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On-line Process and Real-Time Analysis of Biomass Pyrolysis Gases Using Photo Ionization Time-of-Flight Mass Spectrometry

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(Alois Fendt)

It takes two to invent anything. The one makes up combinations; the other one chooses, recognizes what he wishes and what is important to him in the mass of the things which the former has imparted to him.
What we call genius is much less the work of the first one than the readiness of the second one to grasp the value of what has been laid before him and to choose it.

Paul Valéry
in Jacques Hadamard:
The Psychology of Invention in the Mathematical Field

Abstract

Im Rahmen dieser Arbeit wurde eine on-line Prozessanalytik für die Charakterisierung von Flash-Pyrolysegasen aus Biomasse an einem Technikumsreaktor am KIT aufgebaut. Diese basiert auf der Photoionisations-Flugzeitmassenspektrometrie, die eine fragmentationsfreie und schnelle Echtzeitanalyse der organischen Bestandteile der Pyrolysegase ermöglicht. Als Ionisationsverfahren wurden zum einen Resonanzverstärkte Multiphotonen-Ionisation (REMPI), und zum anderen Einphotonenionisation (SPI) eingesetzt. Letzteres wurde mit Hilfe einer kompakten VUV-Lichtquelle mit 126 nm Wellenlänge über einen Excimer-Prozess, angeregt durch Elektronenbeschuss von Argongas, erreicht. Damit lassen sich eine Vielzahl von Verbindungen und Substanzklassen ionisieren, und zwar sowohl aromatische als auch aliphatische Verbindungen. Die Anwendung statistischer Methoden zeigt eine deutlich unterscheidbare Pyrolysegaszusammensetzung für die eingesetzten unterschiedlichen Biomassesorten und Temperaturvariationen. Dies beeinflusst wiederum die Eigenschaften der im Prozess anfallenden Biosyncrudes und ermöglicht damit einen Beitrag für die Optimierung des Gesamtprozesses.

Soft photo ionization time-of-flight mass spectrometry (PI-TOF-MS) is applied for real-time analysis of pyrolysis gases from biomass arising in a technical flash pyrolysis plant at the KIT. There, evolving pyrolysis gases are condensed and the obtained oil is immingled with the pyrolysis coke, providing the so-called biosyncrude, whose consistence is influenced by the composition of the pyrolysis gases. For the direct and on-line monitoring thereof, mass spectrometers with two different ionization methods were coupled directly to the pyrolysis reactor via a heated sampling train. On the one hand, an electron-beam pumped excimer light source (EBEL) is used for generation of VUV light for single photon ionization (SPI), which is a universal method to comprehensively ionize (nearly) all organic molecules. On the other hand, laser-based resonance enhanced multi-photon ionization (REMPI) using UV-photons is an ideal detection method for selective analysis of aromatic species in complex samples.

The miscellaneous biomass feeds showed distinguishable mass spectra with specific patterns. The main components of the pyrolysis gases were cellulose and lignin decomposition products and in some cases N-aromatics. Applying multivariate analysis provides the basis for the optimization of the bioliq® process in respect of the different slurry consistence and the subsequent gasification step.

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Motivation & Introduction

Instrumental techniques for analytical chemistry have undergone a rapid development in the last years. The field of application of analytical methods is exceedingly extensive nowadays. Multitudinous techniques can come into consideration, with their intrinsic characteristics, and advantages and disadvantages, in search for analytical problem-solving. Fundamental targets thereby are improvement of selectivity and performance, enabling measurements in real-time. Within the scope of this work, biomass pyrolysis gases at a technical flash pyrolysis plant are investigated on-line and in real-time, particularly with regard to the optimization of this process for the production of synfuels out of biomass. In this context, the need for bioenergy and its potential is exposed. A large biomass feedstock spectrum can be employed in the “biomass to liquid” (BtL) process introduced here; this influences the consistency and quality of the so-called biosyncrude, a store- and transportable suspension of the arising pyrolysis gases and the remaining char, which in turn is linked to the further process steps and conditions, e.g. the synthesis gas composition. For the analysis of this complex matrix, time-of-flight mass spectrometry combined with soft photo ionization is exceptionally suited due to the nonappearance of fragments and the generally high selectivity of the method. Most notably, an innovative VUV light source (EBEL) for single photon ionization (SPI) has been applied and newly developed here, that allows direct and on-line measurements of the whole width of organic intermediates arising thereby. In addition, laser-based resonance enhanced multi-photon ionization (REMPI) was employed as a highly selective and sensitive method for detection of aromatic compounds. Data analysis is a further crucial aspect; particularly multivariate methods have turned out to be well suited for classification and pattern recognition in such complex matrices.

1.1 The need for bioenergy

In times of a growing world population in conjunction with higher living standards, increasing global primary energy consumption is anticipated, in spite of raising energy efficiency. Furthermore, production of conventional oil and gas predominantly takes place in conflict areas, unfavorably against the background of diminishing and difficult to exploit fossil energy sources. As a consequence, in the future new developments in the field of energy generation or production of chemicals have to focus more on the increased application of regenerative sources. In addition, this would be a benefit in terms of reducing the emissions of the greenhouse gas carbon dioxide. Biomass is the only regenerative energy source containing carbon. However, an argument recently developed is related to the increased biomass utilization for energy production, since a conflict is feared between “food and fuel”, which could lead to a decrease in harvesting of edibles and rising food prices. Hence, particularly the use of rest and waste biomass such as straw and urban waste wood has become of interest for the production of liquid fuels (so called second generation biofuels) and chemicals. Regarding Germany, the future total energy consumption will presumably decrease slightly, but owing to the worldwide situation as well as compliance with the climate goals, expansion of renewable energy resources is inevitable. Thereby, bioenergy (energy from biomass) has the biggest share (around two thirds at the moment) in all renewables[1]. By all means, the German government decided to expand the renewable energy sources significantly up to 2050.[2] The anticipated bioenergy potential for the year 2050 is depicted in Figure 1.

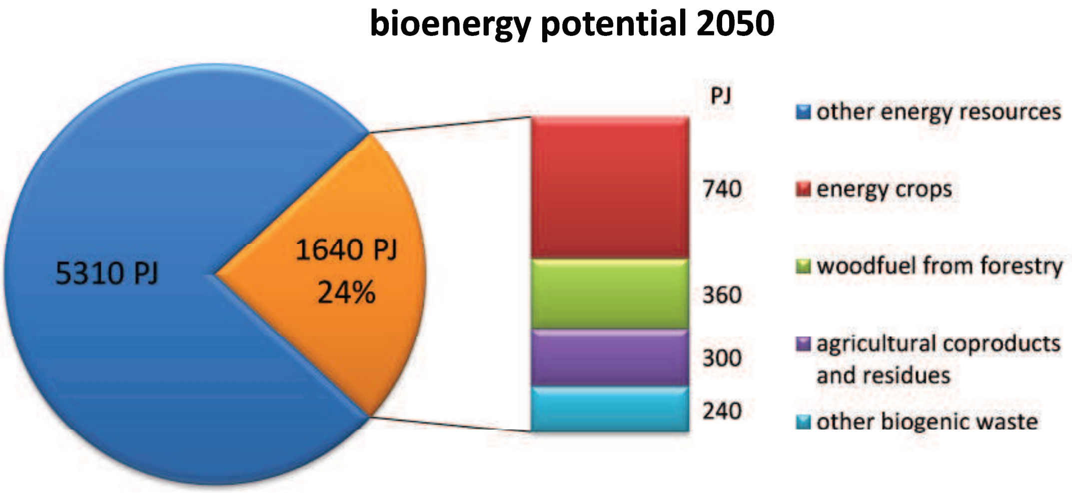

Figure 1: Anticipated[3] bioenergy potential and shares in 2050

The renewable energy shares of the total final energy consumption (8,692 PJ) in Germany 2011 amount to 12.5 % with a biomass share of 8.4 % of total (730 PJ)[1]. The bioenergy share is assumed to rise to around 24 % (1,640 PJ) of the total German energy demand (6950 PJ) in 2050[3]. Thereby, energy crops are to play an essential role. A maintainable degree should be achievable by a well-organized agriculture and forestry management, including the use of fallow land, for example. Furthermore, emissions of the green-house gas CO_2 can only be reduced significantly by biofuels of the second generation[4]. Plenty of possibilities for production of energy from biomass exist, as illustrated in Figure 2.

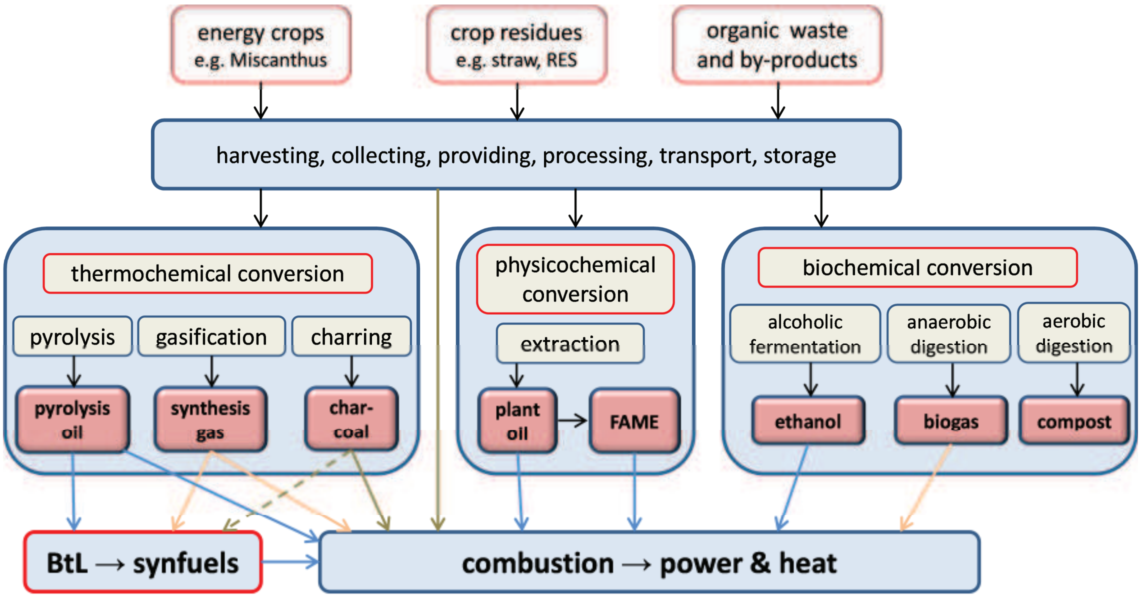

Figure 2: Bioenergy production and conversion routes (freely adapted from Kaltschmitt et al.[5])

However, the largest part of the bioenergy is based on traditional biomass, which is used primarily for cooking and heating in rural areas of developing countries[6]. Beyond that, gasification attracts a high level of interest as it offers higher efficiencies compared to combustion; and fast pyrolysis is interesting as a liquid is produced that offers advantages in storage and transport and versatility in applications, although it is still at a relatively early stage of development[7]. Anyway, particularly in the field of mobility, high energy density is sought. In this respect, synthetic fuels (synfuels) are an optimal solution and purer than petroleum-based fuels[4]. This applies even more to the comparison with direct use of pyrolysis liquids.

