polycyclic aromatic hydrocarbons (PAHs), such as chrysene.[36] Benigni et al. used GC-APLI in combination with high-resolution mass spectrometry for fossil oil analysis deploying 266 nm radiation.[34]

For SPI, VUV radiation needs to surpass the ionization potential of the analyte. By a frequency tripling process using a xenon gas cell (118 nm, 10.5 eV) irradiated with the third harmonic of solid-state Nd:YAG lasers (355 nm, 3.5 eV), pulsed VUV radiation for single-photon ionization mass spectrometry was generated.[37–39] Already in 1999, Zoller studied different coal samples by coupling thermal analysis to SPI-MS.[40] Other more recent studies were done by coupling fluidized bed reactor[41,42] or thermogravimetry[32,33] further elucidated below. In principle, wavelength-tunable VUV radiation is possible by mixing other noble gases to the xenon, such as krypton. Nonetheless, it has been shown that this approach is not easy to operate and far from optimized or commercialized.

At atmospheric pressure conditions, predominantly radiation in the UV wavelength range (200-300 nm) was used so far. Very recently, we introduced gas chromatography coupled to atmospheric pressure single photon laser ionization (APSPLI) mass spectrometry, deploying a Fluorine excimer laser emitting radiation at 157 nm (7.9 eV), investigating a fossil light crude oil.[43] This laser provides a unique source for pulsed VUV radiation without the need of frequency multiplication. Interestingly, this light source was not used for EGA-MS at vacuum conditions. Novel frequency doubling of the third harmonic of a Nd:YAG laser (177.3 nm) also holds the potential to be used in EGA-MS. Even femtosecond laser ionization was proposed for GCMS.[44]

Lamp-based photoionization

Aside from laser-based sources, discharge lamps provide a simplistic, low-cost and convenient source for VUV light used in SPI-MS. Most common are low-pressure rare gas discharge lamps. Here, the VUV radiation is created based on spectral emission lines generated by exciting the gas in the sealed lamp to a plasma. Excitation of the gas can be done by a direct current or radio-frequency-powered field. Depending on the rare gas, different wavelengths are available, such as 129/147 nm (9.6/8.4 eV) for Xenon, 117/124 nm (10.6/10.0 eV) for Krypton, or 105/107 nm (11.8/11.6 eV) for Argon. Another lamp-based source of VUV radiation are deuterium lamps yielding a broad emission spectrum from 112 to 900 nm after arc discharge. Moreover, electron beam-pumped excimer VUV lamps (EBEL) have been reported and utilized for mass spectrometry.[45–49] Comparable to excimer laser technology, also excimer lamps based on rare gas and halogen mixtures have been described. Other VUV light source concepts are microhollow cathode discharge lamps or more sophisticated designs of electron beam-pumped excimer lamps utilizing gas mixtures. Compared to discharge lamps or simple electron beam-pumped sources, these solutions have not been used yet for EGA-MS in energy and fuels research. Exemplary, in situ EGA-MS studies deploying lamp-based photoionization were published by Hu and co-workers investigating the pyrolysis of lignite.[50,51]

For atmospheric pressure photoionization, predominantly radiofrequency-powered Krypton-filled electrodeless discharge lamps are deployed. Classical direct infusion APPI sources, their usage in liquid chromatography coupling, and applications have been described extensively.[52] Here, besides direct photoionization, various reactions can take place. Most dominant are proton and charge transfer reactions in positive polarity and electron capture in negative polarity. Detailed information on the reactions schemes in APPI and APCI can be found in the work of Kauppila et al.[53], Syage et al.[54], and Klee et al.[55] It can be concluded that APPI with adding a dopant leads to similar ion chemistry as APCI. A simplified reaction scheme for APPI is given in Figure 2. In contrast to vacuum photoionization, aside of the molecular ion of the analyte (M^+) also quasi molecular ions, such as protonation products ($[M+H]^+$) or water adducts ($[M+(H_2O)_n+H]^+$), are often found. APPI-MS has been reported in various technical setups since 2007 for gas chromatographic hyphenation. These solutions are generally featuring a heated transferline guiding the GC effluent into a classical API source. Attempts have been made to optimize the effluent transmission, maintaining the sharp separation peaks in GC coupling. Also miniaturized versions, where the ionization takes place inside the transfer capillary, either based on VUV lamps[56] or argon discharge lamps[57], have been reported. Moreover, recent solutions featuring GC-APPI high-resolution mass spectrometry have been published.[58,59] Nonetheless, GC-APPI was only of limited use for energy and fuels research till now. However, Kondily et al. showed the potential together with classical EI or low energy EI for the analysis of fossil feedstock material, a light crude oil fraction. The complementary information allows detecting a broader range of compounds.[59] Figure 3 gives a comparison of EI and PI for selected petrochemically-relevant target compounds. Together with the transition of the energy and fuels community towards alternative feedstocks, novel applications in the field of bio-oils and pyrolysis recycling oils can be predicted. Particularly, the adaption of the ionization behavior using different dopants can be beneficial.

Synchrotron radiation photoionization

When high-energy particles, such as accelerated electrons, are forced by a magnetic field towards a curved path, synchrotron radiation is emitted. This high photon flux and pulsed radiation source covers a very broad energy distribution, from soft low-energy microwave emission to hard high-energetic X-ray radiation. These inherent advantages can be exploited for ionization in mass spectrometric analysis. Synchrotron radiation is generated in large facilities covering multiple beamlines providing certain parts of the electromagnetic spectrum, *e.g.*, also vacuum ultraviolet to ultraviolet radiation (6-100 eV), which span the first ionization energy for almost all organic molecules. Moreover, the tunable light source enables near threshold ionization with minimal excess internal energy and, thus, a soft ionization characteristic with almost no fragmentation preserving the molecular ion peak. Due to the special nature of synchrotron radiation, the abbreviation SVUV has been used in literature for synchrotron vacuum ultraviolet radiation.[60]

Various applications of photoionization mass spectrometry by synchrotron radiation were shown in the last years, such as for basic flame chemistry[61] or on more complex mixtures, such as combustion aerosols.[62] For organic mixtures, photons with an energy from 7-24 eV are commonly used with an average photon flux of 10^{13} photons/s or higher.[63] The radiation is directly guided through a window inside the ionization chamber. High-order harmonic radiation is prior eliminated by a gas filter filled with neon or argon.[64] Photon flux and energy have to be tuned to ionize most organic compounds on the one hand but minimize fragmentation on the other hand. Complex instrumental setups were published featuring synchrotron radiation together with thermal analysis, primarily for solid matrices, such as lignocellulosic biomass or coal.[65,66] Decoupling the ionization region from the mass analyzer by a skimmer setup allows directly performing pyrolysis experiments while causing minimal contamination and maintaining the vacuum at the mass analyzer side. Specifics of the evolved gas analysis concepts are discussed in the following.

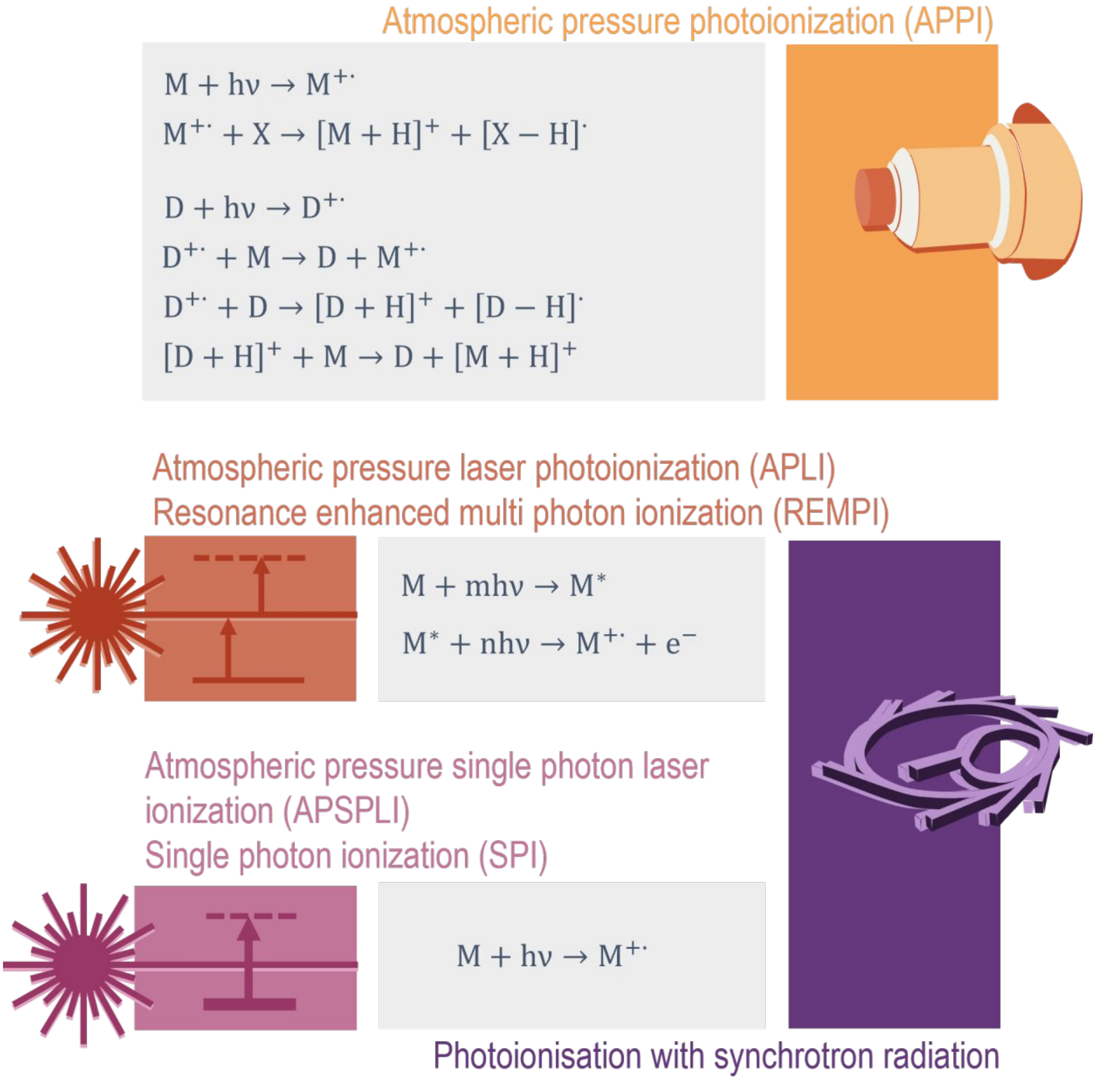

Figure 2: Scheme and ionization reaction pathways for atmospheric pressure photoionization (APPI), atmospheric pressure laser ionization (APLI), resonance enhanced multi photon ionization (REMPI), atmospheric pressure single photon laser ionization (APSPLI), and single photon ionization (SPI).

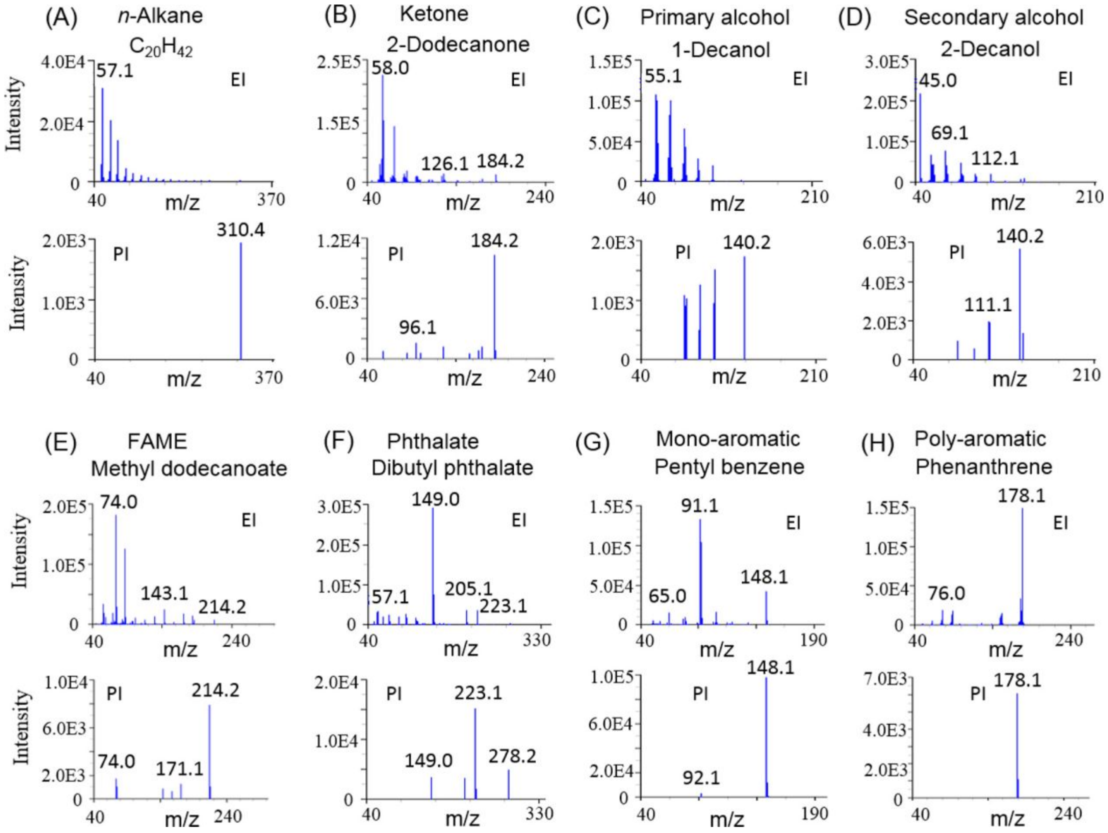

Figure 3: GC×GC-TOF-MS electron ionization (EI) and photo ionization (PI) mass spectra for numerous petrochemically-relevant compounds. EI exposes strong fragmentation behavior generating diagnostic fragments, whereas soft photoionization by a deuterium discharge lamp preserves the molecular information. Reprinted with permission from Giri et al., **2017**, *Anal. Chemistry*, 89, 5395-5403. Copyright 2021 American Chemical Society. [67]

Table 1: Comparison of VUV light sources commonly used in mass spectrometry for single photon ionization. In comparison, ionization energies of organic compounds are commonly in the range of 8-12 eV.

VUV light source	wavelength [nm]	ionization energy [eV]
Deuterium discharge lamp	110-160	7.75-11.3
9th harmonic frequency of Nd:YAG laser	118	10.5
Kr discharge lamp	123	10.1
Argon electron beam pumped lamp	126	9.8
Xe discharge lamp	147	8.4
Fluorine excimer laser	157	7.9

Evolved gas analysis (EGA) techniques

Evolved gas analysis mass spectrometry (EGA-MS) is used since the earliest days of mass spectrometry and is over 70 years old.[68] First reviews on EGA-MS were already written in the 1960s and early 1970s, presenting applications in inorganic, biological, and polymer chemistry but also in petroleum sciences and geological topics.[69] Already in his 1984 review on EGA-MS, Holdiness stated: "Since DIP inlets are available with most MS, little is needed in the way of complicated specialized equipment." Interestingly, the instrumental variety of desorption and pyrolysis techniques has been narrowing down in mass spectrometric coupling during the last decades, and modern solutions are most often featuring gas chromatography[34], pyrolysis gas chromatography[33], thermogravimetric coupling[70], direct inlet probe[71], or other types of resistively heated thermal probes. With the broad introduction of atmospheric pressure ionization (API) in mass spectrometry in the late 1990s and early 2000s, EGA-MS concepts operating at atmospheric pressure have also been brought to market. Here, a substantial number of solutions were presented over the last two decades, including thermogravimetric coupling with API[72,73] or multiple versions of atmospheric pressure direct insertion probes[74,75]. Moreover, modern concepts have developed from simplistic manual experiments to fully automated measurement and data analysis solutions, some featuring autosampler capabilities[71,76]. In the following, the general concepts of the prevalent EGA solutions for mass spectrometric coupling with soft photoionization are briefly presented. Figure 4a schematically summarizes the technical concepts and types of construction, whereas Figure 4b presents the general thermochemical conversion pathways matrices in energy and fuels research underwent.