1.2 Pyrolysis of biomass & Synfuels

For the production of synfuels out of biomass, a series of different technical processes exist[5], which are summarized under the term “biomass to liquid” (BtL). It denotes a process chain that converts biomass to liquid hydrocarbons by way of thermochemical gasification – directly or via an intermediate product – to obtain synthesis gas, and the subsequent fuel synthesis thereof[8]. Many common systems use pyrolysis to achieve this, for example fluid bed reactors, circulating fluid beds (CFBs), vacuum and ablative pyrolysis, and rotating cone. Already in the 1990s several fast pyrolysis technologies reached near-commercial status[7]. On principle, a multitude of products arises during biomass pyrolysis, varying in quantity and composition as a function of process conditions. The latter are generally classified into three groups[9, 10]:

- Charring / Carbonization (conventional slow pyrolysis)
- Fast pyrolysis (moderate temperature and short residence time)
- Flash pyrolysis (high temperature and very short residence time)

Evidently, the heating rate is a key parameter, even though it’s not clearly defined in literature. Anyhow, it is strongly influenced by reactor configuration and feed particle sizes[11]. Aim of fast and flash pyrolysis is maximization of the liquid portion of primary pyrolysis products. At this, up to 75 % of pyrolysis oil are generated, beside gas (roughly 15 %, predominantly CO_2, CO and CH_4) and char (around 10 %). In brief, relevant process parameters to achieve this are summarized as follows[11]:

- Reactor temperatures between 450 and 550 °C, depending on the employed lignocellulosic biomass and the reactor type
- Short residence times in the reactor to suppress secondary reactions
- Rapid quenching of the product gases below 100 °C
- Small (feedstock) particle sizes (best ≤ 3 mm)
- Short contact times of product gas and catalytically active char

Carbonization of wood at low temperatures and long residence times is used since ancient times for production of charcoal. In contrast, direct gasification of biomass is achieved at high temperatures (and also long residence times) with a defined amount of oxygen or steam. The volatile vapors (70 – 86 %) generated thereby are mainly H_2, CO, CO_2, CH_4, hydrocarbon gases, tar, and water vapor. Solid char and ash are also produced[12]. The product spectrum of fast and flash pyrolysis is strongly influenced by the composition of the lignocellulosic biomass, as shown later. For instance, pure lignin yields high char rates (around 50 %)[11], in contrast to pure cellulose. The condensates of the pyrolysis gases are complex and heterogeneous mixtures of more than 300 components, typically consisting of 25 % water[7], 35 % water-soluble monomers, 25 % water-insoluble oligomers and 15 % polar substances[13, 14]. The main constituents in the aqueous phase and the water-soluble fraction are acetic acid and hydroxyacetaldehyde[15]. The water-insoluble part of flash pyrolysis oils (the also called pyrolytic lignin) contains many oligomeric phenol derivatives[13].

In principle, the pyrolysis oils can be used directly[16] as fuels or as source for extraction of particular components thereof, e.g. for smoke flavorings. In this connection, the direct analysis of the condensable pyrolysis gases at their point of origination can open up new possibilities for extraction of materials. However, pyrolysis oils are not suitable for standard engines and vehicles due to impurities and their high inhomogeneity, inconsistent quality and incompatibility with conventional fuels. Furthermore, they are corrosive because of the high content of oxygen compounds, and their storage stability[17] is limited due to phase separation tendency[11] and deterioration, as a result of condensation and polymerization reactions[13]. In contrast, synfuels are not afflicted with these drawbacks and problems, resulting in higher lifecycles and more efficient combustion at engines. Beyond that, BtL fuels are advantageous in terms of land use efficiency. With an ordinary car, it is possible to drive 64,000 km with fuel from biomass grown on one hectare acreage, as reckoned by the FNR (Gülzow, Germany)[18] and depicted in Figure 3. This corresponds to an annual yield of around 4,000 l/ha.[8] This is considerably farther than with first generation biofuels; for example, the cruising range using biodiesel amounts to 23,300 km and 22,400 km for bioethanol, respectively.

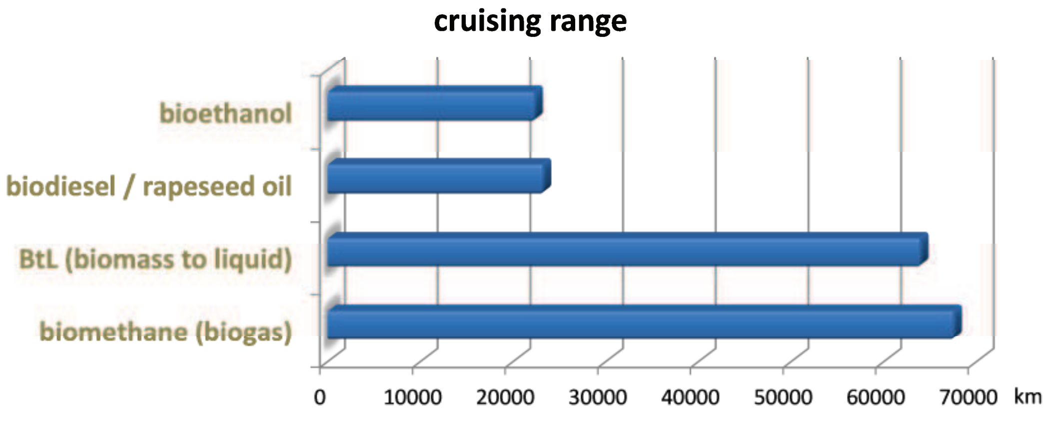

Figure 3: Cruising range with fuel from biomass grown on one hectare acreage[18]

1.3 The bioliq® process

At the Karlsruhe Institute of Technology (KIT), the so called bioliq® process[19-22] was developed. It comprises three fundamental and some intermediary process steps[4, 23] (see Figure 4). First, flash pyrolysis at 500 °C in a twin screw mixer with a heat transfer material such as hot sand is carried out in decentralized plants, converting various kinds of biomass into biochar and pyrolysis gases. The latter are condensed and immingled with the char, providing a pump- and storable suspension, the so-called bioliqSynCrude®. This also called biosyncrude or bioslurry contains about 90 % of the energy stored in the biomass, with an energy density around ten times as high as that of the feedstock[4], entailing reduced transport costs. In this regard, a cost-effective transport over a long distance is not possible particularly for straw and hay[11].

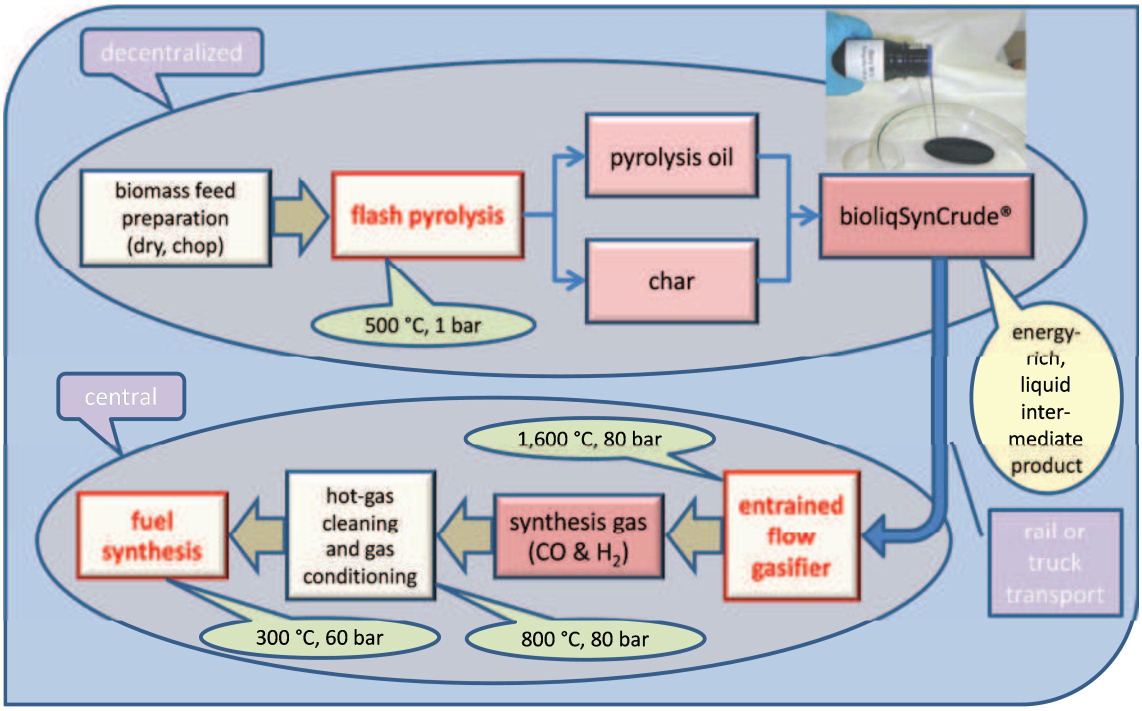

Figure 4: Schematic of the bioliq® process and photo of the bioliqSynCrude® [4]

In a second step, synthesis gas is generated from the biosyncrude in a pressurized entrained flow gasifier[24]. After thorough purification, the tar free synthesis gas can be used directly for a variety of well-known processes such as the Fischer-Tropsch reaction[25-27] or the synthesis of methanol and higher alcohols[28] and dimethyl ether (DME)[29], respectively, which themselves could serve as fuels or as educts of other organic chemicals. The last two steps are implemented in one central large scale plant. The process conditions define the composition of the bio-oils and -chars. This in turn influences the biosyncrude characteristics and the subsequent synthesis gas quality. However, relatively little is known about the primary products in the pyrolysis off-gas or the mechanisms of the thermal decomposition of the biomass feedstock. The latter is complicated by the fact, that preferably a large variety of different biomass should be applied, each of which exhibiting distinct chemical composition and thermal properties. Therefore, it is of interest to learn more about the intermediary gaseous products evolving directly from the pyrolyzed feedstock prior to condensation. For this a direct on-line analysis of the evolved organic species is required.

1.4 Analytical pyrolysis for structural elucidation of biomass

Analytical pyrolysis of biomasses and their basic components (hemi-)cellulose and lignin is an established method for the investigation of the respective structural compositions and is extensively described in literature[10, 30-59], including chemical, mechanistic and kinetic investigations. Due to its simple structure and the quantitatively highest portion in plants (43 – 46 % in wood[13]), cellulose was the first component investigated this way. However, it's still a matter of ongoing research due to the complex sequence of chemical and kinetic reactions during pyrolysis. In general, the pyrolytic decomposition of biomass is simplistically subdivided into primary and secondary reactions, where the volatile fragments generated in the first step react further on[13] (see Figure 5).

Thereby, the decomposition rates of the basic components are different. Cellulose is the thermally most stable one, but once the decomposition started, it reacts comparably fast to gaseous, mainly condensable products[13]. Hemicellulose on the other hand is composed of different polysaccharides, mainly built up of xylose, mannose, galactose, rhamnose and arabinose monomers. It is the chemically and thermally least stable biomass component, in contrast to lignin, which is a complex biopolymer based on phenol derivatives. There, the decomposition extends over a wide span of time[11]. A proposed structure of beech lignin[60] is shown in Figure 6.