These compounds undergo three main processes during heating (Figure 4b). In the first process, which can be observed for temperatures below 300 °C, volatile to semivolatile compounds are evaporated intact. This pathway is often related to the evaporation or desorption phase. The second main process occurs generally at temperatures above 300 °C, when pyrolysis begins and C–C- or C–S-bonds are thermally cracked. Larger petroleum-derived compounds found in heavier fractions reveal especially two pathways for thermal degradation. Species composed of several smaller aromatic cores linked by alkyl bridges preferentially crack at the linkers leaving the remaining alkylation intact. Highly aromatic compounds, which consist of a large aromatic core and peripheral alkylation, preferentially cleave of their alkyl side chains. If the aromatic core is volatile enough, it also can be evaporated, otherwise, it remains as residue.[77–81] The formation of residue is in addition driven by coke formation due to aromatization processes or the presence of highly stable, non-evaporable aggregates.[70]

Pyrolysis and Gas Chromatography Mass Spectrometry (Pyr-GCMS/GCMS)

Strictly regarded, gas chromatography with mass spectrometric detection falls within the general definition of EGA-MS and, thus, is included in the discussion here. GCMS is one of the most prevalent analytical approaches and is routinely used in almost all scientific areas, including fossil petroleum analysis. Because of the compositional complexity of petroleum matrices, comprehensive two-dimensional gas chromatography (GCxGC) has extensively been used here.[82] Nonetheless, GCMS platforms are dominated by harsh electron ionization conducted at 70 eV (EI) and to date only a limited number of soft ionization approaches exist, with chemical ionization, soft electron ionization, and photoionization as the most important schemes. For the general concept of gas chromatography, the reader is directed to excellent recent review articles, discussing applications in biomass and biofuel analysis[18,83], and Tranchida et al. reviewing comprehensive gas chromatography with special emphasis towards ionization techniques[84]. Here, the importance of soft vacuum ionization concepts, such as soft EI, and atmospheric pressure solutions such as GC-APCI, are presented. Soft EI, EI below 15-20 eV, and cold EI, generating vibrationally cold molecules due to a supersonic molecular beam, intend on lowering the amount of excess energy causing fragmentation.[85–87] In 2017, Giri and co-workers evaluated the usage of soft photoionization in comprehensive gas chromatography on a time-of-flight mass spectrometric platform (GCxGC PI TOF-MS).[67] Shortly after, the same group discussed the compositional elucidation of heavy petroleum matrices by GCxGC with EI, PI, chemical ionization (CI), and field ionization (FI). Here, the advantage of PI significantly retaining the molecular ion information was highlighted.[88] Atmospheric pressure ionization sources for gas chromatographic coupling most often rely on APCI[89,90], APPI[58,91], or APLI[34]. In this context, Barrow et al. firstly brought GC-APCI to high-resolution mass spectrometric detection for the characterization of oil sands[90], whereas Benigni et al. showed the sensitivity of APLI towards polycyclic aromatic hydrocarbons in GC-APLI high-resolution mass spectrometry[34]. Very recently, the Fernandez-Lima group expanded the analytical performance for hydrocarbon speciation by additional integration of ion mobility separation.[92] Integration of fast ion mobility separation (~ms) creates new capabilities for untargeted screening of the isomeric and isobaric complexity. In particular, the collision cross section (CCS) information retrieved from the ion mobility spectrometry adds an additional metric not accessible by classical fragmentation and tandem mass spectrometry.

From the injection perspective, soft ionization gas chromatography utilizes the same injector types as their EI analogous, such as split/splitless or programmable temperature vaporizer (PTV) injectors. Notably, pyrolysis gas chromatography, a distinct variation of gas chromatography featuring a specialized desorption and pyrolysis injector inlet, is widely used for the analysis of low amounts (0.1-1 mg) of high viscous and solid sample materials. This thermal degradation conducted in the pyrolyzer inlet extends the utility of gas chromatography towards nonvolatile and larger compounds. Generally, three groups of pyrolyzers can be categorized (Figure 4a): 1) Filament-type solutions, 2) induction-type pyrolyzer (Curie-point, heating the sample by a high frequency magnetic field), and 3) furnace-type pyrolyzer (sample cup placed in a heated furnace). Distinct advantages and disadvantages exist between the concepts. Most importantly, furnace-type pyrolyzers allow for a broad temperature range or continuous ramp-up heating. Particularly, applications in polymer science, environmental analysis, and energy and fuel research are reported. In particular, the contribution of pyrolysis gas chromatography towards the structural understanding of lignocellulosic biomass has to be noted.[93,94] In the here discussed application fields, various studies on petroleum heavy fractions, asphaltenes[33], deposits[32], or coal can be found. Nonetheless, almost no studies on pyrolysis gas chromatography with soft photoionization exist, except for the work of Otto et al.[95] studying crude oils by a custom-made split system allowing EI quadrupole and soft laser-based photoionization time-of-flight mass spectrometric detection and very early introduction of the concept by Genuit et al. in 1985[96]. In this regard, Cole et al. described in 2015 a novel approach for bio-oil analysis utilizing pyr-GCMS with soft APCI.[97]

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) allows to trace the mass loss in real-time as a function of temperature or heating time. For fossil petroleum, petroleum-derived materials or solid fuels, TGA is frequently deployed to determine physical phenomena and bulk parameters. By hyphenating TGA and mass spectrometry, the evolved gas mixture can be chemically characterized. For a typical TGA measurement, almost no sample preparation is needed. An aliquot of the sample material (1-50 mg) is heated by a defined temperature protocol with heating rates of 5-50 K/min, causing slow-pyrolysis processes, up to temperatures of 1,500 °C. Routinely, nitrogen is used as inert gas atmosphere during pyrolysis experiments, but also air or oxygen are used to determine the carbonaceous residue. For further information, the reader is directed to excellent reviews on thermal analysis and thermal analysis mass spectrometry.[7–12]

Classically, TGA is performed at atmospheric pressure creating a natural driving force for sampling when coupled towards vacuum ionization mass spectrometry. Interestingly, the hyphenation is almost exclusively done by an effusive gas stream with transfer times of several seconds. Faster skimmer or Knudsen cell concepts are rarely been found and used for less complex and specific sample materials.[98,99] Zhou et al. presented a nozzle setup sampling the evolved gas mixture as a molecular beam to the ionization region.[100]

In 2009, Geißler et al. and Streibel et al. introduced TGA with soft photoionization mass spectrometry for the description of a variety of solid fuels.[48,49] Fendt et al. used a comparable setup for the analysis of biomass and biochars.[101] Instrumentally, Wohlfahrt et al. expanded the analytical capabilities of TGA PIMS introducing fast gas chromatography after the thermal evaporation process.[102,103] This concept allowed to address isomeric patterns in crude oil desorption and pyrolysis products. More recently, TGA PIMS was deployed for certain challenges in energy and fuels research, such as deposit formation[32] and asphaltenes[33]. In terms of ionization schemes, these studies encompass laser-based VUV SPI or REMPI as well as discharge-lamp solutions. In the field of soft atmospheric pressure ionization mass spectrometry, only a limited number of studies utilizing TGA for petrochemical or solid fuel applications exist. Elbaz et al. combined the data from TGA and ultra-high resolution mass spectrometry, but no direct coupling was presented indicating the need for such a hyphenated system.[104] Here, our contribution in direct hyphenation can be noted, which uses a slight overpressure for sampling.[72] This concept was applied to analyze fossil liquid petroleum samples[72,105], asphaltenes[70,105], bitumen[82] and solid biomass fuels[72].

Direct insertion probe (DIP)

The concept of direct insertion probe (DIP) was already well-established in the very early days of mass spectrometry. In fact, the first publication utilizing DIP-MS dates back to the 1960s. Despite technological improvements in design, user-friendly usage, reproducibility, and sensitivity, the overall concept remained the same. The viscous or solid sample material is placed onto a sample holder, *e.g.*, a micro-vial or glass capillary; the sample holder is subjected inside the ionization volume, *e.g.*, by a rod construction, and directly heated inside. This temperature-resolved measurement gives a very rough separation of the analyte by volatility and boiling point by one theoretical separation plate. Beneficially, some set-ups allow the sample to be heated by a defined heating gradient, which allows studying degradation and evaporation processes in more detail. Most DIP sources are limited in temperature, exemplarily the direct inlet probe from Bruker Daltonics (so-called DirectProbe option for APPI and APCI sources) and the SIM option for LECO time-of-flight mass spectrometers reaches up to 400 and 470 °C respectively, whereas the Waters Corporation analogous (ASAP source) can go up to 650 °C. Self-constructed DIP versions vary drastically in the upper temperature limit. Here, the open direct probe of Kostyukevich can be mentioned, directly evaporating the petroleum sample material up to 400 °C without source housing.[106] Those temperature limits are generally high enough to induce pyrolytic degradation of the given energy and fuels matrix. Nonetheless, for certain applications, such as solid fuel degradation or heavy residues, 400 °C can be seen as a minimal requirement. Exemplarily, it has been stated that residual compounds of heavy petroleum fractions, such as bitumen, cannot be fully pyrolyzed and evaporated due to a temperature limit of 400 °C.[76]

In contrast to atmospheric pressure concepts, DIP was historically performed under vacuum conditions, reducing the effective boiling point according to the Clausius-Clapeyron relationship. Here most often harsh electron impact ionization is utilized, such as in the work of Flego et al. utilizing nominal resolving quadrupole mass analyzer to characterize crude oils[107], bitumen[108], and asphaltenes[109] or Käfer et al. deploying a high-resolution time-of-flight mass spectrometric platform for the chemical description of bitumen[71] and vacuum residues[76]. The reduction of the mean boiling point for polycyclic aromatic hydrocarbons was found to be as high as 300 K.[71] In contrast to thermogravimetric approaches conducted at atmospheric pressure this allowed to detect larger compounds intactly prior their thermal decomposition.

Naturally, in vacuum DIP solutions, thermal treatment is performed by a filament or small furnace heating the sample material. In contrast, atmospheric pressure analogous generally utilize a heated gas stream for evaporating the material and subjecting the analyte towards the ionization region inside the chamber. In comparison to vacuum DIP solutions, the technical realization of atmospheric pressure DIP is simplified as the gate for sample introduction, maintaining the reduced pressure conditions, is not needed. Different atmospheric pressure DIP designs exist, which can be grouped into two categories: 1) combined sample loading and heated gas stream, and 2) separated sample loading and hot vaporizer gas supply. The first allows the preheated vaporizer gas stream to flow along the side of the sample, most often loaded to a melting point glass capillary, in a combined probe, whereas the latter directs the heated gas stream onto the sample material sitting on a rod or bearing probe geometry (Figure 4a). It should be noted that the terminology “direct insertion probe” (DIP) encompasses concepts, such as direct probe, direct inlet probe, or atmospheric solids analysis probe, and is generally referring to the same EGA concept.

Other custom-made concepts

In this chapter, EGA techniques not clearly classifiable to the aforementioned concepts will be discussed. Predominantly custom-made concepts can be grouped in this category, largely including the EGA of products from different thermochemical batch reactors. For this reason, the reader is strongly directed towards the work of Anthony Dufour and co-workers, as well as Fei Qi and co-workers extensively publishing in this field over the last decade.

Already 2012, Weng et al. presented a custom-made biomass pyrolysis apparatus featuring a horizontal pyrolysis chamber with a quartz tube furnace.[66] The evolved gas mixture is sampled by a nitrogen gas stream through a repeller plate with a 3 mm inner diameter aperture. Ionization is performed by tunable SVUV radiation described above and detection by a quadrupole time-of-flight mass spectrometer. This setup was used in various studies for the investigation of coal[110,111] and biomass pyrolysis[65] later with an optimized smaller orifice skimmer[65].

A sort of continuation of this work conducted in the group of Fei Qi can be seen in the group of Anthony Dufour with a more sophisticated design of the thermochemical reactor. Here, Jia et al. introduced the combination of a microfluidized-bed reactor with soft photoionization mass spectrometric detection of lignocellulosic biomass pyrolysis products.[41,42,112] Technically, a gaseous aliquot of the reaction products is sampled by a deactivated fused silica capillary (100-530 µm inner diameter) and a custom-made heated connector interface operated at 300 °C. The evolved gas is transferred into the vacuum ionization source of the mass spectrometer by a heated transfer line (250 °C). Very recently, this setup was extended by a complex double reactor design with integrated catalytic steps for the conversion of algal biomass.[113] Interestingly, this EGA concept was also hyphenated towards synchrotron radiation in 2020 by Yang et al. for studying the pyrolysis behavior of solid fuels.[114]

Custom tubular furnace systems[115] and more complex catalytic reactor evolved gas monitoring[116] have also been used in combination with discharge lamp based photoionization mass spectrometry or vertical furnace geometries. Another concept was presented by Kostyukevich et al. reporting an open thermal desorption design featuring atmospheric pressure photoionization (Krypton-discharge lamp, 10/10.6 eV).[106] A desorbing unit equipped with heating wire and temperature gauge is closely placed to an extended inlet capillary and the APPI lamp. Disadvantageous, the simplistic open API geometry causes strong oxidation artifacts from reactions of the evaporated compounds with atmospheric oxygen and moisture. Hence, unknown complex mixtures can hardly be addressed with this approach. Encapsulated API designs with a high flow rate of dry Nitrogen allows to largely avoid these unwanted ionization by-products. These artifacts are a result of the chemical ionization pathway in APPI and reveal the close similarity of APPI and APCI, particularly when using dopants or working at ambient moisture conditions. Moreover, a very unusual EGA technique can be seen in the so-called thermo-optical carbon analyzer, sometimes also referred to as elemental carbon organic carbon analyzer. Despite this instrumentation particularly developed for the analysis of carbonaceous aerosols and widely used in particulate matter research, also studies on the mass spectrometric detection of the evaporated gas mixture were reported.[117,118] As an example, hyphenation towards vacuum photoionization time-of-flight mass spectrometry (SPI/REMPI-TOF-MS) allowed addressing the chemical profile of engine feed fuels, such as heavy fuel oil and diesel fuel.[119]