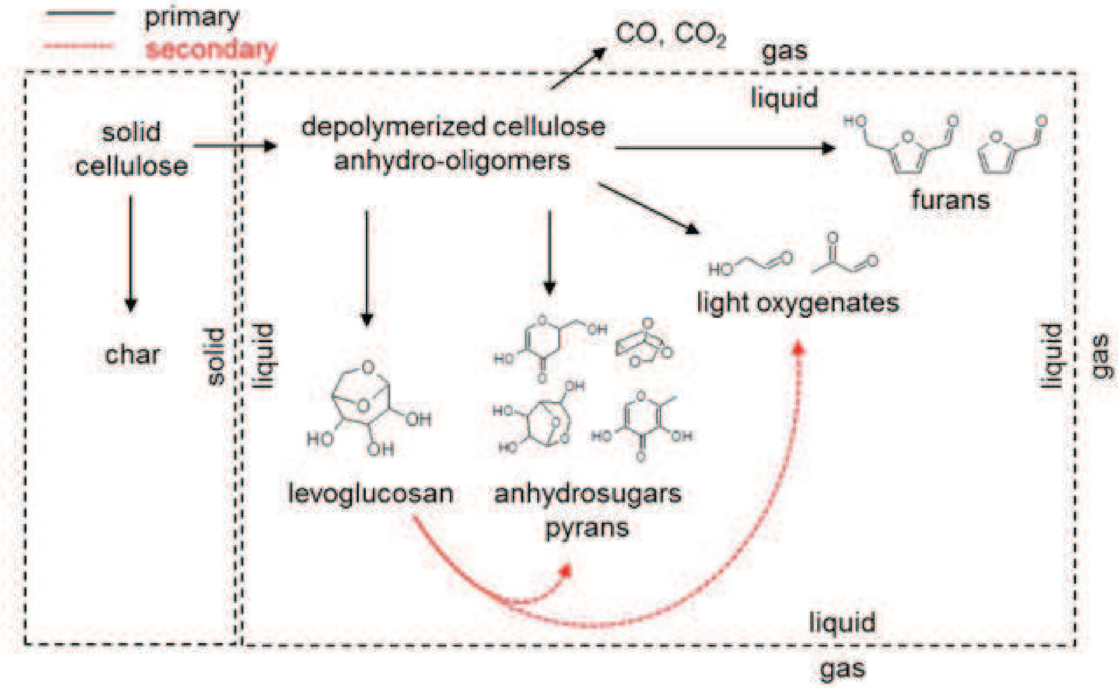

Figure 5: Primary and secondary pathways in cellulose pyrolysis[61], yielding furan derivatives and light oxygenates

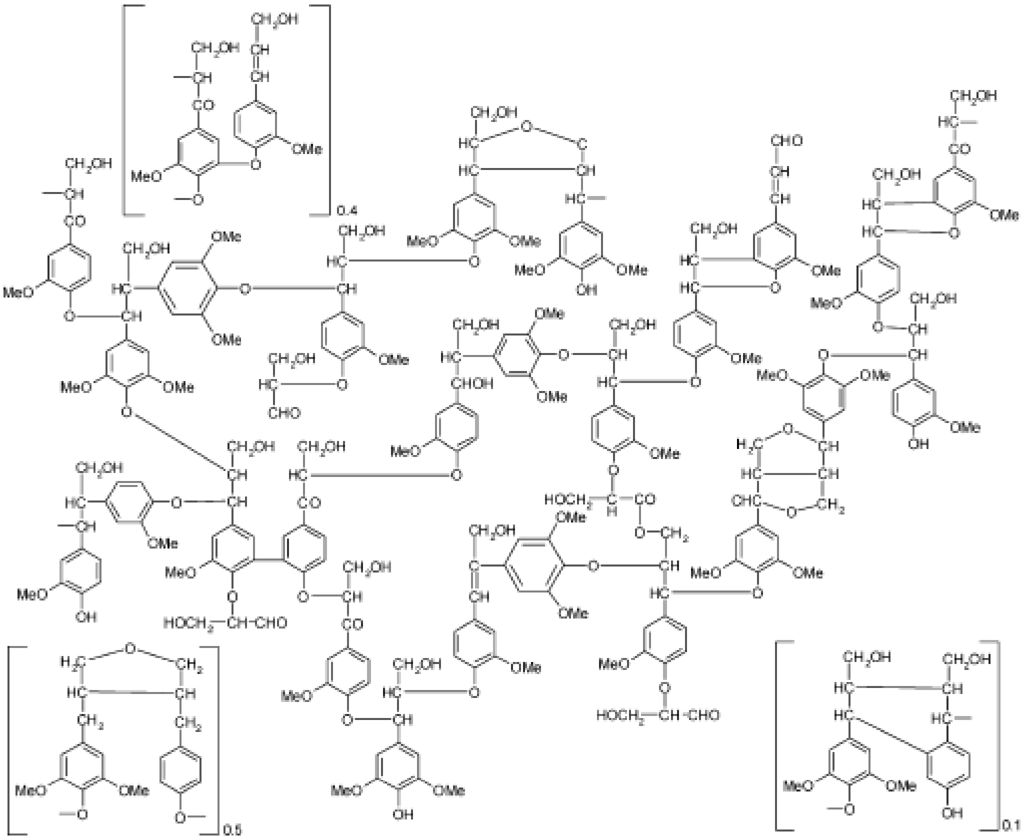

Figure 6: A proposed structure of beech lignin[60] with different phenolic substructures

Various techniques have been applied to reveal the structural information and decomposition rates of whole biomass as well as of the basic components. On the one hand, thermogravimetric analysis can be utilized[43, 62-75]; however, the evolved gas characteristics and kinetics strongly depend on the employed heating rates and on experimental conditions[76, 77] in general, and mostly differ from fast and flash pyrolysis, respectively. On the other hand, products arising at high heating rates have been investigated using fluidized bed systems[78-80], and mainly by applying analytical (Curie-point) pyrolysis-gas chromatography / mass spectrometry with electron ionization (Py-GC/MS). Additionally, off-line methods, e.g. GC/MS characterization of biomass-based pyrolysis oils[81, 82], or off-line pyrolysis-gas chromatography with flame ionization detection (Py-GC/FID)[38] have been applied. An overview of mass spectrometric investigations of lignins, including soft ionization techniques, is given by Reale et al.[51].

However, predictions about expected product spectra at thermochemical biomass decompositions are still far from being reliable despite all efforts. This has two main reasons: First, the high reactivity of the volatile, condensable products; second, the low thermal conductivity of biomass, hampering an isothermal pyrolysis[13]. Thus, an on-line and real-time analysis of pyrolysis gases prior to condensation is of great importance.

Anymore, even if similar analytical methods have been applied already, no reports about direct on-line measurements in a technical scale and with such a variety of biomass feeds could be found in literature. Moreover, it should be noted that pyrolytic lignins differ considerably from milled wood lignins[13] (MWLs), which are often used in analytical pyrolysis. Nonetheless, analytical pyrolysis has proven to be an useful technique for structural elucidation, in particular for lignin; that predominantly consists of three monomers, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which again are structurally based on hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties[83]. Aryl-ether bonds (especially the β-O-4) are the most frequent bond types[13]. Based on these works[33-38, 40-42, 48-51, 54-57, 81, 82, 84-89] as well as on own laboratory Py-GC/MS measurements (2.5), the assignment of the mass spectrometric peaks obtained at the biomass pyrolysis gas measurements has been carried out. The most important pyrolysis products (with IPs below 9.81 eV) are listed in the annex. With the analytical techniques applied here (see next chapter), derivatives of the respective lignin based groups can be identified and classified, as shown below (2.3).

1.5 Photo ionization time-of-flight mass spectrometry

Among the various techniques in mass spectrometry, time-of-flight mass spectrometry (TOF-MS) enables a very fast and highly sensitive detection of molecules, allowing the investigation of pyrolysis dynamics. In this context, the ionization method is a crucial point. The customarily employed electron ionization (EI) would lead to fragmentation of the molecules and make an interpretation of the resulting mass spectra nearly impossible in this complex mixture investigated here. In contrast, soft photo ionization leads to nearly fragment-free mass spectra, depicting only molecular ions. As a result, this allows the direct analysis of the whole width of organic compounds arising in the biomass pyrolysis process. Moreover, the matrix gas nitrogen and other highly concentrated small molecules are suppressed. On the one hand, single photon ionization (SPI) is a “universal” ionization technique, since all compounds are ionized whose ionization energies or potentials (IPs) are below the energy of the applied VUV photon. Thereby, ionization is carried out directly in one step, as schematized in Figure 7 (left side).

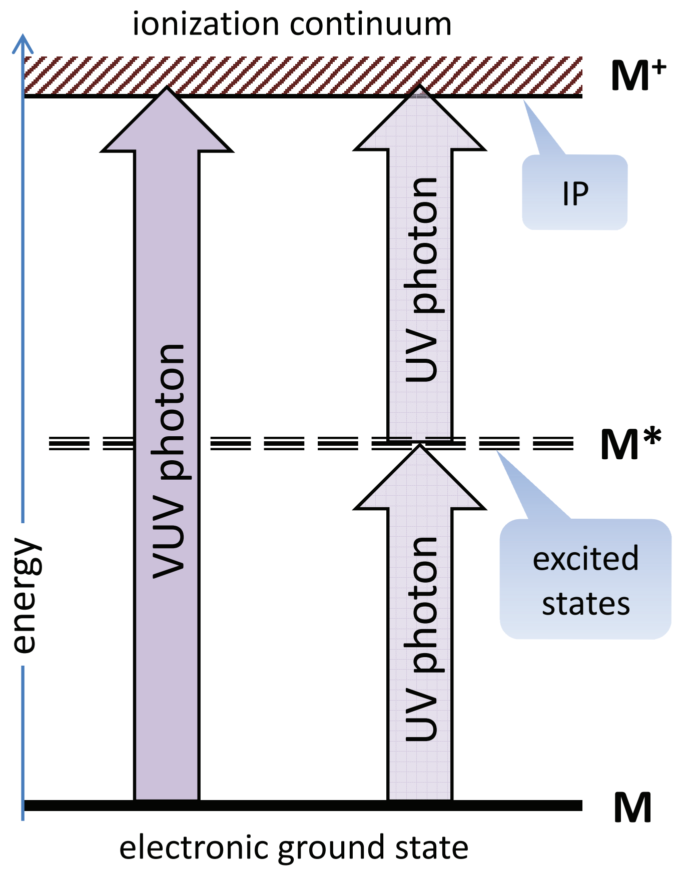

Figure 7: Scheme of the SPI (left) and the REMPI ionization mechanism

On the other hand, resonance enhanced multi-photon ionization (REMPI)[90-95] with laser generated pulsed UV-photons enables a selective and very sensitive detection. REMPI utilizes a two photon absorption[96], whereby the one photon energy is in resonance with an excited electronic state, from which the absorption of the second photon can lead to ionization, if the combined energy of the two photons matches the ionization potential of the molecule. The applied wavelength strongly influences the ionizability of the investigated molecules; in the 240 – 270 nm UV-range, for example, this scheme is selective for (poly)aromatic compounds. Here, a Nd-YAG-Laser (BIG SKY ULTRA, Quantel, Les Ulis Cedex, France) with two frequency doubling units at 266 nm, 10 ns pulse width and 10 Hz repetition rate with a power density of approximately 7 x 10^6 W/cm² was employed. Despite this wavelength being highly selective for aromatic compounds one has to take into account that the ionization cross sections of the compounds may differ widely.

VUV photons for SPI can be produced in different ways, using:

- Synchrotron radiation (very broad usable spectrum, but stationary)
- The 3rd harmonic (118 nm) of a 355 nm laser[97-101]
- Commercial VUV photoionization sources, either with a 10.6 eV Kr discharge lamp[102], or with a deuterium lamp, yielding a narrow intense Lyman-α atomic line at 121.567 nm as well as a weak broadband continuum of Werner and Lyman molecular bands at around 130 and 160 nm, respectively[103]
- The Lyman-α emission of atomic hydrogen (121.6 nm) in He or Ne – H_2 mixtures via dielectric-barrier discharge[104-106] (DBD) excited by radio frequency, or via microwave discharge[107], or by ionizing particle beams[108]
- VUV excimer light sources, based upon radiative decay of rare gas excimers generated by DBD lamps[109] or electron-beam pumping (see below)

Here, SPI with a continuous beam of VUV photons is achieved using an electron-beam pumped excimer light source (EBEL)[110-116]. Thereby, energetic electrons excite and ionize the rare gas atoms. In successive processes, excited diatomic rare gas molecules (excimers) are formed in three-body collisions involving a metastable rare gas atom and two ground-state atoms[117]. As a result of the high gas pressure, the excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The emitted VUV light (the so-called second excimer continuum[112, 118]) is first collimated and then focused on the effusive gas inlet using two MgF_2 lenses. The rare gas volume was filled with argon (6.0, 2 bar abs.) and purified continuously using a heated gas getter, yielding an emission maximum at 126 nm (9.8 eV center photon energy available for ionization). In principle it is possible to vary the ionization energy (between 121.6 and 147 nm) by replacing the argon filling with other rare gases or rare gas mixtures[98], thus enhancing the selectivity of VUV ionization, and allowing to keep the ionization energy below the appearance energy of fragments. In any case, this allows an almost fragmentation-free ionization of the majority of organic compounds. The basic structure of EBEL consists of a 0.7 × 0.7 mm^2 ceramic silicon nitride (SiNx) foil of only 300 nm thickness that separates the rare gas volume ($p > 1$ bar) from a vacuum chamber containing an electron gun. The latter generates a 12 keV electron beam which is directed into the rare gas through the SiNx foil with low-energy loss. The EBEL schematic is depicted in several publications[110, 113, 119].