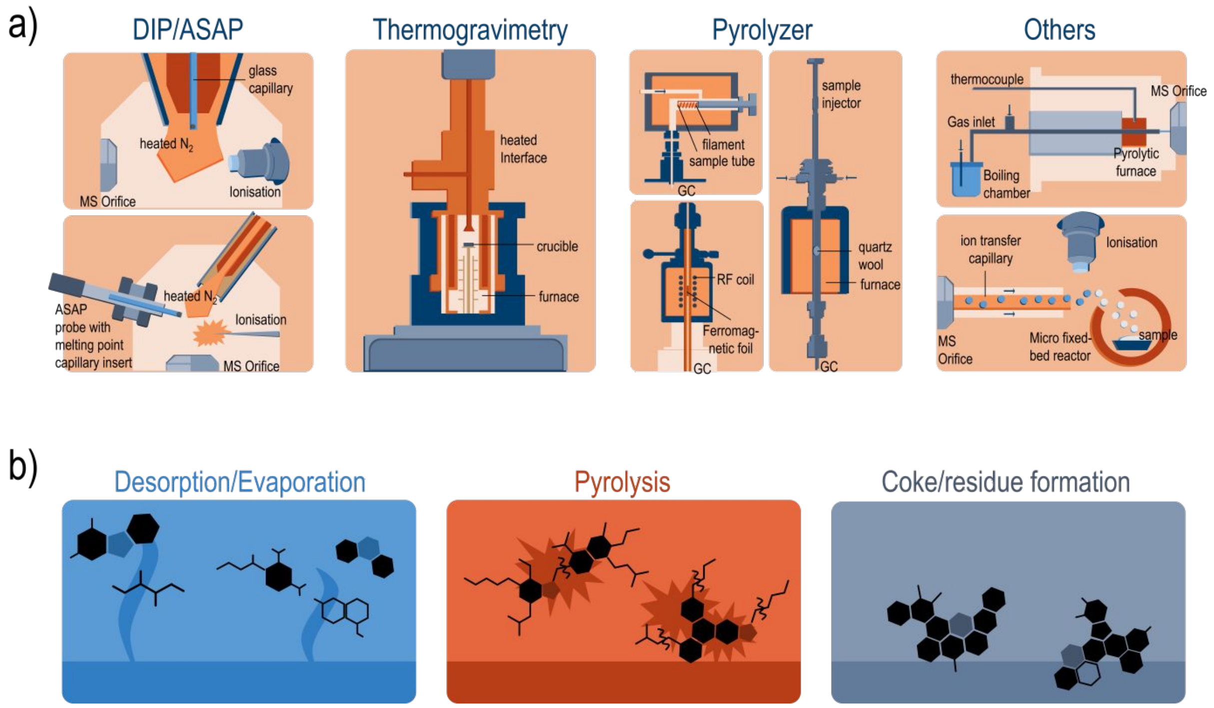

Figure 4: a) Schemes of different evolved gas analysis concepts utilized for soft ionization mass spectrometric hyphenation. Direct insertion probe (DIP) can basically be conducted with the sample holder being integrated in the heating device or heated by an external gas stream. Various thermogravimetric concepts with one or multiple horizontal or vertical balance arms. Here the simplest and most common vertical concept is shown. Pyrolyzer utilized for pyrolysis gas chromatography can be differentiated into three main groups: 1) Filament-type solutions, 2) induction-type pyrolyzer (Curie-point, heating the sample by a high frequency magnetic field), and 3) furnace-type pyrolyzer (sample cup placed in a heated furnace). Other concepts are schematically represented by furnace (up) or reactor (down) type setups. b) Schematic representation of the three main processes during the thermal treatment of petroleum, including the intact desorption of smaller, evaporable compounds, the degradation by pyrolysis of larger, less-volatile constituents into evaporable thermal fragments, and the formation of high aromatic coke residue.

Energy and fuels applications

In this section applicative studies of EGA with soft ionization, primarily photoionization, mass spectrometry are summarized. Categorization was done based on the sample type and put into context to other publications.

Liquid fossil petroleum and distillates

Gas chromatography is one of the most widely used techniques for the molecular description of fossil petroleum. Consequently, novel gas chromatographic hyphenations towards soft ionization mass spectrometry are often introduced analyzing liquid fossil petroleum matrices. Classically, the comparable low heteroatom content and stable hydrocarbons are particularly suitable for gas chromatographic analysis. Barrow et al. showed in 2014 that the hyphenation of GC to ultra-high resolution mass spectrometry allows to address the isobaric complexity as well as the isomeric diversity of liquid samples related to the Athabasca (Canada) oil sand industry.[90] Double bond equivalent versus carbon number visualization of oxygenated compound classes (CHO_{2-4}) were used to address the chemical space finding evidence for dicarboxylic acids and pointing out the reduced fragmentation compared to traditional EI systems. In the coming years, this hyphenation was used multiple times with APCI, APPI and APLI to address polar constituents in South African diesel fuels[120], shipping fuels[89,121], light crude oils[43,59], shale oils and heavy sweet crude oil[34]. Kondyli and Schrader could show that GC-APPI significantly increases the number of detected CHO_x and CHS_x-class compounds in a light crude oil and is able to elucidate the alkylation profile of dibenzofurans and benzothiophenes.[59] Generally, the full potential of GC-APPI/APCI/APLI is explored utilizing a high-resolution mass spectrometric platform giving access to the exact *m/z* values and consequently allowing elemental composition attribution. These techniques can be seen as a complementary approach to classical GC equipped with EI, inducing another ionization selectivity and broaden the chemical space accessible by the analysis. This is particularly advantageous for very heterogeneous complex mixtures, such as heavy fossil fractions, recycling pyrolysis oils or bio-oils.

Another approach for unraveling the chemical complexity of fossil petroleum was taken by Giri and co-workers operating GCxGC with vacuum PI.[67,88] Here, a base oil sample set comprised of solvent refining, hydrocracked, catalytically dewaxed and synthetic oils was investigated. Particularly the isomeric pattern of branched alkanes and cycloalkanes could be identified with higher confidence. Moreover, they demonstrated the correlation between base oil composition and physical properties, a highly valuable feature to tune refinery processes.[67] Compared to traditional one-dimensional gas chromatography, comprehensive gas chromatography significantly enhances the peak capacity, ultimately allowing better separation capabilities in complex mixture analysis. Classical mass spectrometric hyphenation relies on hard electron ionization and, thus, good separation is needed to deconvolve the characteristic fragmentation profiles utilized for chemical attribution. Hence, GCxGC increases data reliability strongly. Moreover, improved identification of the separated compounds is also beneficial in soft photoionization techniques. Tunable vacuum ultraviolet ionization by a synchrotron beamline allowed the group of Goldstein to individually access the contribution of aromatic and aliphatic species to the hydrocarbon classes of four crude oils and receive information “that goes beyond the typical GCxGC separations…”.[122–124] In this context, Nowak et al. altered the energy of the VUV beam between 10.5 and 9 eV to ionize hydrocarbon isomers of four crude oils (North Sea, Gulf of Mexico, Texas, and Azerbaijan). It could be shown that 10.5 eV is able to ionize aromatic and aliphatic crude oil hydrocarbons, whereas 9.0 only ionizes aromatic hydrocarbons. Consequently, this allowed to distinguish those compound classes efficiently. The authors conclude the system is potentially be applied “to oil spills, microbial transformations, and environmental impacts”.[122]

Beside other, this setup was used to study changes in crude oil chemical composition during biosouring and perchlorate treatment[125], engine emissions and engine oils[126], as well as lubricating oils[127]. Goldstein and co-workers could show the chemical similarity between the molecular profile of primary organic aerosol and lubricating oil, stating “Lubricating Oil Dominates Primary Organic Aerosol Emissions from Motor Vehicles”.[127] A one dimensional GC concept with vacuum laser photoionization was very recently presented by Kösling et al. on a high-resolution Orbitrap mass spectrometer platform efficiently ionizing aromatic constituents of diesel fuel and heavy fuel oil. Here, the high-resolution mass spectrometry allowed to resolve narrow mass splits within the spectra of the fossil petroleum matrices allowing confident assignment of the signals towards the alkylated homologue rows of various PAHs (Figure 5).[128] Very recently, light crude oil (CPC Blend from Kazakhstan) was characterized on the molecular level by newly introduced atmospheric pressure single photon laser ionization (APSPLI). In this work, we conclude that the novel APSPLI concept is able to ionize a broad compositional space, particularly useful for the description of petroleum matrices.[43]

As outlined above, thermal analysis allows reaching higher temperatures causing intended pyrolytic degradation of the analyte. This feature is particularly useful for heavier crude oils or distillates, which are less applicable for GC analysis. TGA coupling with vacuum photoionization was deployed in the last dozen years towards a variety of fossil crude oil matrices.[47–49] Geißler et al. nicely depict the two phases of the thermal analysis of fossil petroleum matrices by showing two-dimensional graphs of temperature versus *m/z*. A characteristic evaporation ellipse was found for the desorption of crude oil hydrocarbons below 350 °C dominated by alkanes, cycloalkanes and alkylated aromatics, and a second pyrolytic distribution revealing smaller thermal degradation products above 400 °C mainly featuring alkenes and alkylated PAHs.[49] Those characteristic desorption and pyrolysis molecular pattern accessed by REMPI and SPI were revealed to be different between Californian and Turkish crude oil.[47] Wohlfahrt et al. brought the TG-PIMS concept on a new level by incorporating a fast chromatographic separation of the evaporated gas mixture prior to mass spectrometric analysis. SPI ionization by an EBEL allowed specifying the isomeric pattern of a Turkish and Greek crude oil, for instance, separating C7-alkylated benzene derivatives from another unknown compound with the same nominal mass.[102]

More recently, ultra-high resolution mass spectrometric detection and soft atmospheric pressure ionization enabled to resolve the isobaric complexity.[72] Aside of crude oils[72,129], heavy crude oils and their solvent fractions (SARA – saturates, aromatics, resins, asphaltenes)[105,130] were studied as well as the parent crude oils to asphaltenes[33]. Collision-induced dissociation (CID) leads to a dealkylation process and structural information on the aromatic core could be obtained. The fractions revealed completely different chemical profiles, in terms of compound classes and temperature-profiles. Aromatics were dominated by CH- and CHS-class compounds, whereas the resin fraction revealed a significant higher proportion of CHO_x- and CHS_xO_y-class constituents. Correlation of the molecular profile with physico-chemical bulk properties of the parent crude oil allowed to find certain relations: Total sulfur weight content strongly correlates positively with the abundance of sulfur-containing species (CHS, CHS_2) or a negative correlation between API gravity and mean DBE of the desorption step. Finally, it could be concluded that EGA-HRMS is a valuable complementary approach for the SARA-fractions of crude oils, particularly by enlarging the structural information using CID.[105]

Without the mass loss information and limited in upper temperature but with higher throughput and easier handling, DIP APCI and APPI MS were used in multiple studies for fossil petroleum analysis.[74,131] Afonso and co-workers extensively studied the characteristics of DIP (and the Waters Corporation analogous ASAP) for the analysis of vacuum gas oils[131], polyalphaolefins[132], lubricants[133] but also polymers[134,135]. Comparison of the results received by DIP and direct infusion approaches, such as ESI, APCI and APPI, on vacuum gas oils revealed the suitability of the DIP approach for speciation of aromatic sulfur-containing compounds. Farenc et al. found that direct infusion APPI and ASAP yielded comparable mass spectra. Vacuum gas oils prior (feed) and after (effluent) catalytic hydrotreatment (HDT) were investigated, allowing to trace the substantial reduction of sulphur on the molecular level by molecular maps of the CHS_1-class (carbon number versus DBE).[131] In combination with thin-layer chromatography, DIP mass spectrometry was able to identify polymer additives, such as polyisobutylene derivatives, in gasoline. Here, the authors highlight the capabilities of structural elucidation of additives within complex hydrocarbon matrices with minimal sample preparation.[136]

Solid fuels, residues and char

Solid and high-viscous matrices are particularly challenging for most analytical systems, including classical mass spectrometric concepts. EGA concepts combining the desorption of smaller, volatile compounds and the intended thermal degradation by pyrolysis at elevated temperature are especially useful for those matrices. In the following, applicative studies of EGA-MS with soft ionization, primarily photoionization, for lignocellulosic biomass, petroleum related deposits and heavy residues, as well as asphaltenes, are covered.

Chemically unraveling the pyrolysis reactions and products of biomass thermal degradation is heavily researched.[93,94] Only a minor fraction of the studies are performed by EGA-PIMS or comparable platforms. Primarily cellulose, hemicellulose and lignin are investigated.[137] Dufour and co-workers used a tunable synchrotron PIMS[137] developed in China[66] to study the pyrolysis of oak and miscanthus biomass or pine wood[65]. With higher pyrolysis temperature ramping from 300 to 700 °C more details on the pyrolysis chemistry could be revealed, such as the decrease of oxygen content in high molecular weight species or the formation of homologous (delta *m/z* 14, CH_2) series pyrolytically derived from PAHs. The authors conclude the “potential for process control to get wanted products”.[137] Dufour et al. studied the effect of cellulose structure and ash content on primary tar formation. In this context, they found a new major intermediate product at *m/z* 128 acting as precursor for the generation furanone-based species. Based on tandem mass spectrometry they hypothesized for *m/z* 128 the structure 5-methyl-4-oxotetrahydrofuran-2-carbaldehyde or a position isomer.[137] Comparable studies on biomass thermal degradation, but with a lamp- and laser-based PI, were published reporting temperature resolved tracing of the characteristic phenolic thermal degradation products.[45,101] Results of those investigations were stated to be integrated in the optimization of the bioliq® process (a pyrolytic liquidification process of residual biomass to gasoline) of wider bandwidth of products. Principle component analysis of the SPI-MS spectra for the various investigated biomasses (corn, miscanthus, rice/wheat/rye/barley/oat straw, hay, softwood, hardwood, and other) allowed to clearly differentiate the molecular profiles. 4-vinylphenol, phenol, *m/z* 180 (*e.g.*, 4-vinylsyringol/coniferyl alcohol), allylsyringol and guaiacol being the species with the highest significance for the separation also detectable in REMPI.[45] This applicative context of directly analyzing the evaporated species from biomass thermal conversion was intensively investigated by Jia et al. utilizing a micro fluidized bed reactor (MFBR).[112,138,139] The products of the fast pyrolysis of heartwood, sapwood and bark from Douglas fir (softwood) and oak (hardwood) were studied with the MFBR. Specific marker compounds were found for each wood zone. These chemical differences were related to the chemical composition (lignin, carbohydrat, and minerals content) of the respective sample material. Exemplarily, for the hardwood, it was found that the wood zones have a higher impact on the pyrolysis products from the carbohydrates (cellulose/hemi-cellulose) than those from the lignin.[112] Investigating the catalytic fast pyrolysis of biomass, PIMS could reveal the superior selectivity of hierarchical zeolite catalysts towards the generation of aromatic compounds.[138] Zhou et al. explored the pyrolysis of pine wood by SVUV and TG time-of-flight MS primarily reporting species with *m/z* 20-220. The same group of Fei Qi and co-workers investigated co-pyrolysis of lignin and lignite exploring synergetic effects by TG-PIMS. Combined pyrolysis of biomass and low-rank coals significantly affected the evaporated molecular pattern but, more importantly, an enhanced production of volatiles and decrease of the total char yield was found.[140] This approach is particularly interesting for industrial realization of pyrolysis processes generating high valuable liquid products and minimized contents of waste char. In the same year, the group presented the near-atmospheric pressure PI concept used for real-time monitoring of biomass pyrolysis. High-resolution mass spectrometry allowed to explore the molecular pattern of the oxygenated compounds dominating the spectral response.[141] Time/temperature-resolved analysis of Van Krevelen diagrams (O/C versus H/C) allowed the authors to trace the degradation in general, whereas tandem mass spectrometry (MS/MS) was able to structurally elucidate selected target compounds. Here, the fragmentation of $C_6H_8O_3$, reported as typical marker of cellulose, was discussed in detail and reporting the same structure as Dufour et al.[137] Very recently, Chen et al. online monitored the in-situ products from biomass pyrolysis by a custom-build reactor design featuring a direct orifice sampling in front of APPI-MS. Besides model compounds, such as guaiacylglycerol-β-guaiacyl ether, poplar wood was investigated. The authors highlight the capability for analysis at operando conditions reducing secondary reactions substantially. Interestingly, the authors compared the chemical pattern of the condensed pyrolysis liquid, measured via direct infusion ESI and APPI, with the online monitoring, finding larger dimeric and trimeric lignocellulosic pyrolysis products with higher abundance using the EGA-MS approach.[142] Very recently, Liu et al. characterized the so-called “phenol pool” of Zeolite-catalyzed lignin pyrolysis by EGA-PIMS in a fixed-bed reactor setup under isothermal mode.[143]