In this connection, an orthogonal acceleration TOF-MS is particularly suited for the use of continuous light sources such as the EBEL due to the special type of construction with pulsed (around 70,000 Hz) orthogonal extractor plates, as illustrated in Figure 8 and a series of papers[110, 119, 120].

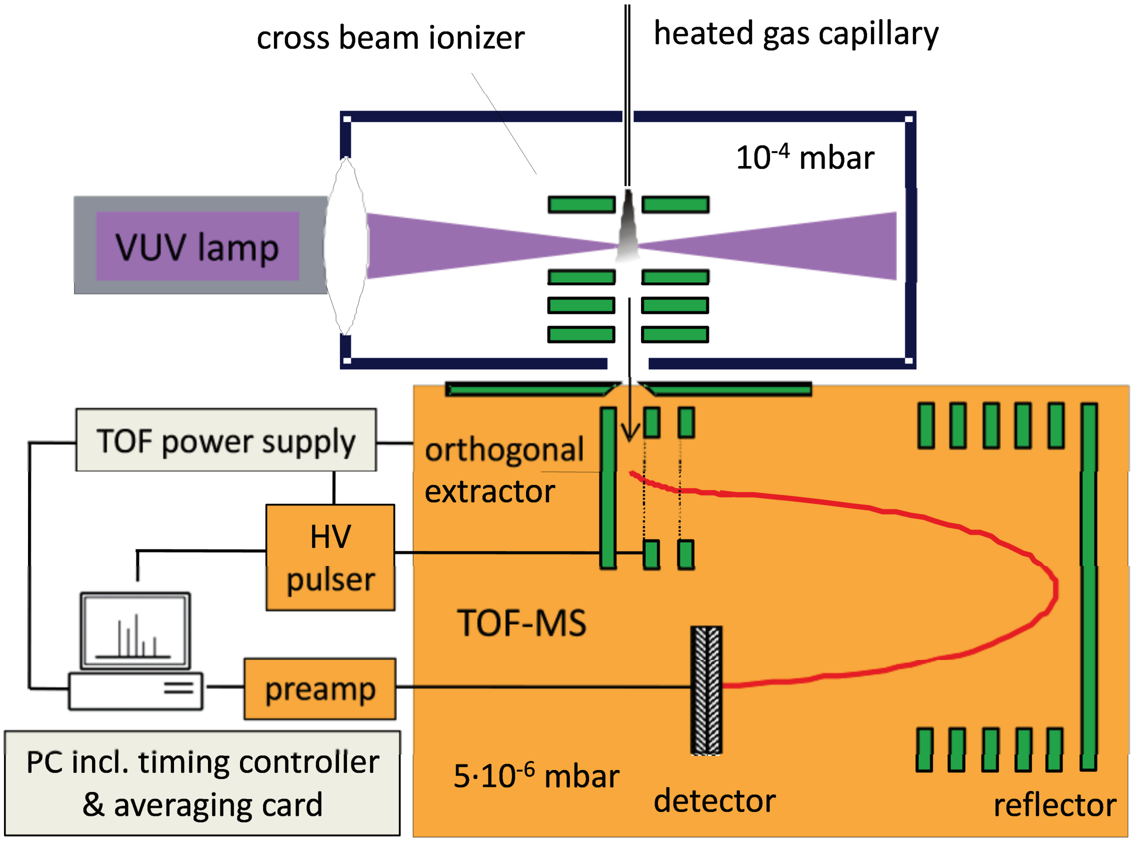

Figure 8: Scheme of the orthogonal acceleration TOF-MS in combination with the EBEL VUV light source

2

Objectives and Conception of this Work

With respect to a great variety of biomass feeds and, on a limited scale, for process variations operated in a technical flash pyrolysis plant at the KIT, the employed analytical technique should have the ability to point out the different flash pyrolysis gas characteristics, and to contribute to the optimization of the bioliq® process with a view to the biosyncrude consistency and quality, respectively. For this, time-of-flight mass spectrometry using soft photo ionization methods as outlined above is applied for real-time investigation of organic intermediates, allowing the direct and on-line monitoring of the pyrolysis gases. Ionization is carried out by single photon ionization (SPI) as well as by resonance enhanced multi-photon ionization (REMPI). Both techniques have been applied to investigate pyrolysis and other thermal processes before, for instance for pyrolysis of tobacco, oils and polymers[121, 122], as well as coffee roasting[96, 123] and waste incineration plants[124-127]. However, differing pyrolysis and product gas characteristics are expected for the here employed biomass feedstock. Hence, the first measurements have been carried out using an established mobile REMPI- & SPI-TOF-MS. Furthermore, a compact mobile mass spectrometer specifically designed for use in field measurement campaigns was built up and tested in combination with the newly developed EBEL-VUV light source. Moreover, an optimized new high temperature inlet was constructed and implemented. The mass spectrometers were adapted to the heated sampling train of the pyrolysis plant. The results are interpreted with regard to the specific pyrolysis gas characteristics of the respective biomass feeds and process variations, in particular using multivariate data analysis. For the assignment of the mass spectrometric peaks, own laboratory Py-GC/MS measurements have been conducted. For comparison with the technical plant and a better understanding of pyrolysis processes, laboratory experiments have been conducted, in addition, namely thermogravimetric analysis and laboratory oven pyrolysis.

2.1 Setup of the mobile REMPI- & SPI-TOF-MS

Due to the different nature of the ionizing photons and their generation, i.e. short laser pulses for REMPI and a continuous VUV beam for SPI, two different time-of-flight mass spectrometers (TOF-MS) have been applied for the detection of the molecular ions. For the REMPI and the first SPI-MS measurements, a mass spectrometer (Reflectron CTF10, Kaesdorf, Munich) was employed that has been proved and tested in comparable measuring campaigns; for use of SPI, the EBEL VUV light source and an accessory HV pulser for the extractor plates had to be mounted, as depicted in Figure 9 (with a previous EBEL model).

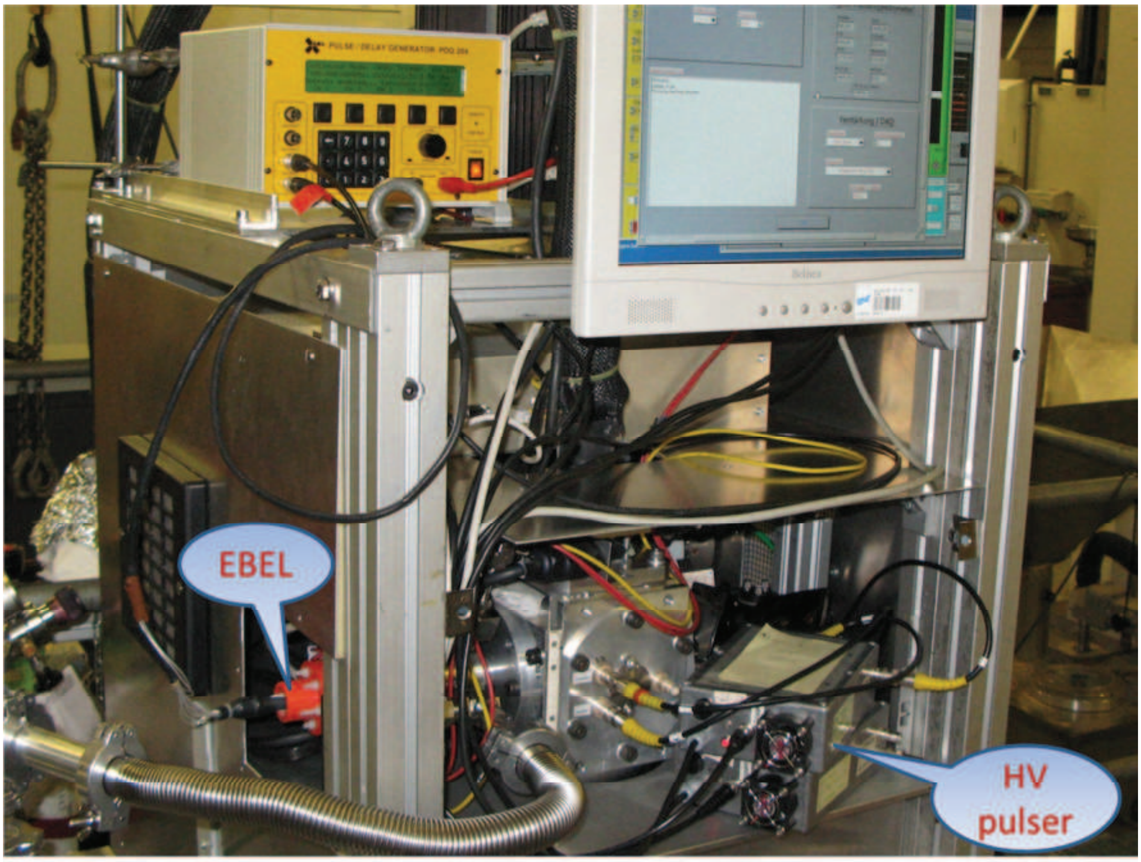

Figure 9: Setup of the mobile REMPI- & SPI-TOF-MS with mounted VUV light source EBEL

Starting from the second measurement campaign, the SPI-MS measurements were achieved with a mobile orthogonal acceleration TOF-MS (C-TOF, TOFWERK AG, Thun, Switzerland), as depicted in the lower right part of Figure 10 (see also Figure 13). During the course of the three measurement campaigns, the mass spectrometric systems were continuously optimized. In the third campaign, where only SPI measurements have been performed, a newly developed EBEL version (see Figure 10, left side) was employed, leading to improved sensitivity. Thereby, improved performance and higher stability and durability than earlier models as well as easy adaptability to different kinds of focusing systems have been achieved. Based on the established concept of the EBEL and hitherto existing operational experience, this model has been developed and constructed anew using 3D-CAD software, but also commercially available vacuum components have been employed where possible.