DIP high-resolution mass spectrometry offered a commercially available solution to study the molecular pyrolysis pattern of biomass extensively reported by Castilla et al.[73,75] Ion mobility mass spectrometry allowed to gain structural isomeric information, whereas high-resolution mass spectrometry was able to resolve the isobaric complexity (Figure 6). The additional analytical dimension given by ion mobility spectrometry helped to chemically characterize different biomass pellets (beech, crepito, miscanthus). Detailed exploration with MS/MS was given for certain marker molecules, such as Vanillin and Syringol.[73] As for the work of Zhou et al.[141], time/temperature-resolved Van-Krevelen diagrams were used but extended by a combination with the results from multivariate data analysis (PCA loadings) allowing for visualization of the compositional space characteristic for beech and maple/oak.[75] Very recently, pyrolysis PIMS was used to unravel the pyrolysis pathways of another high-abundant biomass source, microalgae. This development strongly linked to the increasing attempts for the generation of pyrolysis oils based on algae broadens the chemical space by the substantial contribution of lipids and proteins. The monitored aromatic compounds were reported to be resulted by proteins, the dehydrogenation of cyclic alkenes, or Diels-Alder reaction of unsaturated fatty acids. The authors presented suggestions for the industrial applications for these chemical products and product mixtures.[144]

In the application field of residues and deposits in petroleum refining, Grimmer et al. used thermogravimetry coupled to SPI and REMPI-MS for the description of steam cracker fouling and coking residues.[32] Samples obtained from downstream and upstream of the cracking oven were investigated revealing a broad degradation pattern of the polymeric-like structures beginning at 130 °C. Dominantly, retro-Diels-Alder products (cyclic dienes and alkenes) were detected and REMPI revealed the aromatic nature of a heavier pattern, most likely belonging to styrenic constituents. The authors presented first attempts to quantify the Diels-Alder-reaction products based on the SPI data, an important feature for industrial applications in optimizing the refining process.[32] Lacroix-Andrivet and co-workers were able to investigate polymer-modified bitumen, a heavy vacuum residue in petroleum refining, by DIP high-resolution mass spectrometry. The characteristic polymer degradation pattern, such as of the styrene−butadiene−styrene copolymer, could be observed next to the ultra-complex evaporation profile of the bitumen chemical space. Interestingly, Kendrick mass defect and carbon number versus DBE visualization allowed to map the additive efficiently.[74] Moreover, also chemical changes in the complex bitumen matrix during short-term aging were investigated combining GCxGC-MS and TG-APCI-MS. Oxidation processes were revealed to be prevalent for the CH- and CHS-class compounds. The study highlights the aging behavior of nitrogen-containing compounds, such as carbazoles, for which a significant reduction was found, indicating condensation or oxidation processes.[82] Asphaltenes, a high-aromatic heavy solvent fraction of petroleum causing substantial flow assurance problems, is heavily investigated in the literature, particularly the molecular architecture. TG-HRMS was able to significantly contribute to this field by studying the molecular pattern received from intended pyrolysis of the highly aromatic constituents with soft atmospheric pressure chemical ionization.[33,70,105] Evaluation of the molecular-resolved profile of the intended pyrolysis products was found to be a measure for the dominance of island- (one large condensed aromatic core) or archipelago-type (multiple aromatic cores bridged by aliphatic linkers) species.[70] Moreover, it was found that deploying a lighter paraffinic solvent for asphaltene precipitation causes a higher abundance of species emitted in the desorption phase. They belong mainly to CHO_x-class compounds from the maltene fraction occluded and coprecipitated with the asphaltenes.[105]

Coal was found to be heavily investigated by EGA-MS in general but also to be an important application field of EGA-PIMS.[48,50,51,110,111,116,140,145–149] This finding is due to the tremendous complexity of this combustible sedimentary rock, and state-of-the-art analytical instrumentation is required for molecular-level insights into thermal degradation processes. In this framework, the group of Fei Qi used pyrolysis SVUV-MS already in 2013 for the investigation of bituminous coals. The authors conclude that the different pyrolytic molecular pattern might have resulted from the differences in the structure of the macromolecular coal network. These molecular patterns are dominated by alkylated series (delta *m/z* 14, CH_2) of common core structural motives, such as phenol, methoxyphenols, naphthalenes, phenanthrenes, and larger PAHs. Moreover, the authors performed temperature- and photon energy-resolved experiments, finding distinct differences partially explained by isomer-dependent ionization energies not resolved by mass spectrometry (Figure 7).[110] Comparing the pyrolysis patterns of anthracite and bituminous coals accessed by pyrolysis lamp- or laser-based PIMS, it was revealed that coal rank variation can be easily differentiated.[40,146] More recently, also applicative studies mixing solid fuels, such as biomass and coal, were reported investigating the pyrolysis reactions in a more realistic reactor setup. This work is extending the study of Zhou et al.[140] exploring the changes in the emitted molecular profile in co-pyrolysis and co-combustion setups. It was found that the coal has little to no effect on the production of furfuryl alcohol in processing of a coal-corn residue blend.[148] Increasing capabilities of the instrumental setups and molecular simulations could be shown to be combined for elucidating emission pathways in brown coal pyrolysis.[111] Also the influence of mineral additives to the pyrolysis of Chinese coals was studied by EGA-PIMS. Specifically, in this work the effect of iron oxide on the pyrolysis of Hongshaquan and Daliuta coals was studied deploying different mixing ratios from 10:1 to 2:1 (Fe_2O_3: demineralized coal). Increase of Fe_2O_3 content promoted the emission of lighter products, such as alkenes and aromatic hydrocarbons, and inhibiting the generation of bi-phenols. Moreover, pyrolysis peak temperature significantly decreased.[145]

Alternative feedstock energy materials

Analysis of the pyrolysis products from the thermal conversion of alternative feedstocks, such as waste plastics, or biomass, is not extensively presented by EGA-PIMS so far. Consequently, this chapter also leads over to the future perspectives closing remarks. In a first attempt, liquid products from the pyrolysis of alternative energy feedstocks are more often subjected towards classical GCMS analysis adapting column polarity or adding derivatization steps allowing to evaporate the functionalized constituents intactly.[83,150–152] Interestingly, the very recent review article of Staš et al. featuring GCxGC in pyrolysis bio-oil research is not mentioning photoionization at all.[83] Regarding ionization, Herztog et al. has shown the benefits of APPI and APLI for bio-oil analysis.[153] Hung et al. recently presented GCxGC with Orbitrap-based high-resolution mass spectrometry for the chemical description of bio-oils. Despite using hard electron ionization nicely allowing for spectral database search in the NIST library, the authors conclude that a soft ionization could provide tremendous support.[154] Recently, the group of Fei Qi and co-workers stronger moved into the field of bio-oil research by studying the hydrodeoxygenation of model compounds over a nitrogen-doped carbon supported palladium catalyst. The group reports an efficient deoxygenation of lignin model compounds at the same time preserving the aromaticity, stating “extremely advantageous for the concept of selective conversion of lignin into value-added aromatic chemicals”.[155]

Most often, not the pyrolysis liquids but the solid residues of the thermal conversion processes are investigated by EGA-PIMS, such as biochars, partially discussed in the previous chapter.[101] Fendt et al. pointed out the strong release of a broad chemical profile, including aromatic constituents, from EGA-MS of softwood and hardwood chars.[101] Very recently, we could highlight the importance of EGA-MS for chemical description of plastic pyrolysis chars finding the strong presence of compounds originated from the plastic additives. In this work, derivatives of benzophenone, a common additive in plastic packaging as an UV blocker to prevent photodegradation (UV stabilizer), were found (Figure 8).[156] Other plastic additives, such as flame retardants, colorants, or plasticizers, are expected to largely contribute to alternative feedstock pyrolysis oils. Recently, nitrogen-containing species in plastic pyrolysis oils were reported at the molecular level and linked to additives, such as hindered amine light stabilizers (HALS).[157]

Waste tires are considered as important source for recycling and act as substantial alternative feedstock. This waste made of natural and synthetic rubber, carbon black, textile material, steel, Sulphur, and additives, can be thermo-chemically converted (pyrolyzed), generating tire pyrolysis oils having a comparable calorific value to petroleum.[158] Thermal degradation of waste tires leads to broad and complex chemical composition, dominated by hydrocarbons, classically requesting in-depth characterization.[159,160] Interestingly, also PAHs, from the cyclization and aromatization of the thermal degradation product butadiene, and amines as well as thiophenes, from additives and manufacturing accelerators, were found.[161] Prospectively, studying the chemical composition of this alternative feedstock will be of high interest for evolved gas analysis soft photoionization mass spectrometry in the framework of a circular economy, particularly taking into account the vital field of co-pyrolysis together with other feedstocks, such polymers and biomass.

The challenge for most of the EGA-MS concepts is to evaporate the functionalized constituents intactly or to have a fundamental knowledge on the pyrolytic decomposition reactions and pathways. We assume these conditions are not met yet for the novel application field of alternative feedstocks limiting the current application of EGA-PIMS. Nonetheless, soft ionization techniques have been deployed, such as GC-APCI high-resolution mass spectrometry for chemical description of pyrolysis oils from German brown goal. Identification of isomerically resolved n-alkylated phenols was possible. Moreover, homologous series of alkyl and alkylene carboxylic acids, dihydroxy benzene and alkoxy alkyl phenols were detected.[162]

Synopsis for energy and fuels matrices

Figure 9 is schematically giving the energy and fuels matrices reviewed in this article covering classical fossil petroleum, such as crude oils and their solvent and distillation fractions, solid fossil fuels, such as coal, biomass-based alternative feedstocks, such as lignocellulosic biomass, and other alternative sources, such as waste plastic. Generally, no specific EGA-MS methodology for a certain matrix can be determined, but a rough guideline should be given in the following. Table 2 is summarizing the discussed EGA-MS concepts as additional reader guidance.

From a sample introduction perspective, volatile and semi-volatile mixtures are ideally suited for GC. Here, soft photoionization can be seen as a complementary technique to the structural speciation by harsh EI. Particularly, for compounds not giving a molecular ion, such as saturates and naphthenes, soft single photon ionization is beneficial. This is the case for classical fossil distillates but also for hydrogenated alternative feedstock matrices, such as bio-oils after the HDO process or hydrated vegetable oils (HVOs). Furthermore, atmospheric pressure ionization concepts, such as APPI/APLI/APCI can induce a certain selectivity, especially by using dopant reagents. This approach can be advantageous for trace compounds, such as nitrogen- and sulphur-containing aromatics residual to the hydrodenitrogenation (HDN) and hydrodesulphurization (HDS) in classical fossil petroleum refining. This aspect can also be of high analytical interest for contaminants in novel recycling fuels, *e.g.*, from additives or halogenated compounds received from polymer recycling. Finally, the superior selectivity and sensitivity of vacuum REMPI for aromatic constituents is of high interest for aviation fuels and other critical application areas demanding low PAH contents.

DIP/ASAP and TGA concepts are particularly useful for solid fuels or high viscous sample materials. Consequently, beneficial application areas are vacuum residues of classical petrochemical refining, such as bitumen and vacuum gas oils but also critical solvent fractions, such as asphaltenes. Moreover, these concepts can be used to study and mimic the transformation process of alternative feedstocks, such as biomass. Here, particularly the ionization features of atmospheric pressure sources are beneficial to sensitively target polar and semi-polar constituents, such as methoxyphenols from biomass pyrolysis or nitrogen-containing aromatics from algae bio-refining. For studying other degradation products, such as small alkenes/paraffin's from polymer pyrolysis or aldehydes and alcohols from biomass thermal degradation, vacuum based SPI can be deployed.

Consequently, for a comprehensive molecular picture in EGA-MS for complex petrochemical matrices and products from alternative feedstocks the combination of ionization concepts is highly anticipated. Here, a recommended workflow can be the combination of universal photoionization schemes (SPI) utilizing either SVUV or laser/lamp-based solutions and selective ionization concepts, such as REMPI or dopant-assisted APPI.

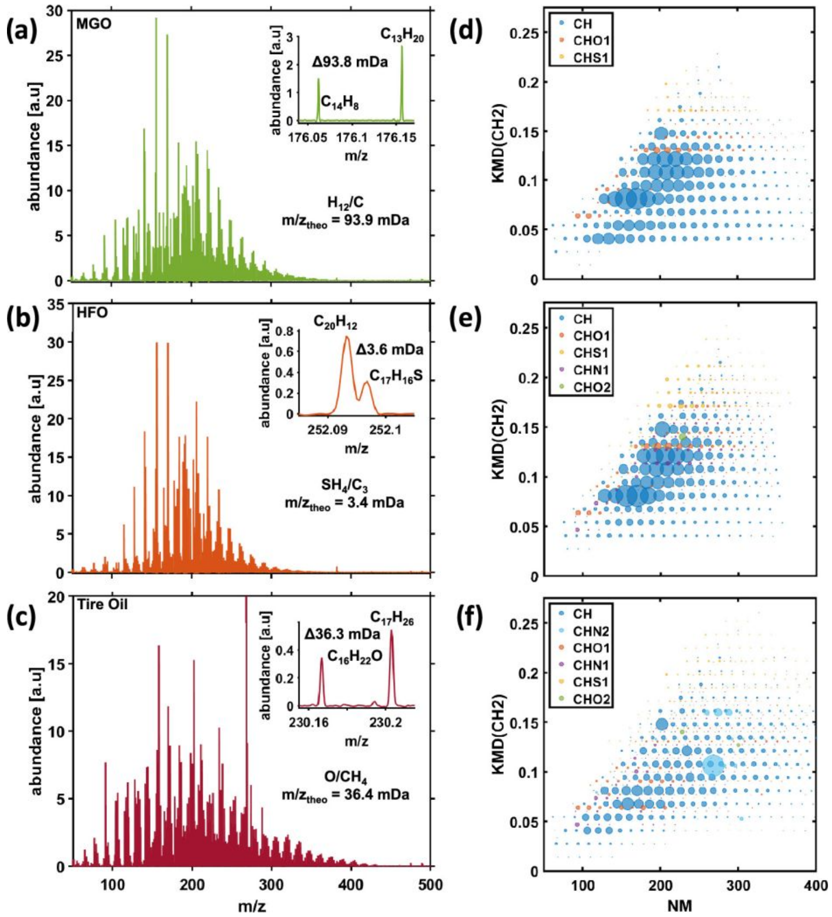

Figure 5: Average mass spectra of three different petrochemical materials investigated by GC-REMPI Orbitrap FTMS. (a) Marine gas oil (MGO), (b) heavy fuel oil (HFO), and (c) tire oil are depicted on the left side. Characteristic isobaric interferences are shown in insets. These mass splits can be resolved and chemically attributed due to the high mass resolution and mass accuracy of the Orbitrap mass analyzer. Kendrick mass defect plots of (d) MGO, (e) HFO, and (f) tire oil. The compound classes are color coded. Reprinted with permission from Kösling et al., **2021**, *Analytical Chemistry*, 93, 9418-9427. Copyright 2021 American Chemical Society.[128]

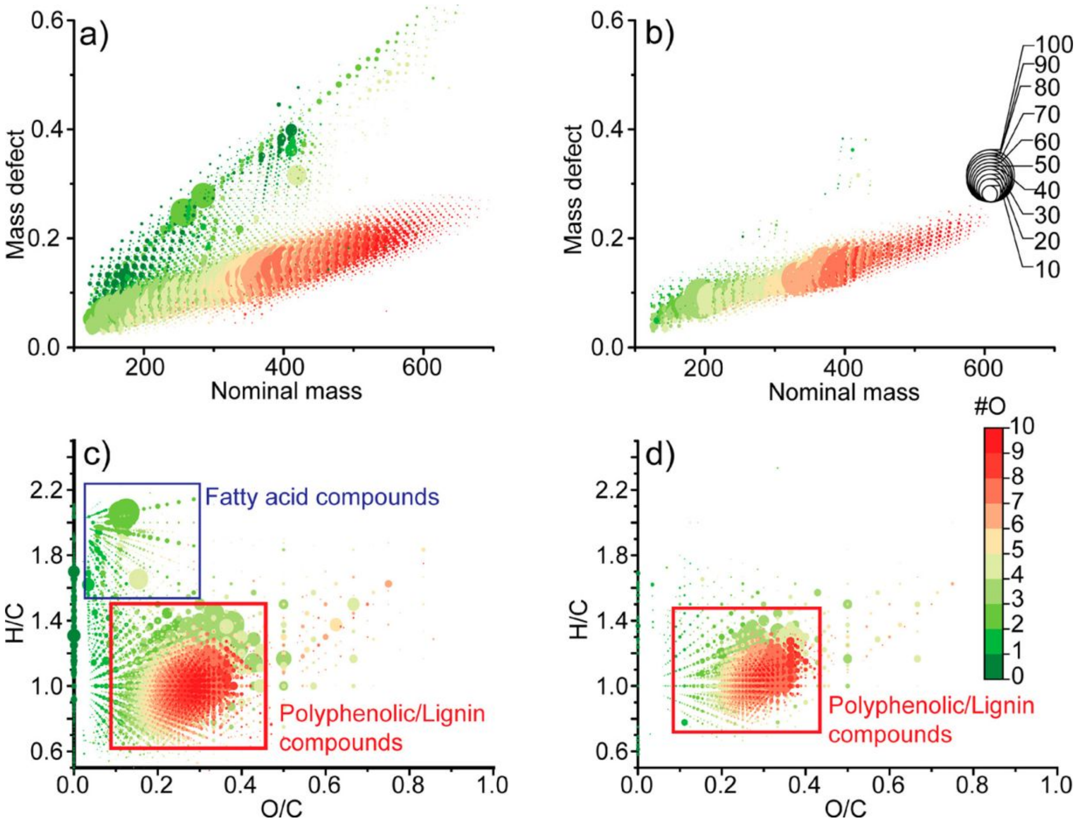

Figure 6: Comparison of DIPAPPI and DIP-APCI for the molecular description of lingocellulosic biomass pyrolysis products. Nominal mass versus mass defect with oxygen number color-coded and relative intensity coded as dot-size: (a) DIP-APCI and (b) DIP-APPI. O/C Van Krevelen diagram with oxygen number color-coded and relative intensity coded as dot-size: (c) DIP-APCI and (d) DIP-APPI. Reprinted with permission from Castilla et al., **2020**, *JASMS*, 31, 822-831. Copyright 2021 American Chemical Society.[75]

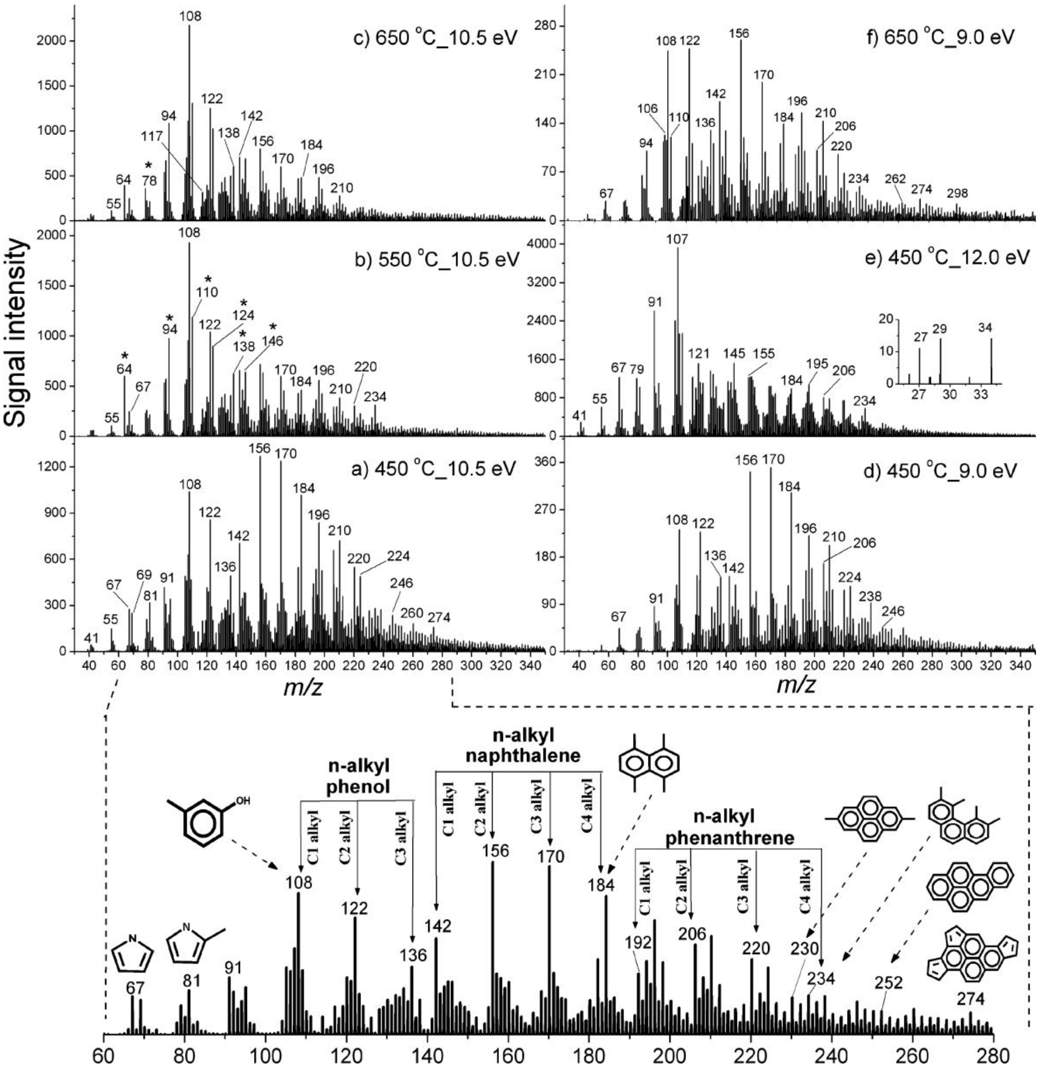

Figure 7: Mass spectra of the evolved gas mixture from coal pyrolysis ionized and analyzed by SVUV and quadrupole time-of-flight mass spectrometry at different photon energies and pyrolysis temperatures. Characteristic molecular profiles can be depicted dominated by alkylation series of aromatic core structures, such as phenol, naphthalene and larger PAHs. Reprinted with permission from Jia et al., 2013, *Energy & Fuels*, 27, 694-701. Copyright 2021 American Chemical Society.[110]

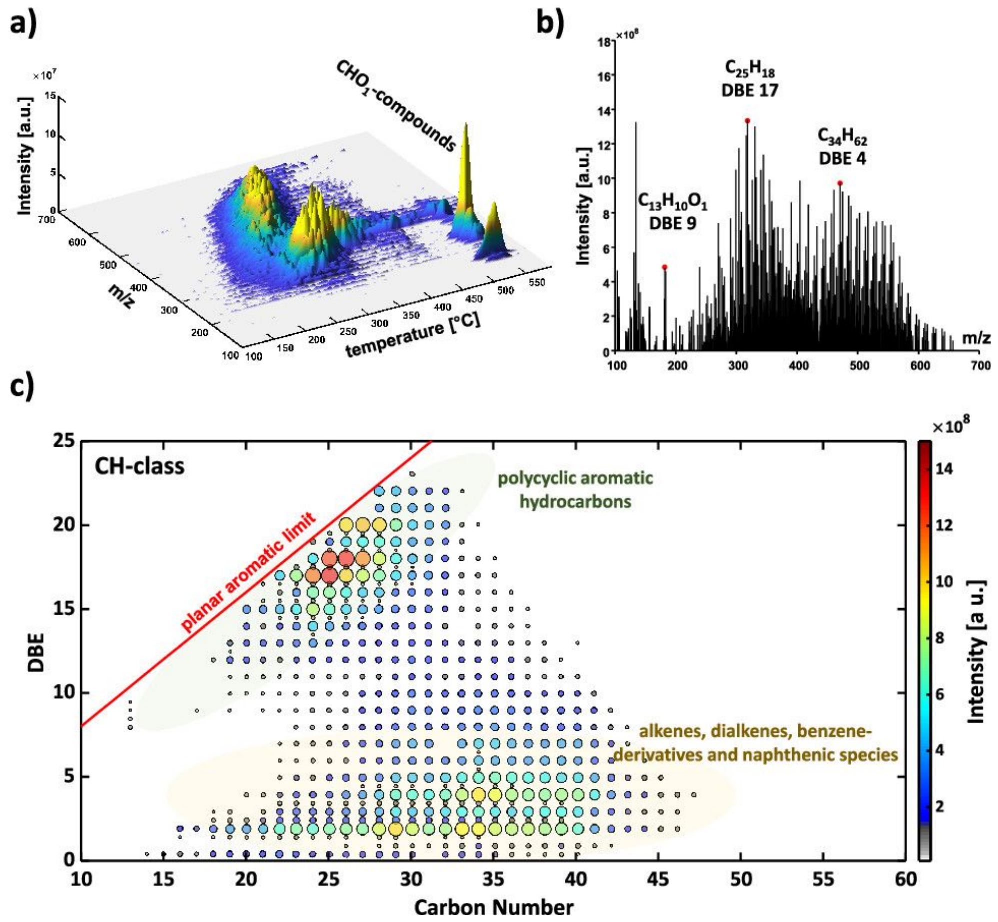

Figure 8: Results of evolved gas analysis by thermogravimetry coupled to high-resolution mass spectrometry for plastic (PE) pyrolysis chars. (a) survey data visualization of the mass spectrometric response (temperature versus *m*/*z*), (b) average mass spectrum of the attributed elemental compositions, and (c) DBE versus #C diagram of the CH class. Two distinct chemical distributions can be found, one at higher DBE values with a comparably low #C spread and another at low DBE of 0–5 with a high #C spread. Reprinted with permission from Friederici et al., 2021, *Energy & Fuels*, DOI: 10.1021/acs.energyfuels.1c01994. Copyright 2021 American Chemical Society.[156]

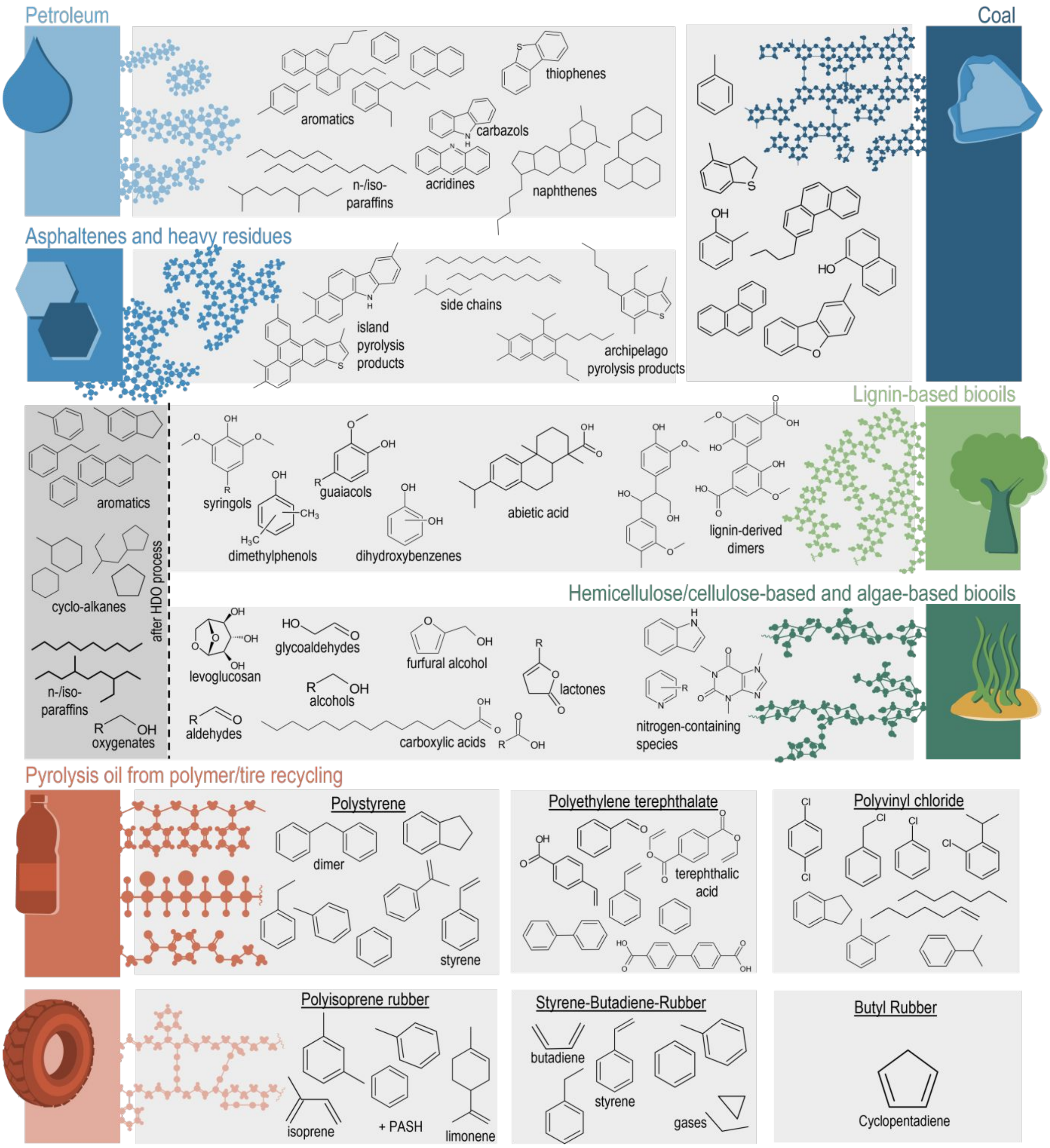

Figure 9: Energy and fuels matrices covered in this review article, spanning from 1) classical fossil petroleum, primarily composed of saturated, naphthenic, and aromatic hydrocarbons; 2) coal pyrolysis products, featuring high-aromatic hydrocarbons with a high abundance of oxygen- and sulfur-containing compounds; 3) lignocellulosic and other biomass-based degradation and pyrolysis products with a high content of oxygen, further upgraded by hydrodeoxygenation (HDO); and 4) other alternative pyrolysis oil sources in the context of recycling, such as waste plastic or tire thermochemical conversion.