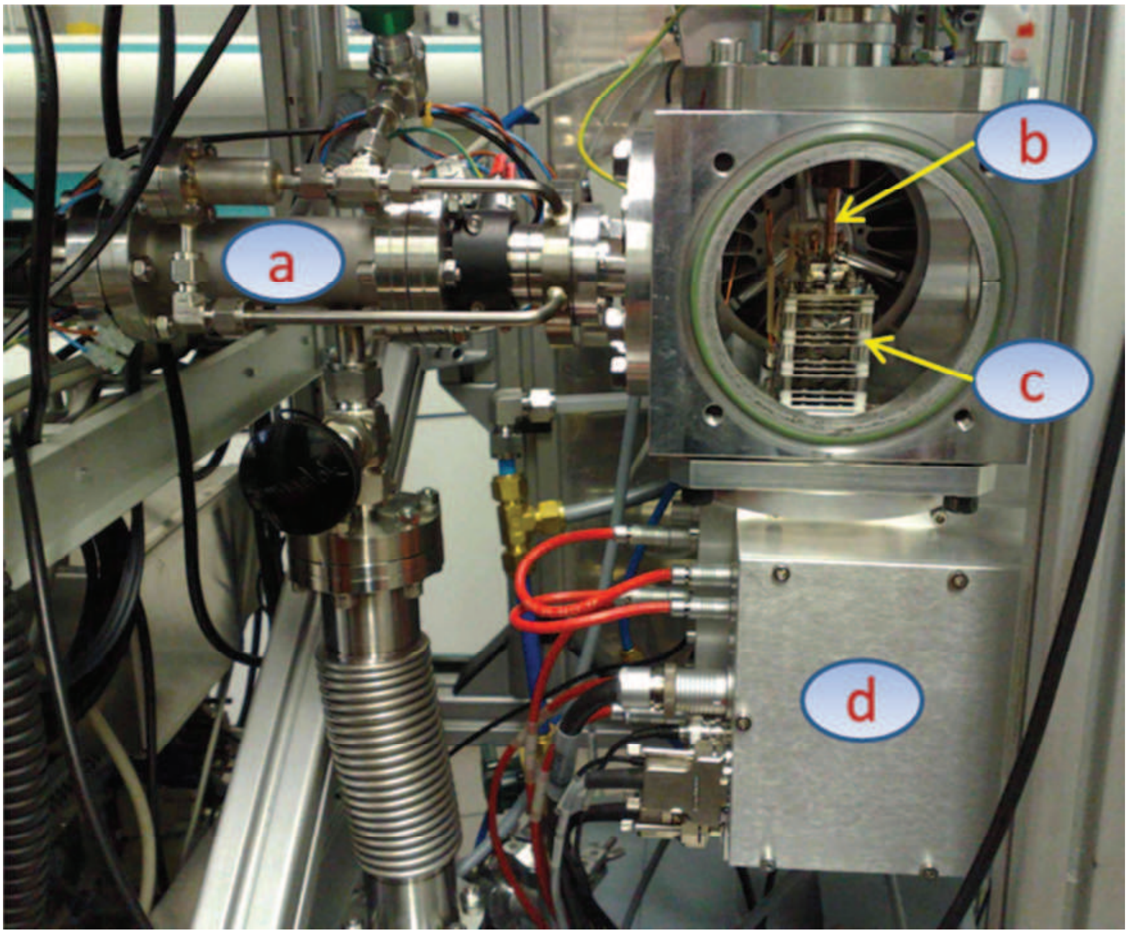

Figure 10: Photo of the SPI-TOF-MS with the newly developed EBEL VUV light source (a), the high temperature inlet (b), and the electrostatic lenses (c) as part of the orthogonal acceleration TOF-MS (d)

The pyrolysis gases are sampled directly by a capillary that runs in a heated hose (300 °C) and serves as a restriction between the atmospheric pressure conditions and the vacuum of the mass spectrometer. The ionizing photons hit the pyrolysis gases immediately underneath the inlet needle, where an effusive molecular beam is formed. In this context, an optimized new high temperature inlet was constructed and implemented, as apparent in the upper part of the ionization source. There, the generated ions are accelerated into the TOF-MS via electrostatic lenses.

2.2 On-line pyrolysis gas measurements

Experiments have been accomplished at the technical flash pyrolysis plant at KIT North Campus with a throughput of 10 kg per hour, which consists of a twin screw mixer (Lurgi-Ruhrgas) and a two-stage biomass feeding. Thereby, chopped biomass is filled in a storing tank, then funneled in a nitrogen purged reservoir and conveyed to the reactor by a screw. Hot steel balls are supplied as heat exchanger; in addition, metal doped alumina balls have been tested, too. The pyrolysis products arise via suction and are cooled in several stages, yielding char mainly in the first stage and pyrolysis oil in the following. The steel balls are led back from the end of the mixer to the reactor via a heat exchanger.

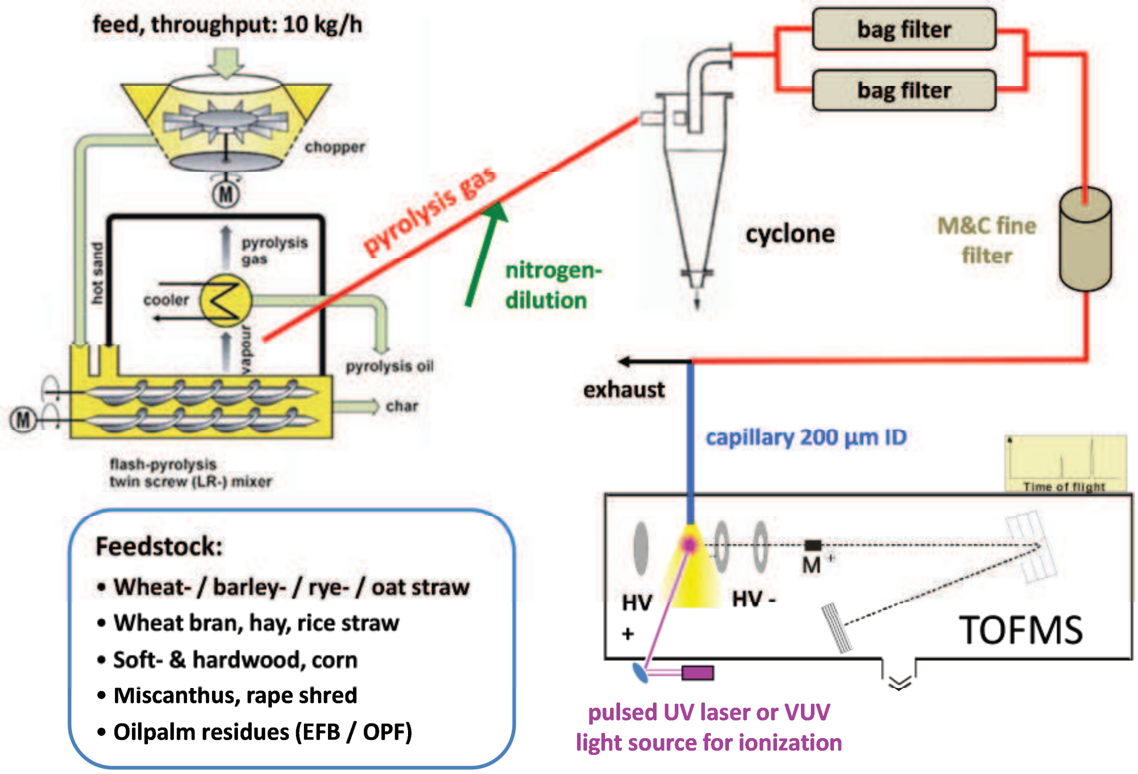

Figure 11: Scheme of the on-line pyrolysis gas measurements with a photo ionization TOF-MS coupled to the heated sampling train at the pyrolysis plant

For the online analysis of the primary organic biomass pyrolysis products at the technical pilot plant, a heated sampling train had been conceived and developed at the KIT. Thereby, the main challenge is the fact that the pyrolysis gas is very rich in both coarse and fine particles. These particles must be removed from the gas stream to prevent clogging of the last component of the sampling train, a deactivated quartz capillary with an inner diameter of 200 µm. For this purpose, a series of particle filter devices has been mounted. The sampling train begins directly at the exhaust of the pyrolysis reactor. The pyrolysis gas is immediately diluted by nitrogen as carrier gas. This is followed by a cyclone for removing the coarse particles. After the cyclone, the sampling path is divided in two parallel lines, each containing a bag filter. If one of the filters is saturated, the gas stream could be switched to the parallel line thus allowing the continuation of the sampling process. At last there are two fine particle filters in line. Finally, the sampled gases reach the afore mentioned capillary, that runs in a heating hose to the ion source of the respective mass spectrometric system. The scheme of the on-line pyrolysis gas measurements is depicted in Figure 11.

In Figure 12, the coupling of the mass spectrometers to the flash pyrolysis plant at the KIT is shown. On the upper right side, the mobile SPI-MS instrument can be seen, hiding the REMPI-MS in the background (for this, see Figure 23).

Figure 12: Overall view of the coupling of both mobile mass spectrometers to the technical flash pyrolysis plant at the KIT[128]

The coupling to the sampling train (see Figure 13), which is heated to not less than 300 °C throughout the entire line, is achieved by heated Swagelok tubings and fittings. To maintain a constant pyrolysis gas flow passing by at the capillary, a laboratory pump with 5 l/min flow rate is used.

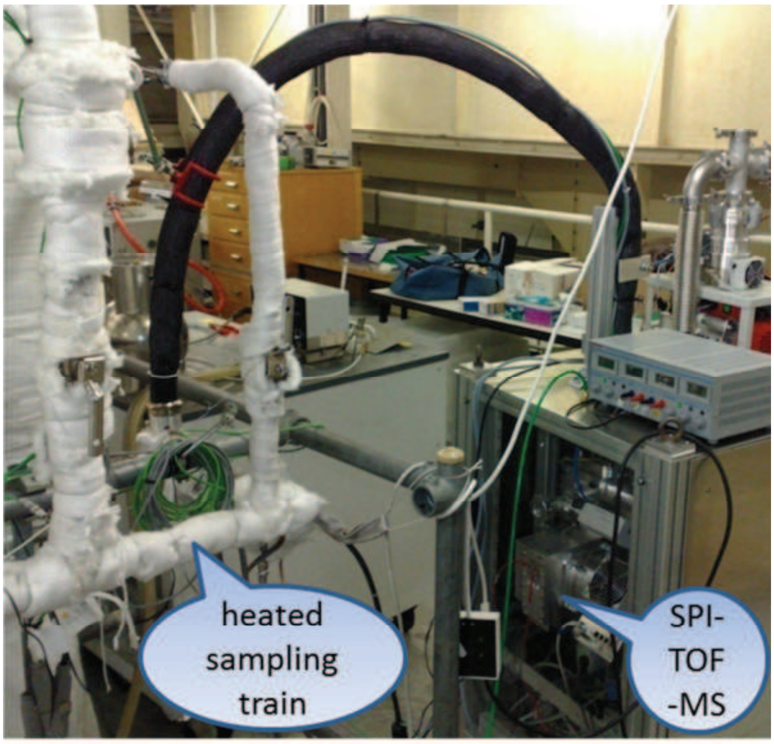

Figure 13: Coupling of the SPI-TOF-MS to the heated sampling train

A large variety of biomass feedstock has been investigated with the described experimental setup, comprising several kinds of straw and corn, soft- and hardwood, hay, wheat bran, rice straw (from Egypt), rape extraction residue (RES), oil palm residues (EFB & OPF) and Miscanthus. Straw (from wheat, barley, rye and oat), hay, wood, RES and bran were from the surrounding area of Karlsruhe, corn cobs and corn stover from South Africa. All samples are chopped and in a range of sizes between 1 and 3 mm. By default, a pyrolysis temperature of 500 °C was applied. As process variations, temperatures have been changed to 450 and 550 °C. Furthermore, other heat exchanger material has been employed, consisting of doped alumina. By closing and re-opening the valve to the reactor, a residence time of around 140 s in the sampling train could be determined, which is in good agreement with the theoretically estimated value of 128 s. Furthermore, the course of pyrolysis gas measurements is depicted in Publication 1 for five different biomass feeds in succession. The selected nominal masses represent major pyrolysis products and demonstrate the varied signal intensity ratios in the mass spectra.

2.3 Data analysis & Overview of results

First of all, the mass spectra obtained by the on-line pyrolysis gas measurements had to be interrelated with the pyrolytic products of the technical flash pyrolysis pilot plant. However, the applied analytical techniques implicate that the mass peaks cannot be clearly assigned to certain compounds. For this reason, literature studies (see also 1.4) as well as own Py-GC/MS measurements (see 2.5) have been conducted. Furthermore, the selectivity of REMPI provided additional information for the mass assignment. The measurements revealed a series of typical pyrolysis products described in literature. In Figure 14, the mass spectra of both ionization techniques are compared at the example of wheat straw. In case of REMPI, exclusively phenol derivatives can be seen. With SPI, ketones, aldehydes and furan derivatives from (hemi-)cellulose decomposition emerge, in addition.

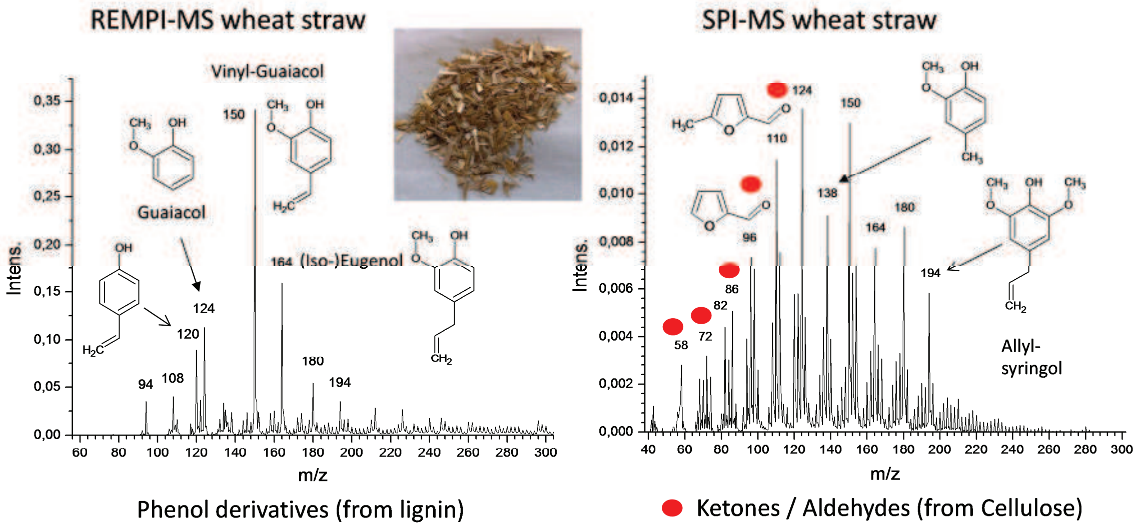

Figure 14: REMPI- and SPI-MS spectra of wheat straw revealing phenol derivatives from lignin and ketones and aldehydes from cellulose in case of SPI-MS

For comparison, process GC data provided by the KIT of wheat straw and the transition of hardwood to softwood (indicated by a red line) are shown in Table 1. Even though the data provide important information about the content of small gas molecules (which are not ionized with the soft ionization techniques), it is obvious that they are not a sufficient data basis for the differentiation of the biomass feeds.

Table 1: Process GC data of wheat straw and the transition of hardwood to softwood

19.11.2007		Educt:	wheat straw									
Neon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	CO [%]	Methane [%]	CO_2 [%]	Ethylene [%]	Ethane [%]	Propane [%]	C4's [%]	C5+ [%]	Time
0,84	1,51	0,64	39,74	18,66	4,07	32,04	0,23	0,64	0,46	0,37	0,81	12:20
1,04	1,82	0,27	30,94	20,50	4,88	37,47	0,27	0,77	0,56	0,45	1,03	12:40
0,84	1,25	5,13	42,09	16,29	3,77	28,13	0,20	0,61	0,42	0,34	0,94	13:02
1,01	1,72	0,30	30,40	20,49	4,88	38,09	0,27	0,77	0,56	0,46	1,05	13:21
1,13	1,97	0,23	30,08	20,20	5,53	37,51	0,29	0,87	0,62	0,47	1,11	13:39
0,69	1,10	6,94	43,51	15,54	3,21	26,71	0,17	0,51	0,35	0,31	0,94	14:08
1,08	1,76	0,21	29,34	20,54	4,94	39,02	0,26	0,76	0,55	0,39	1,15	14:31
0,82	1,44	0,34	39,93	18,02	4,07	32,63	0,20	0,63	0,44	0,35	1,12	14:50
0,88	1,33	0,33	36,81	18,67	4,25	34,79	0,21	0,68	0,47	0,38	1,20	15:16
0,93	1,58	0,22	34,24	19,18	4,45	36,31	0,23	0,72	0,50	0,39	1,25	15:35
0,93	1,55	1,46	35,71	18,81	4,40	34,27	0,23	0,70	0,49	0,39	1,06	Mean
22.11.2007		Educt:	hard- and softwood									
Neon [%]	Hydrogen [%]	Oxygen [%]	Nitrogen [%]	CO [%]	Methane [%]	CO_2 [%]	Ethylene [%]	Ethane [%]	Propane [%]	C4's [%]	C5+ [%]	Time
0,53	1,61	1,36	40,49	20,80	3,20	30,55	0,20	0,30	0,26	0,17	0,52	9:53
0,60	1,41	0,00	35,62	24,00	4,04	32,62	0,26	0,37	0,31	0,15	0,61	10:10
0,60	1,63	0,56	35,99	24,08	4,04	31,26	0,27	0,37	0,31	0,14	0,75	11:14
0,73	1,73	0,40	26,08	28,74	4,96	35,16	0,34	0,45	0,40	0,17	0,82	11:32
0,56	1,56	0,56	40,31	21,97	3,77	29,55	0,26	0,34	0,30	0,04	0,78	11:51
0,50	1,45	0,94	53,20	17,20	3,04	22,25	0,20	0,26	0,24	0,00	0,73	12:08
0,53	1,19	1,47	57,12	16,12	2,84	19,36	0,19	0,23	0,22	0,09	0,63	12:28
0,55	1,58	1,27	57,54	16,01	2,92	18,79	0,19	0,24	0,23	0,10	0,59	12:49
0,67	1,85	1,08	50,38	19,58	3,60	21,31	0,24	0,29	0,29	0,12	0,60	13:09
0,85	2,25	0,68	40,97	25,01	4,61	23,84	0,31	0,37	0,37	0,15	0,60	13:35
0,61	1,63	0,83	43,77	21,35	3,70	26,47	0,25	0,32	0,29	0,11	0,66	Mean

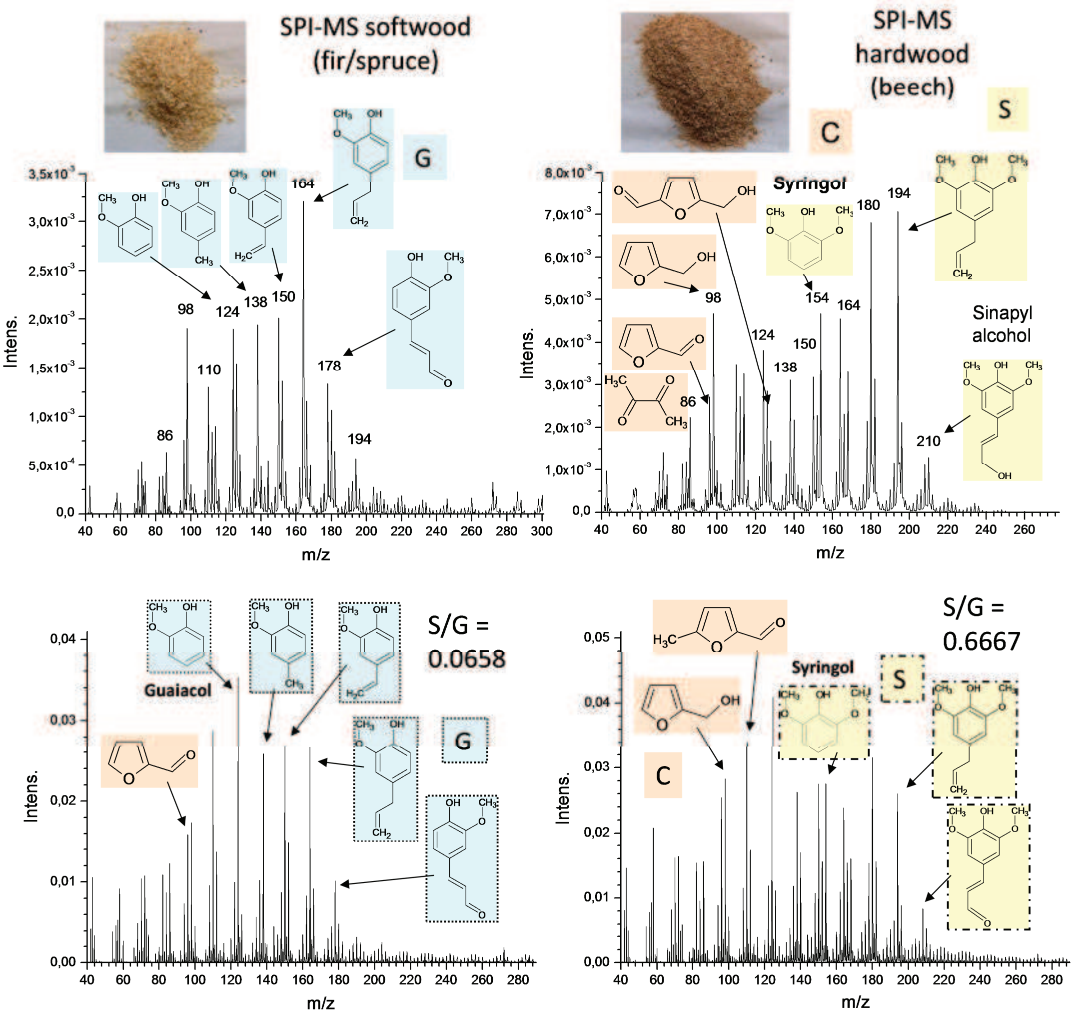

Figure 15: SPI mass spectra of soft- and hardwood obtained at the 1st (at the top) and the 3rd campaign by comparison

In Figure 15, the SPI mass spectra of soft-and hardwood pyrolysis gases obtained at the 1st and the 3rd measurement campaign are compared. Even though the intensity ratios are slightly differing, it becomes apparent that the mass spectrometric patterns are highly similar for the same feed, but significantly varying for a different biomass. The compounds have been arranged in groups for a first characterization[129], according to the biopolymer they are originating from. The “C” group (cellulose decomposition products) comprises ketones, aldehydes and furan derivatives. Lignin is subdivided into three groups (q.v. 1.4): “H” (hydroxybenzene derivatives), “G” (guaiacol based) and “S” (syringol derivatives). In literature, the S to G ratio is described[38, 54, 56, 57], particularly for the differentiation of soft- and hardwood, owing to the different lignin structure of the two kinds of wood. Here, the ratios have been calculated to S/G = 0.0658 and 0.6667, respectively. At hardwood pyrolysis, around ten times more syringol derivatives arise compared to softwood.

REMPI- and SPI-MS spectra of the energy crop Miscanthus are shown in Figure 16. Strikingly, 4-vinylphenol (*m/z* = 120), belonging to the “H”-group shows the highest signal intensity here. Furthermore, the ratio of the H group is calculated to be 10.2 % relating to the sum of all mass peaks, the total ion signal (TIS); for G and S it is 16.4 % and 5.8 %, respectively. The S/G value of 0.3565 lies in between soft- and hardwood.