Table 2: Overview of evolved gas ionization soft ionization mass spectrometry, highlighting the evolved gas analysis technique, ionization scheme and application area. The articles are grouped based on the primary EGA technique. Publication date from 2011-2021 covered. Abbreviations: APCI – atmospheric pressure chemical ionization, APPI – atmospheric pressure photoionization, APSPLI – atmospheric pressure single photon ionization, APLI – atmospheric pressure laser ionization, ASAP – atmospheric solid analysis probe, CI – chemical ionization, DIP – direct inlet probe, EI – electron ionization, ESI – electrospray ionization, FBR – fixed bed reactor, FI – field ionization, FTICR-MS – Fourier-transform ion cyclotron resonance mass spectrometry, GC – gas chromatography, GCxGC – two-dimensional comprehensive gas chromatography, IMS – ion mobility spectrometry, MFBR – microfluidized bed reactor, PI – photoionization, pyr – pyrolysis, REMPI – resonance enhanced multiphoton ionization, SARA – saturates, aromatics, resins and asphaltenes, SPI – single photon ionization, SVUV – synchrotron vacuum ultraviolet, TOF-MS – time-of-flight mass spectrometry.

Evolved gas analysis approach	Ionization	Application	Authors	Year
gas chromatography	SVUV PI	hydrocarbons	Isaacman et al.[123]	2021
gas chromatography	APCI	oil sand extracts	Barrow et al.[90]	2014
gas chromatography	SVUV PI	Lubricating oils, aerosols	Worton et al.[127]	2014
gas chromatography	APCI	diesel fuel, heavy fuel oil	Schwemer et al.[89]	2015
gas chromatography	APCI	various diesel fuels	Smit et al.[120]	2015
gas chromatography	SVUV PI	Gulf of Mexico crude oil	Worton et al.[163]	2015
gas chromatography	APLI	standard reference crude and shale oils	Benigni et al.[34]	2016
gas chromatography	APCI	Brown coal pyrolysis oil	Zuber et al.[162]	2016
gas chromatography	APCI	diesel fuel, heavy fuel oil	Rüger et al.[121]	2017
gas chromatography	SPI	petroleum base oils	Giri et al.[67]	2017
gas chromatography	SVUV PI	crude oil	Nowak et al.	2018
gas chromatography	SVUV PI	crude oil	Nowak et al.	2018
gas chromatography	SPI, CI, FI	petroleum base oil	Giri et al.[88]	2019
gas chromatography	APPI	light crude oil fraction	Kondyli and Schrader[59]	2019
gas chromatography	CI	biofuel	Hung et al.[154]	2020

Evolved gas analysis approach	Ionization	Application	Authors	Year
gas chromatography	APSPLI (APLI at 157 nm)	light crude oil	Rüger et al.[43]	2021
thermogravimetry	SPI	polymers	Saraji-Bozorgzad et al.[164]	2011
thermogravimetry	SPI	crude oils	Wohlfahrt et al.[102]	2013
thermogravimetry	SPI/REMPI	biomass, biochar	Fendt et al.[101]	2013
thermogravimetry	SVUV PI	bituminous coal	Jia et al.[110]	2013
thermogravimetry	SVUV PI	Rice husk and rice straw biomass	Sun et al.[165]	2013
thermogravimetry	APCI	crude oil, heavy fuel oil, diesel fuel	Rüger et al.[72]	2015
thermogravimetry	SVUV PI	Cotton and flax fabrics biomass	Wang et al.[166]	2015
thermogravimetry	SVUV PI	biomass, solid fuels	Zhou et al.[100]	2016
thermogravimetry	SPI	crude oil	Wohlfahrt et al.[103]	2016
thermogravimetry	APCI	heavy crude oils and SARA fractions	Rüger et al.[105]	2017
thermogravimetry	SPI	elemental sulfur	Varga et al.[98]	2017
thermogravimetry	APCI, REMPI, SPI	asphaltenes, parent crude oil	Rüger et al.[33]	2018
thermogravimetry	SPI, REMPI	steam cracker fouling and coking residues	Grimmer et al.[32]	2019
thermogravimetry	SPI	Kraft lignin and lignite	Zhou et al.[140]	2019
thermogravimetry	SPI	Cellulose and polyethylene	Zhou et al.[167]	2019
thermogravimetry	APCI	bitumen and bitumen ageing	Neumann et al.[82]	2020
thermogravimetry	APCI	asphaltenes (island- and archipelago-enriched)	Neumann et al.[70]	2021
thermogravimetry	SPI, REMPI	LDPE pyrolysis char	Friederici et al.[156]	2021
thermogravimetry	SPI	hemicellulose	Dai et al.[168]	2021
direct insertion probe	APCI, APPI	solid fuel: lignocellulosic biomass	Castilla et al.[75]	2020
direct insertion probe	APCI	bitumen, polymer modified bitumen	Lacroix-Andrivet et al.[74]	2021
direct insertion probe	APCI	solid fuel: lignocellulosic biomass	Castilla et al.[73]	2021

Evolved gas analysis approach	**Ionization**	**Application**	**Authors**	**Year**
pyrolyzer	SPI, REMPI	biomass (lignin, (hemi)cellulose)	Fendt et al.[45]	2012
pyrolyzer	SVUV PI	biomass	Weng et al.[66]	2013
Pyrolyzer	SVUV PI	biomass	Weng et al.[65]	2013
pyrolyzer	SVUV PI	biomass	Dufour et al.[137]	2013
pyrolyzer	REMPI	crude oils	Otto et al.[95]	2015
pyrolyzer	SPI	polypropylene	Wang et al.[115]	2015
pyrolyzer (MFBR)	SVUV PI	Biomass	Jia et al.[42]	2015
pyrolyzer	SPI	lignite	Li et al.[50]	2015
pyrolyzer	SPI	lignite	Zou et al.[51]	2015
pyrolyzer	SPI	bituminous coal	Zhu et al.[116]	2016
pyrolyzer	SPI, REMPI	biomass tar	Jia et al.[41]	2016
pyrolyzer	SPI	polypropylene	Wang et al.[169]	2016
pyrolyzer (FBR)	SPI	miscanthus, douglas fir and oak biomass	Le Brech et al.[170]	2016
pyrolyzer	APPI	crude oil	Kostyukevich et al.[106]	2016
pyrolyzer	SPI	bituminous and anthracite coal	Xu et al.[146]	2017
pyrolyzer (MFBR)	SPI	biomass	Jia et al.[112]	2017
pyrolyzer (MFBR)	SPI	biomass	Jia et al.[138]	2017
pyrolyzer (MFBR and FBR)	SPI	biomass	Jia et al.[139]	2017
pyrolyzer (flow reactor)	SVUV PI	guaiacol (lignin model compound)	Liu et al.[171]	2018
pyrolyzer	APPI	biomass	Zhou et al.[141]	2019
pyrolyzer (MFBR)	APPI	biomass	Chen et al.[142]	2019
pyrolyzer	SPI	coal-related model compounds	Zhou et al.[172]	2019
pyrolyzer (double MFBR)	SPI	algal biomass	Jia et al.[113]	2020
pyrolyzer	SPI, SVUV PI	coal	Zhu et al.[147]	2020
pyrolyzer	SPI	Biomass	He et al.[173]	2020
pyrolyzer	SVUV PI	Biomass	Li et al.[174]	2020
pyrolyzer (FBR)	SPI	coal and biomass	Weng et al.[148]	2020

Evolved gas analysis approach	**Ionization**	**Application**	**Authors**	**Year**
pyrolyzer (MFBR/STR)	SVUV PI	Biomass	Yang et al.[114]	2020
pyrolyzer	SVUV PI	brown coal	Zheng et al.[111]	2020
pyrolyzer	SPI	algal biomass	Niu et al.[144]	2021
atmospheric pressure solid analysis probe	APCI	crude oils	Ahmed et al.[175]	2011
atmospheric pressure solid analysis probe	APCI	polymers	Smith et al.[176]	2012
atmospheric pressure solid analysis probe	APCI	lubricants	Barrère et al.[133]	2014
atmospheric pressure solid analysis probe	APCI	crude oils	Ahmed et al.[129]	2014
atmospheric pressure solid analysis probe	APCI	vacuum gas oils	Farenc et al.[131]	2016
atmospheric pressure solid analysis probe	APCI	polyolefins	Farenc et al.[177]	2017
atmospheric pressure solid analysis probe	APCI	crude oils and SARA fractions	Tose et al.[130]	2017
atmospheric pressure solid analysis probe	APCI	pyrolysis oils derived from oil shales	Järvik and Oja[178]	2017
atmospheric pressure solid analysis probe	APCI	polyalphaolefins	Mendes Siqueira et al.[132]	2018
atmospheric pressure solid analysis probe	APCI	gasoline polymeric additives	Beaumesnil et al.[136]	2020
atmospheric pressure solid analysis probe	APCI	diesel, biomass	Rüger et al.[179]	2021

Future research directions and perspectives

This review highlights recent publications in the field of evolved gas analysis coupled to soft ionization mass spectrometry, particularly photoionization, for the molecular description of energy and fuels matrices covering classical fossil fuels, heavy residues and deposits, solid fuels, such as coal and lignocellulosic biomass, as well as pyrolytic bio- and waste oils. The concept of the deployed PI schemes, from simple discharge lamp-based solutions to utilizing large-infrastructure synchrotron facilities, was outlined as well as the variations in EGA techniques, covering simple DIP concepts up to sophisticated hyphenation on industrial pyrolysis reactors. Since the last decade, it can be concluded that EGA-PIMS has seen increased attraction (Figure 1). Technical demands in instrumental construction modifying the EGA scheme, light source, or mass spectrometric platform caused substantial research in this direction. More importantly, challenges in applying EGA-PIMS for novel energy and fuel sources will be a driver for research, certainly due to the stimulus of a changing landscape in energy supply towards carbon neutrality.

In this respect, the different EGA-MS methodologies have shown individual capabilities with specific advantages and disadvantages. On the one hand, gas chromatographic concepts, such as PyrGC, GC and GCxGC MS offer the highest degree of isomeric speciation, allowing exact compound identification, particularly for GCxGC with its increased peak capacity. On the other hand, classical GC injectors require liquid sample injection with minimal water content, challenging for solid fuels or raw bio-oils with high water content. In contrast, direct inlet probe systems (DIP/ASAP) are regarded as robust and rapid characterization technology with minimal sample preparation. Moreover, DIP/ASAP is frequently available for commercialized instrumentation with soft atmospheric pressure ionization and high-resolution mass spectrometric detection, less common in PyrGC, exemplarily. HRMS allows resolving complex mixtures and attributing chemical formulae, giving access to in-depth chemical information. Here, MS/MS also adds an structural dimension by the ability to record fragmentation spectra. Custom-build concepts can close individual gaps between the more common EGA methodologies offering unique capabilities. Here, SVUV approaches can be named, with the unique capability of almost freely scanning through the VUV and UV spectral range with high photon flux. Also, the coupling of online EGA-MS devices towards reaction vessels gives unique insights. Tracing the evolved molecular pattern during pyrolytic conversion processes of alternative feedstocks is not applicable with the other mostly laboratory-bound instrumentation. TGA concepts can be seen as an intermediate approach mimicking conversion and pyrolysis process with precise temperature control and minimized sample masses in the laboratory.

Photoionization has shown great advantages in studying complex mixtures. The soft ionization preserving the molecular ion was found to be of particular value for addressing the molecular evaporation profile. The selectivity and sensitivity of the REMPI process towards aromatic constituents are of high value, whereas the universality of SPI enables a comprehensive description. Future research might put more effort into studying the wavelength dependence for tunable light sources, such as SVUV and optical parametric oscillators (OPO). Significant wavelength dependence of the REMPI cross-section was found for heteroatom-containing species, such as nitrogen-containing PAHs (N-PAHs). Those N-PAHs are frequently found in pyrolysis oils from protein-rich biomass, such as algae, and, thus, tunable REMPI can be particularly interesting studying the thermochemical conversion of these alternative feedstocks. Matrix-effects common to classical atmospheric pressure ionization sources, such as MALDI and ESI, heavily deployed in the context of energy and fuels research, are substantially lower in PI. Moreover, based on the knowledge of the cross-section, photoionization provides the possibility of direct quantification. These cross-sections are mainly reported for PAHs, a key compound class in fossil fuel research. Future studies might determine cross-sections increasingly for oxygen-containing species, enabling quantification attempts in the field of bio-oils and lignocellulosic biomass pyrolysis. Combined with the capability of EGA-PIMS to trace reactive intermediate species and radicals, valuable information for chemical modeling and engineering can be gained. In 2016, Jia and co-workers published the comparison of different EGA-PIMS platforms for studying biomass pyrolysis and concluded the problem of isomeric speciation solved in sophisticated SVUV approaches by scanning photon energies.[138] Isomeric identification can also be addressed in reactor or thermal analysis coupled to fast gas chromatography, which needs to be further explored in the future.[102,103,180]

In the context of the increased usage of heavier fossil oil sources, including the analysis of heavy residues, such as vacuum gas oils or bitumen, as well as asphaltenes, the authors believe that vacuum direct inlet probe designs hold an enormous potential. Interestingly, this concept was prevalent almost half a century ago but might experience a comeback. Shifting the effective boiling point of larger components allowing them to be evaporated prior thermal decomposition bears a solid analytical power, easier accessing the true molecular profile. As a drawback, information on diagnostic pyrolysis products is reduced. Certainly, for novel applicative challenges, such as undertaking pyrolysis of rather heterogeneous waste for recycling, multiple analytical platforms will be required.[181] In this context, the commercialization of several DIP platforms from large analytical instrumentation vendors over the last decade was seen. Easy access to a robust evaluated solution will further increase the utilization of EGA-PIMS. Nonetheless, for energy and fuels research, we are looking forward seeing broader capabilities for temperature ramping, higher upper-temperature limits or, apart from lamp-based APPI, also laser-based photoionization schemes.