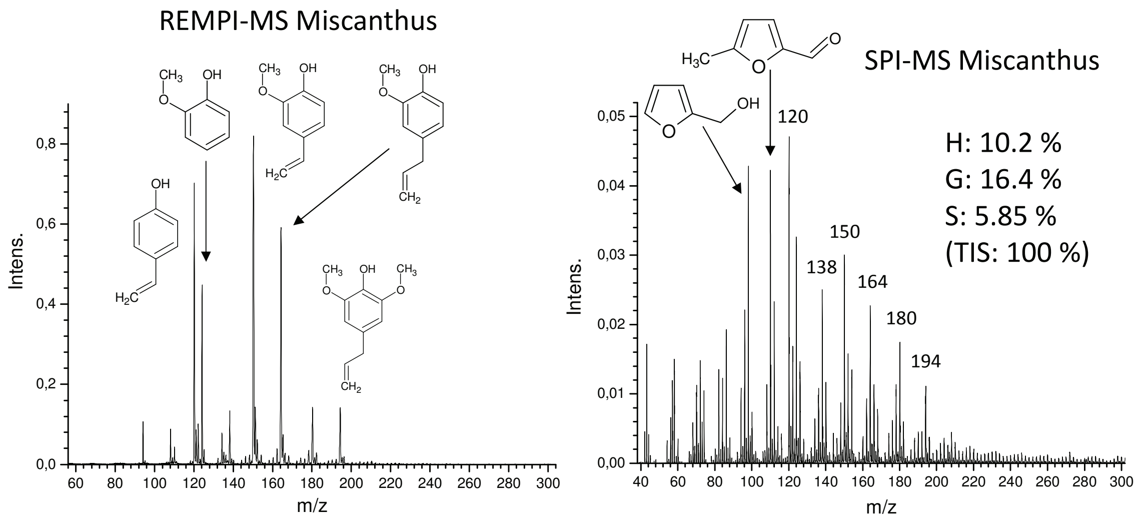

Figure 16: REMPI- and SPI-MS spectra of the energy crop Miscanthus

In the spectrum of corn cobs (Figure 17), *m/z* = 120 is the highest peak, too, pointing out a similar biomass structure (both belong to the Poaceae family). Aside, the SPI-MS spectrum of empty fruit bunches (EFB) is shown. There, a characteristic peak at *m/z* = 94 (phenol) is standing out. EFB is one of the solid wastes that are rapidly increasing in the palm oil industry[130].

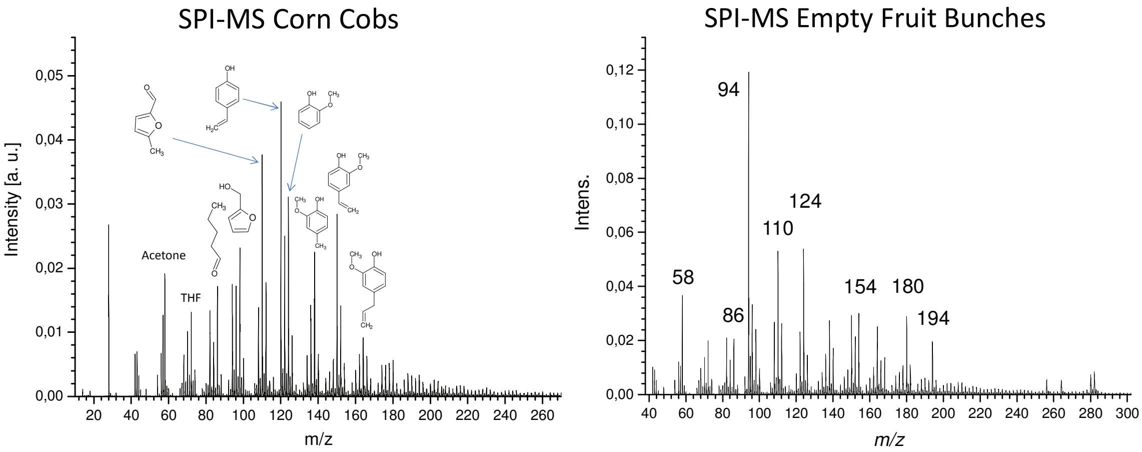

Figure 17: SPI-MS spectra of corn cobs and empty fruit bunches (EFB), showing distinct mass spectrometric patterns

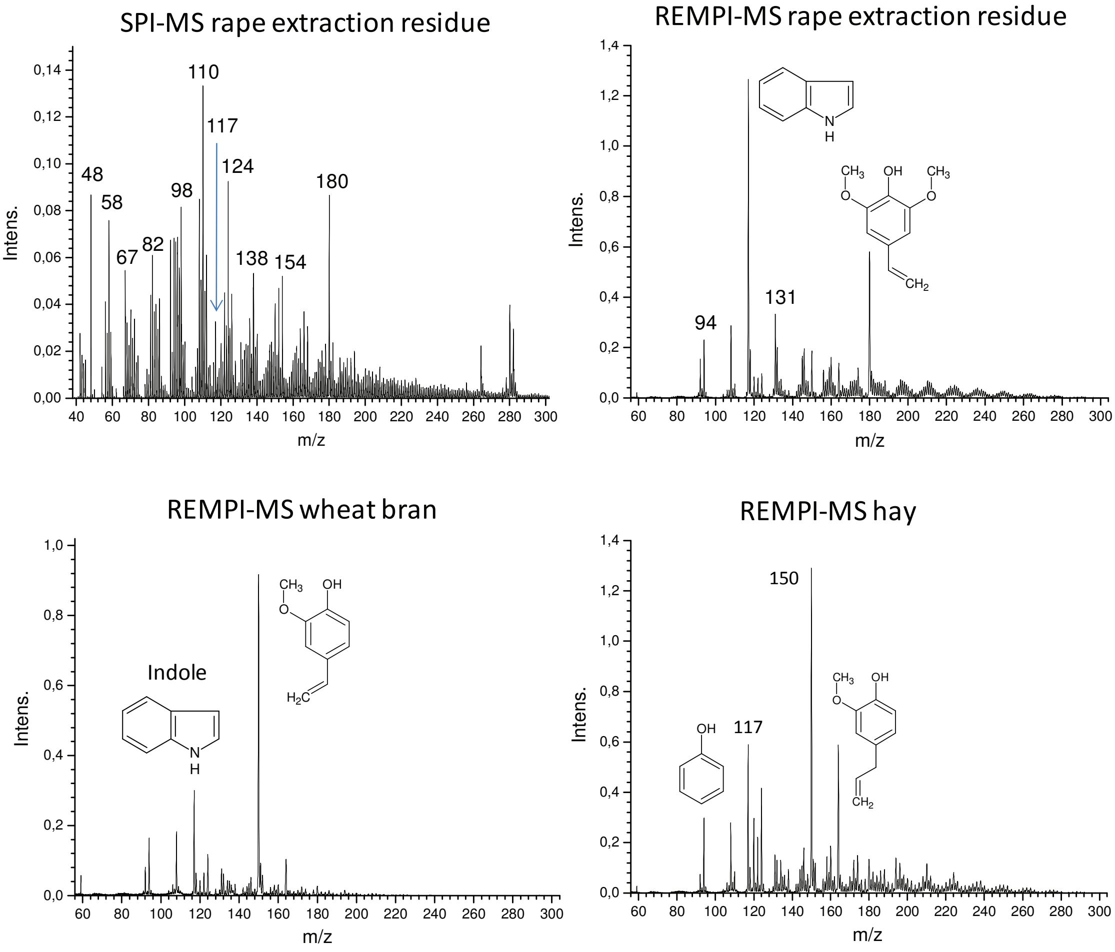

Figure 18: MS spectra of rape extraction residue, wheat bran and hay, revealing additional nitrogen containing compounds

In Figure 18 (upper part), the SPI- and REMPI spectra of rape extraction residue (RES) are depicted. In the former, a completely different and highly complex pattern arises, including a series of additional substances, most of which are nitrogen-containing, e.g. pyridinol[131] (*m/z* = 95), pyrrole (*m/z* = 67), indole[132] (*m/z* = 117), ethylamine (*m/z* = 45) and propylamine (*m/z* = 59), and others such as methanethiol[96, 100] that are formed by the decomposition of proteins[131, 133]. In the REMPI spectrum, indole is the highest peak owing to its high ionization cross-section, whereas most of the other (protein) decomposition products do not appear. In the REMPI mass spectra of wheat bran and hay (lower part) considerable indole peaks occur, too, indicating a certain amount of proteins there. In this connection, CHONS analysis of wheat bran chars (also from other biomass feeds) are listed by Kornmayer[11], showing a considerable nitrogen content, too. Furthermore, in both graphs the highest peak is observed for 4-vinylguaiacol (*m/z* = 150), but they are well distinguishable by the higher signal intensities of 4-vinylphenol, guaiacol and (iso-)eugenol in case of hay.

Anyway, even though the mass spectra show significant patterns for the different biomass feedstocks, a mathematical description is necessary. For this, Principal Component Analysis (PCA) as well as Cluster Analysis have been carried out (see following chapter).

2.4 PCA & Cluster analysis

The SPI mass spectra obtained at the third measuring campaign have been evaluated statistically by applying multivariate data analysis. The underlying data have been averaged over at least 15 minutes and range normalized before applying Principal Component Analysis (PCA) and Cluster Analysis (k-means algorithm, distance type (absolute) correlation), using the program The Unscrambler (CAMO Software AS, Oslo, Norway). In the underlying data matrix, the different biomasses and process conditions are listed in the rows. In the first columns, category variables are listed, enabling a differentiation by color (see Publication 1). The following columns contain the normalized signal intensities for the respective nominal masses (up to *m/z* = 400).

In the Scores plot (Figure 19), the distinguishability of the different biomass sorts becomes apparent. Furthermore, Cluster Analysis, as depicted with special symbols, precisely differentiates the ten biomass species irrespective of the heat exchanger material; therefore, it’s evident that the alternative heat exchanger leads only to marginal differences in the pyrolysis gas composition.

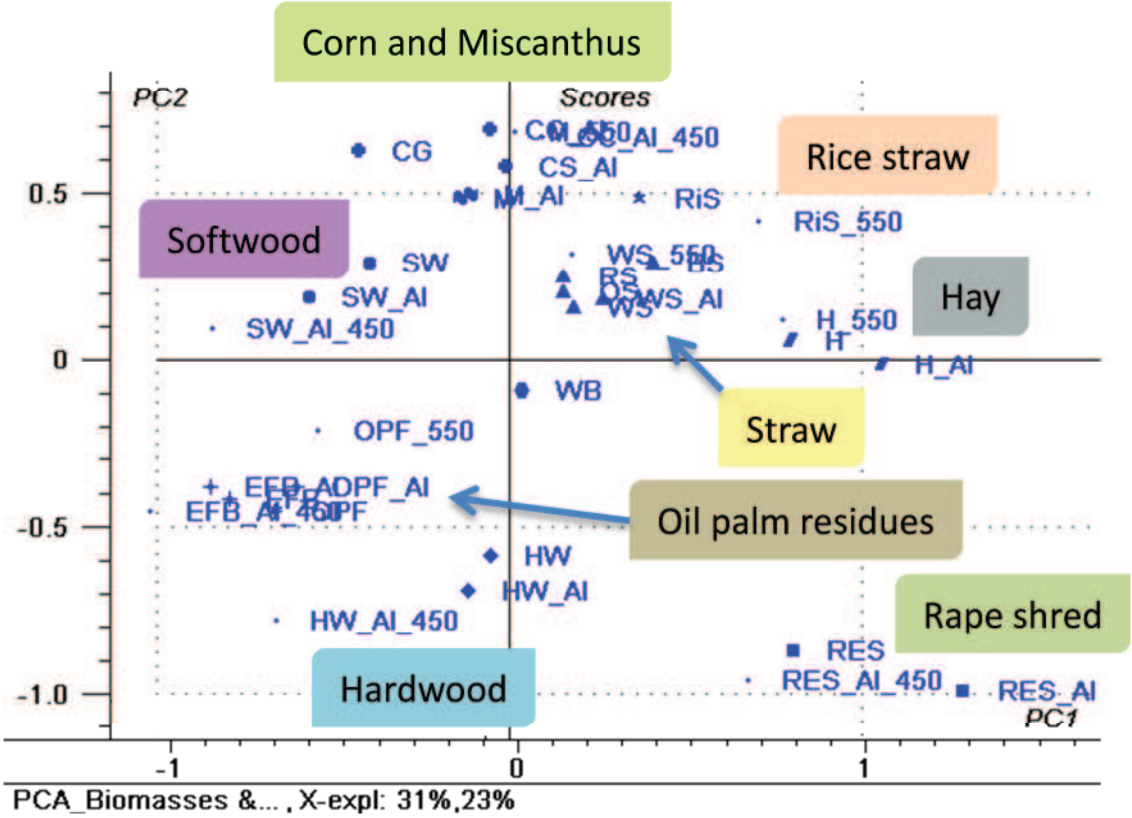

Figure 19: PCA Scores plot & Cluster analysis, illustrating the distinguishability of the different biomass species and the influence of process parameters