Modern developments on the side of the mass spectrometric detection have shown a movement towards higher resolving power, enabling the separation of isobaric constituents. In this field, we will see stronger influence of Fourier-transform mass spectrometry (FTMS) and high-resolution time-of-flight (HR-TOF) mass analyzers. Fossil fuel research has always been the key example for revealing the necessity of high resolving power and high mass accuracy. The difficulty in interpreting spectra is drastically reduced and elemental composition attribution directly enables chemical conclusions. This will be of high value for unknown pyrolysis products and patterns from fossil and novel challenges. Here, particularly the occurrence of certain heteroelements, not reported in classical fossil fuel analysis, such as phosphorous, silicon, halogens, and boron, will make sum formula attribution strategies using HRMS a prerequisite to study those matrices. Boron-containing species can frequently been found in bio-oils, whereas halogen- and silicon-containing species are prominent in certain polymer waste pyrolysis oils and caused by additives, flame retardants and plasticizers.[182,183]

From an applicative perspective, some research fields have not or only rarely been touched by EGA-PIMS. Engineering developments in the field of recycling and attempts in a circular economy (bio and other pyrolysis oils) can be strongly supported by elucidation of the molecular profile by EGA-PIMS. Here, the increasing field of studying co-pyrolysis by EGA-PIMS needs to be mentioned, exemplarily the study of Weng and Zhou et al. performing co-pyrolysis of cellulose and polyethylene over magnesium oxide[184] or zeolite-based catalysts[167]. Thermal conversion of sample type mixtures can be of great benefit for shifting the product range towards certain chemical classes, *e.g.*, pyrolyzing cellulose biomass together with polypropylene over an all-silica mesoporous catalyst to increase the yield of furans.[185] Comprehensive gas chromatography with PIMS has not been yet deployed largely for studying bio-oils or plastic pyrolysis oils. Due to its high analytical potential, EGA-PIMS will have a widespread usage in fundamental and applied research in novel challenges in energy and fuels research within the next decade.

Supporting Information

The Supporting Information is available free of charge at XXX

- description details for the creation of Figure 1

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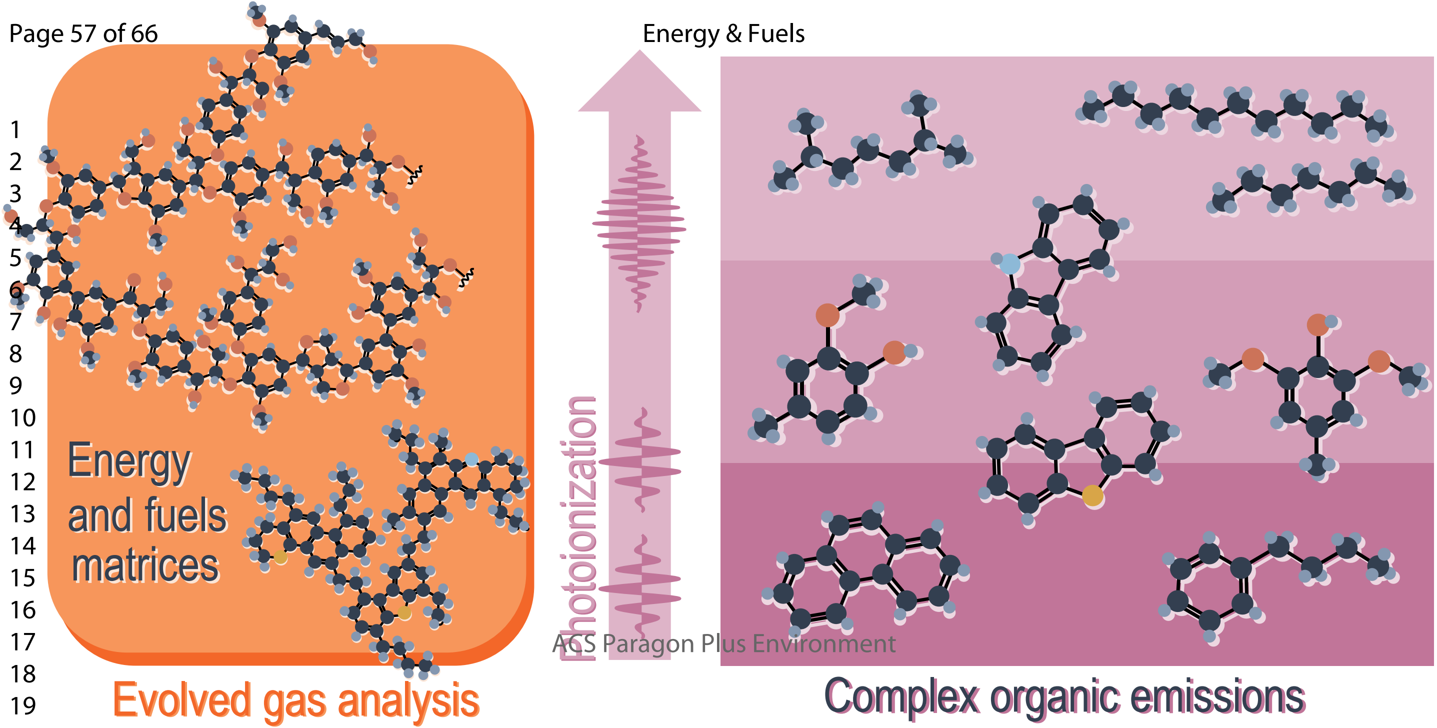

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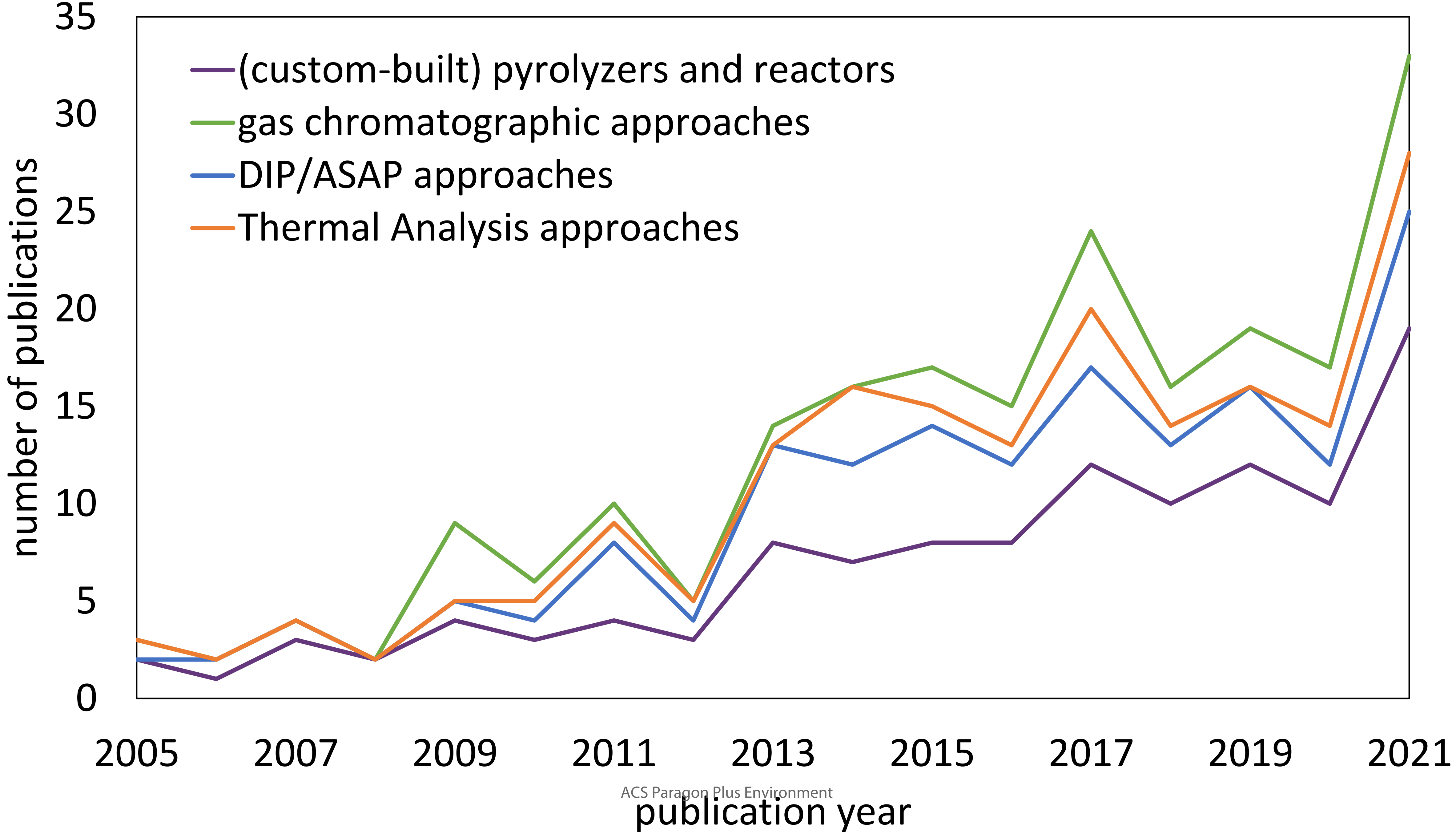

(custom-built) pyrolyzers and reactors
gas chromatographic approaches
DIP/ASAP approaches
Thermal Analysis approaches
number of publications
0
5
10
15
20
25
30
35
2005
2007
2009
2011
2013
2015
2017
2019
2021
publication year

Atmospheric pressure photoionization (APPI)

$$M + h\nu \rightarrow M^{+\cdot}$$

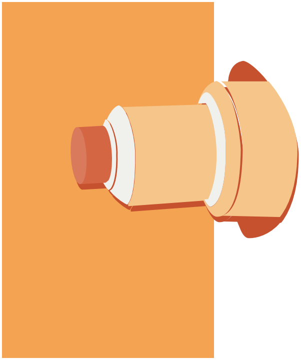
$$M^{+\cdot} + X \rightarrow [M + H]^{+} + [X - H]^{\cdot}$$

$$D + h\nu \rightarrow D^{+\cdot}$$

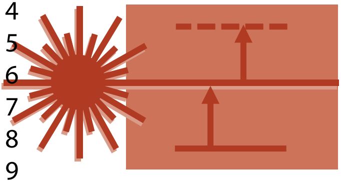
$$D^{+\cdot} + M \rightarrow D + M^{+\cdot}$$

$$D^{+\cdot} + D \rightarrow [D + H]^{+} + [D - H]^{\cdot}$$

$$[D + H]^{+} + M \rightarrow D + [M + H]^{+}$$



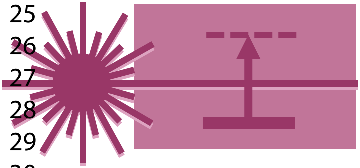
Atmospheric pressure laser photoionization (APLI)
Resonance enhanced multi photon ionization (REMPI)



$$M + mh\nu \rightarrow M^{*}$$

$$M^{*} + nh\nu \rightarrow M^{+\cdot} + e^{-}$$

Atmospheric pressure single photon laser ionization (APSPLI)
Single photon ionization (SPI)



$$M + h\nu \rightarrow M^{+\cdot}$$

Photoionisation with synchrotron radiation

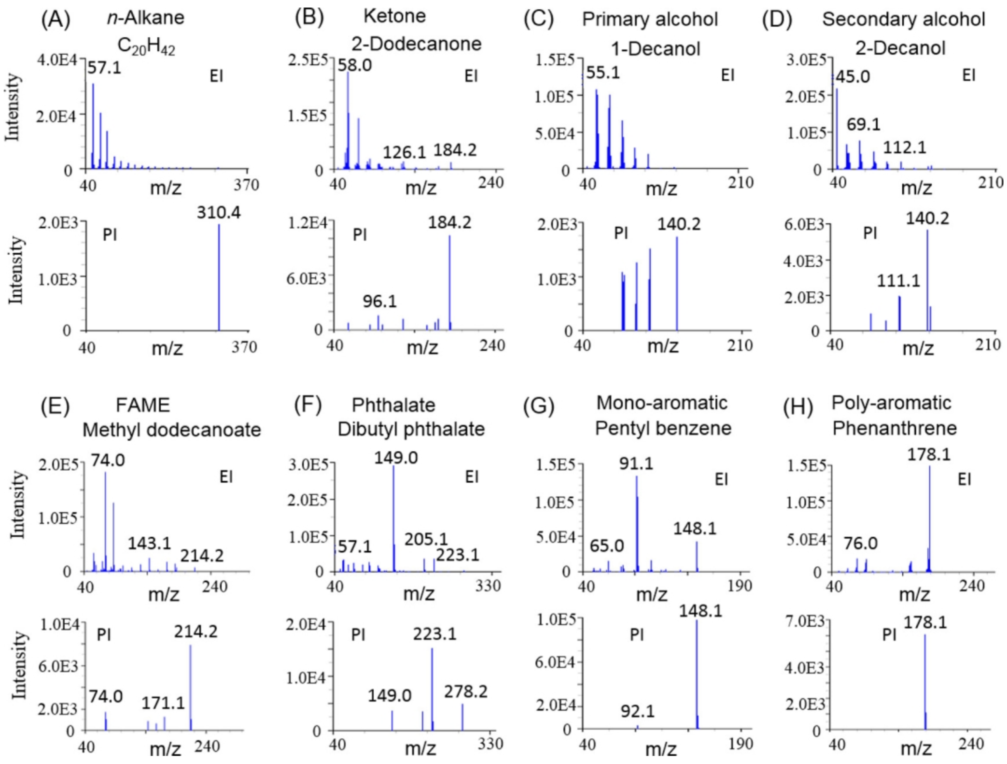


Figure 3: GC×GC-TOF-MS electron ionization (EI) and photo ionization (PI) mass spectra for numerous petrochemically-relevant compounds. EI exposes strong fragmentation behavior generating diagnostic fragments, whereas soft photoionization by a deuterium discharge lamp preserves the molecular information. Reprinted with permission from Giri et al., **2017**, *Anal. Chemistry*, 89, 5395-5403. Copyright 2021 American Chemical Society.


a)
DIP/ASAP
glass
capillary
heated N_2
Ionisation
MS Orifice
heated N_2
ASAP
probe with
melting point
capillary insert
Ionisation
MS Orifice
Thermogravimetry
heated
Interface
crucible
furnace
Pyrolyzer
filament
sample tube
GC
RF coil
Ferromag-
netic foil
GC
sample
injector
quartz
wool
furnace
GC
Others
thermocouple
MS Orifice
Gas inlet
Boiling
chamber
Pyrolytic
furnace
ion transfer
capillary
Ionisation
MS
Orifice
Micro fixed-
bed reactor
sample
b)
Desorption/Evaporation
Pyrolysis
Coke/residue formation

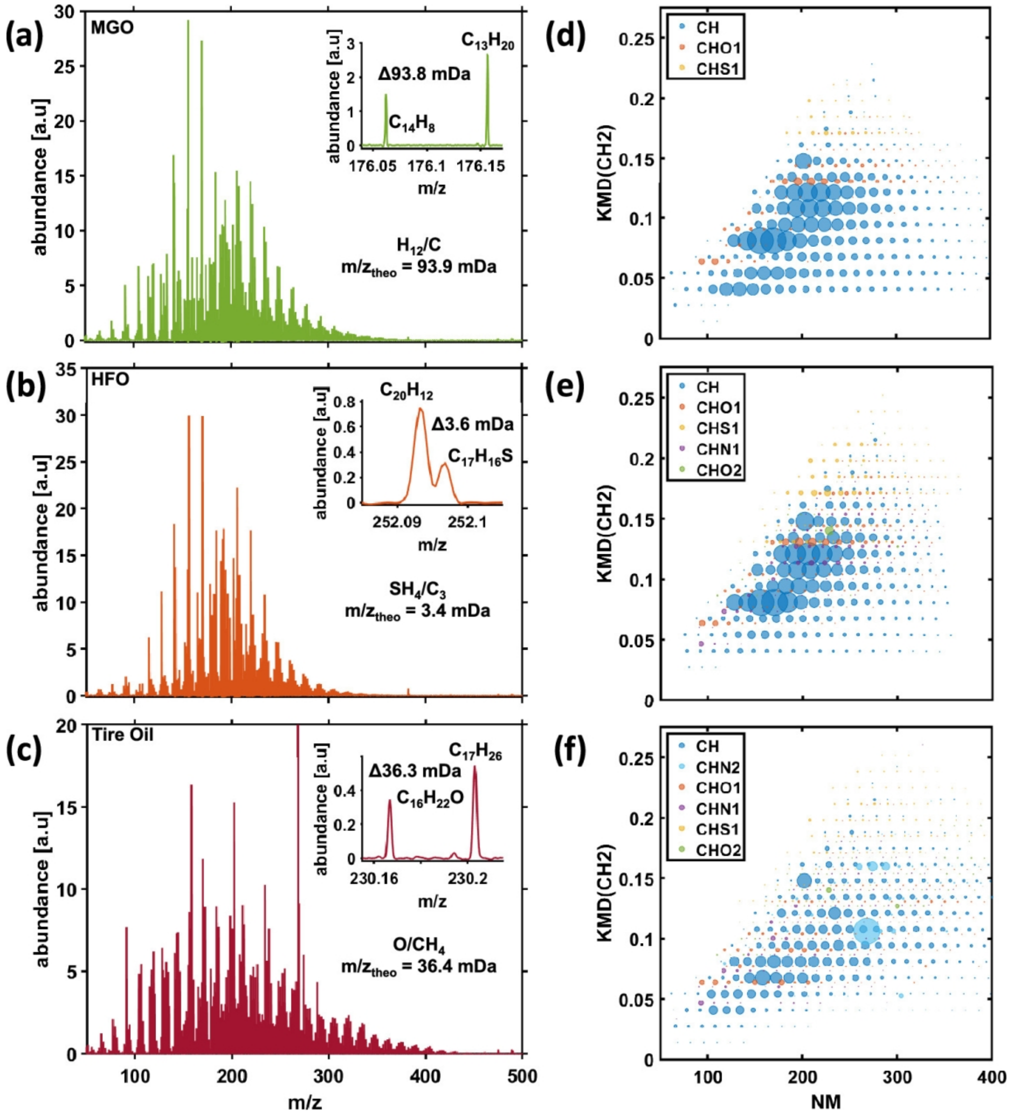


Figure 5: Average mass spectra of three different petrochemical materials investigated by GC-REMPI Orbitrap FTMS. (a) Marine gas oil (MGO), (b) heavy fuel oil (HFO), and (c) tire oil are depicted on the left side. Characteristic isobaric interferences are shown in insets. These mass splits can be resolved and chemically attributed due to the high mass resolution and mass accuracy of the Orbitrap mass analyzer. Kendrick mass defect plots of (d) MGO, (e) HFO, and (f) tire oil. The compound classes are color coded. Reprinted with permission from Kösling et al., **2021**, *Analytical Chemistry*, 93, 9418-9427. Copyright 2021 American Chemical Society.

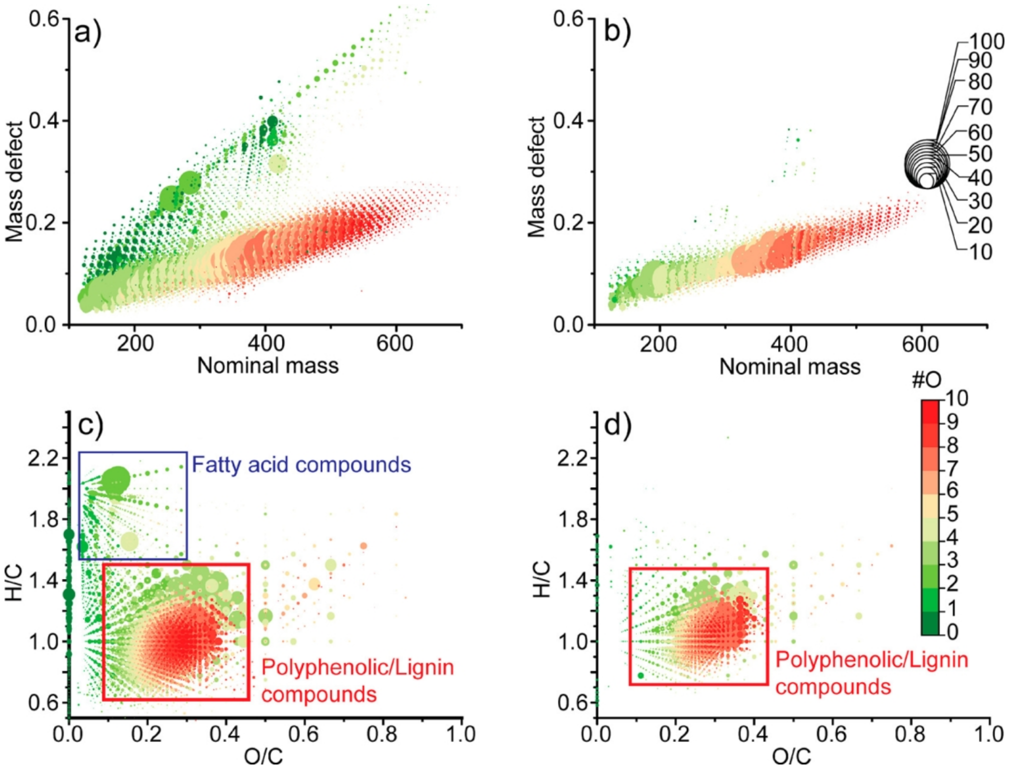


Figure 6: Comparison of DIPAPPI and DIP-APCI for the molecular description of lingocellulosic biomass pyrolysis products. Nominal mass versus mass defect with oxygen number color-coded and relative intensity coded as dot-size: (a) DIP-APCI and (b) DIP-APPI. O/C Van Krevelen diagram with oxygen number color-coded and relative intensity coded as dot-size: (c) DIP-APCI and (d) DIP-APPI. Reprinted with permission from Castilla et al., **2020**, *JASMS*, 31, 822-831. Copyright 2021 American Chemical Society.

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Figure 7: Mass spectra of the evolved gas mixture from coal pyrolysis ionized and analyzed by SVUV and quadrupole time-of-flight mass spectrometry at different photon energies and pyrolysis temperatures. Characteristic molecular profiles can be depicted dominated by alkylation series of aromatic core structures, such as phenol, naphthalene and larger PAHs. Reprinted with permission from Jia et al., **2013**, *Energy & Fuels*, 27, 694-701. Copyright 2021 American Chemical Society.

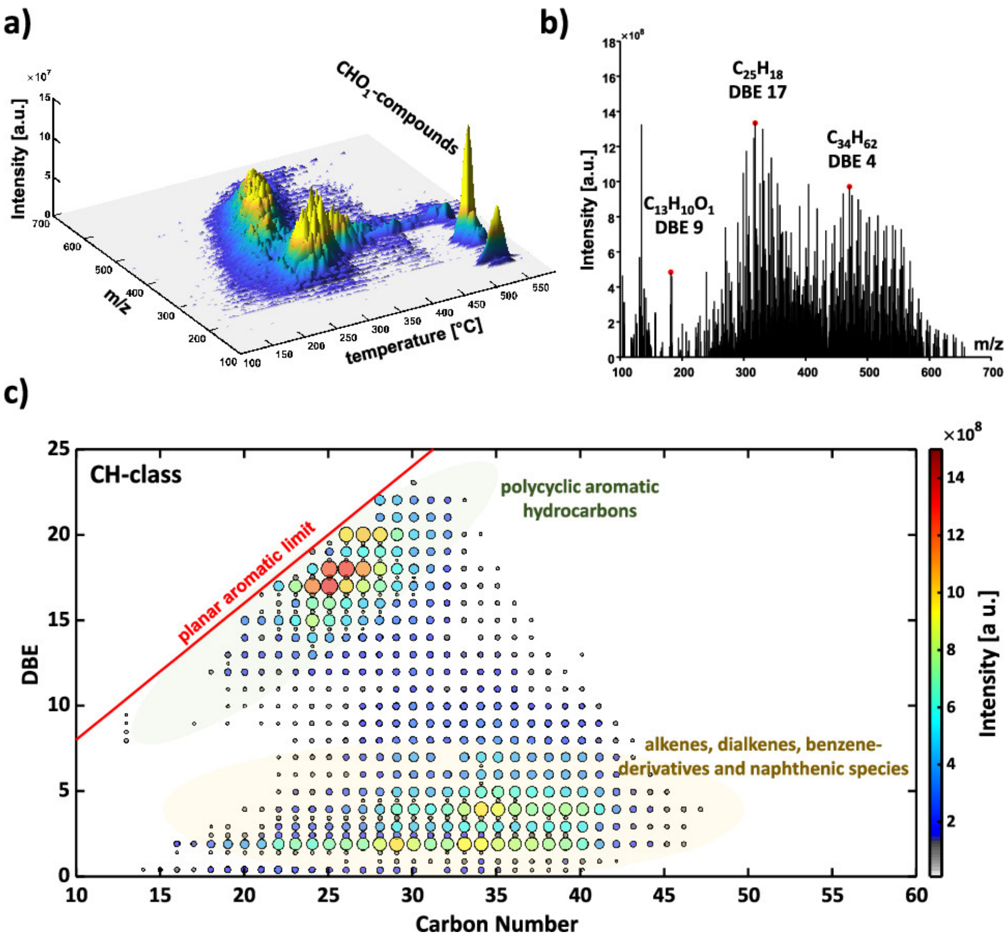
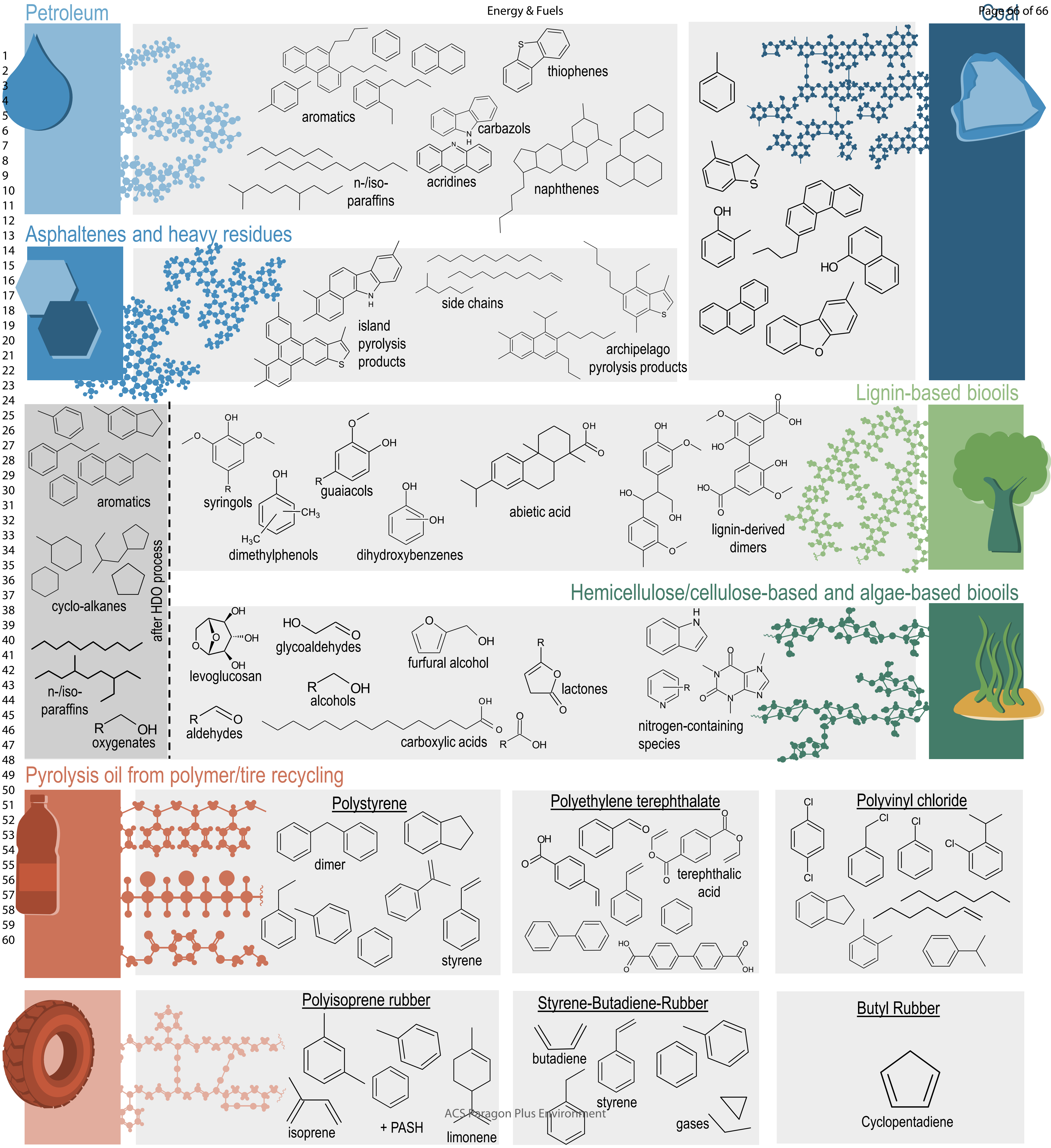


Figure 8: Results of evolved gas analysis by thermogravimetry coupled to high-resolution mass spectrometry for plastic (PE) pyrolysis chars. (a) survey data visualization of the mass spectrometric response (temperature versus *m/z*), (b) average mass spectrum of the attributed elemental compositions, and (c) DBE versus #C diagram of the CH class. Two distinct chemical distributions can be found, one at higher DBE values with a comparably low #C spread and another at low DBE of 0–5 with a high #C spread. Reprinted with permission from Friederici et al., **2021**, *Energy & Fuels*, DOI: 10.1021/acs.energyfuels.1c01994. Copyright 2021 American Chemical Society.


Petroleum
aromatics
thiophenes
carbazols
n-/iso-paraffins
acridines
naphthenes
Coal
Asphaltenes and heavy residues
island pyrolysis products
side chains
archipelago pyrolysis products
Lignin-based biooils
syringols
guaiacols
dimethylphenols
dihydroxybenzenes
abietic acid
lignin-derived dimers
aromatics
cyclo-alkanes
n-/iso-paraffins
oxygenates
after HDO process
Hemicellulose/cellulose-based and algae-based biooils
levoglucosan
glycoaldehydes
furfural alcohol
lactones
alcohols
aldehydes
carboxylic acids
nitrogen-containing species
Pyrolysis oil from polymer/tire recycling
Polystyrene
dimer
styrene
Polyethylene terephthalate
terephthalic acid
Polyvinyl chloride
Polyisoprene rubber
isoprene
+ PASH
limonene
Styrene-Butadiene-Rubber
butadiene
styrene
gases
Butyl Rubber
Cyclopentadiene