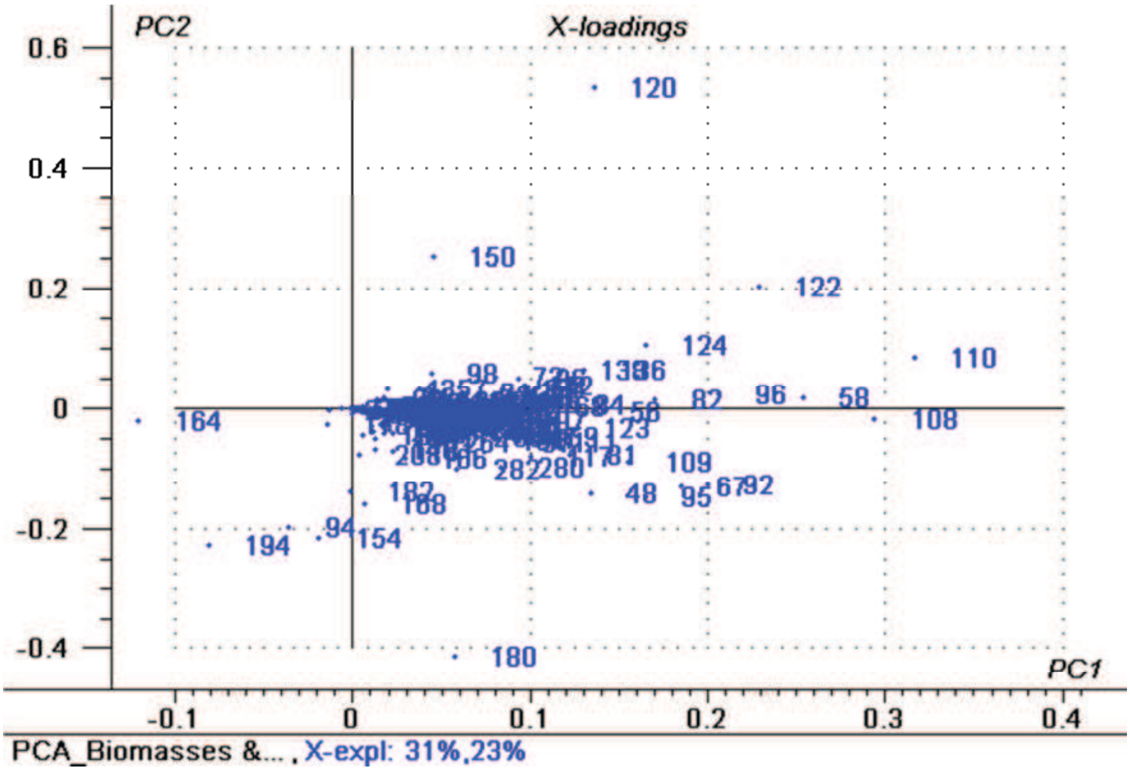

Figure 20: PCA Loadings plot, showing the nominal masses and their influence

The Loadings plot (Figure 20) shows the nominal masses and their influence on the calculation of the respective PC. The Loadings values represent the variance of the underlying compounds for the respective Principal Component and interrelate to the respective position in the Scores plot. Anymore, a ranking list of the biomass pyrolysis products was generated (see Table 2) by adding the absolute Loadings values of the Principal Components (of all biomasses and process conditions), weighted by their explained variances (see lines in the lower parts of the figures). In addition, the detectability of the listed products with REMPI at 266 nm wavelength is indicated, too.

Table 2: Ranking list of the biomass pyrolysis products with nominal masses and detectability with REMPI at 266 nm wavelength (+ moderate, ++ good, +++ very good)

Priority	Nominal mass	Biomass pyrolysis products	Ionization with REMPI@266 nm
1	120	4-Vinylphenol	++
2	94	Phenol	++
3	180	4-Vinylsyringol / Coniferyl alcohol / Guaiacylacetone	+++
4	194	Allylsyringol	++
5	124	Guaiacol	++
6	110	5-Methylfurfural / Catechol	- / +
7	164	(Iso-)Eugenol	+++
8	122	Xylenol / Ethylphenol / Methylanisole	++
9	150	4-Vinylguaiacol	+++
10	108	Methylphenol (Cresol) / Anisole	++
11	154	Syringol	
12	92	Toluene	++
13	95	Pyridinol	
14	138	4-Methylguaiacol	+
15	67	Pyrrole	
16	58	Acetone	
17	98	Dihydromethylfuranone / 2-Furanmethanol	
18	48	Methanethiol	
19	96	Furfural	
20	168	Methylsyringol	+

PCA has also been used to analyze the variability within the Poaceae family, which implies hay, Miscanthus and all kinds of straw and corn (see Publication 1). Moreover, the influence of the sampling train has been investigated, too. For that purpose, the measurement results of wheat straw (Figure 21) and hardwood have been apportioned into ten equal parts of two and three minutes, respectively. It’s obvious from the top right Scores plot that the variations within the course of the wheat straw measurement (clearly in the main window) are very small in comparison with the other kinds of straw.

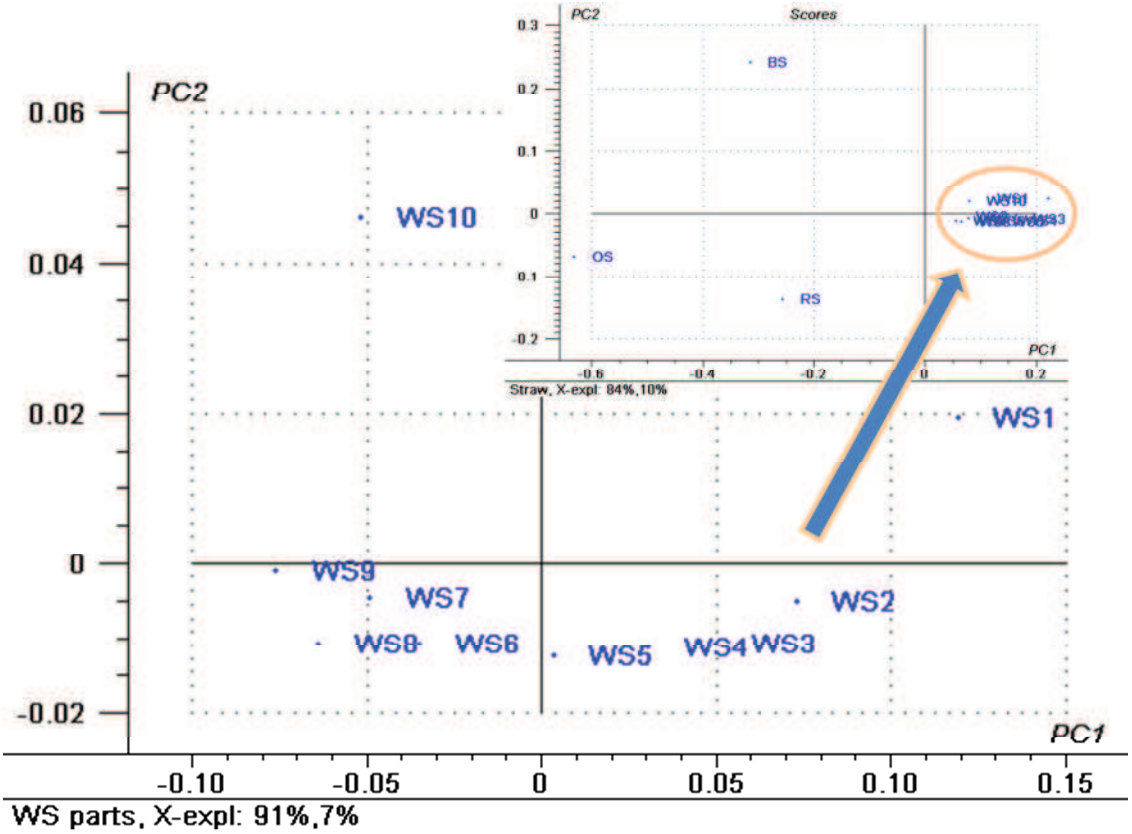

Figure 21: PCA to analyze the influence of the sampling train by apportioning of wheat straw (WS) measurement results into ten equal parts (below) and comparison with other kinds of straw (BS: barley straw, OS: oat straw, RS: rye straw)

2.5 Py-GC/MS measurements

For the assignment of the mass spectrometric peaks, own laboratory Py-GC/MS measurements using a double-shot pyrolysator (PY-2020iD, Frontier Laboratories) have been accomplished. Thereby, small amounts of biomass are pyrolyzed, the gases are separated (see Figure 22, left side) in a gas chromatograph and detected with an electron ionization mass spectrometer. The detected pyrolysis decomposition products are consistent with the findings in literature[33-38, 40-42, 48-51, 54-57, 81, 82, 84-89], where the investigation of biomass pyrolysis products has been mainly carried out by analytical (Curie-point) Py-GC/MS, too, and a series of phenol derivatives from lignin, and furan derivatives, ketones and aldehydes from cellulose and other polysaccharides (hemicellulose) are described (see also 1.4). Here, the lignin decomposition products could be confirmed, and, furthermore, constitutional isomers could be detected, for example eugenol and iso-eugenol (*m/z* = 164), and coniferyl alcohol, 4-vinylsyringol, guaiacylacetone and propioguaiacone at *m/z* = 180, respectively. On the right side of Figure 22, the identification of coniferyl aldehyde (*m/z* = 178) on the basis of the fragment pattern is shown exemplary for softwood.

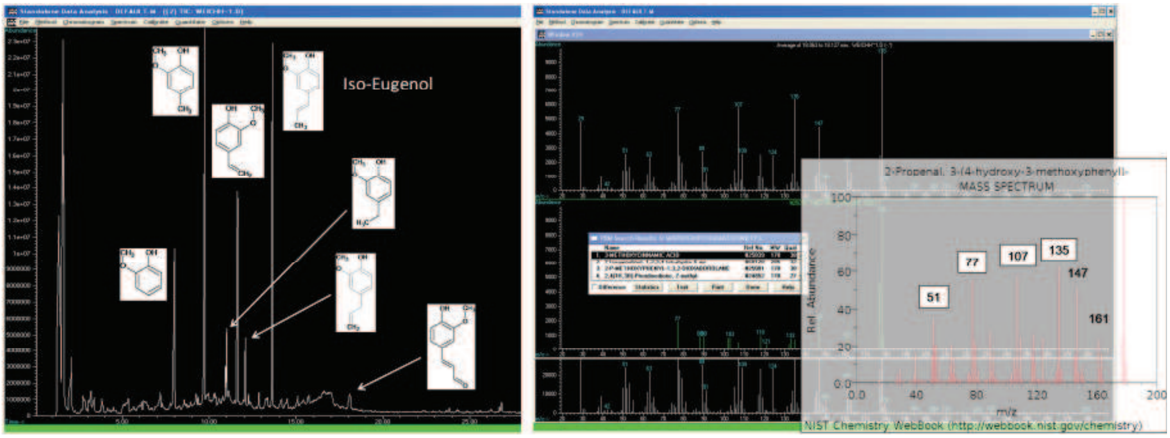

Figure 22: Py-GC/MS analysis of softwood and identification of peaks

2.6 Thermogravimetric Analysis (TA)

Thermogravimetric Analysis (TA) has been applied as a preparatory study for the measurements at the technical pyrolysis plant as well as for biomass pyrolysis experiments at low heating rates (10 K/min) and for characterization of biochars. The instrumental setup is depicted in Figure 23 and described in detail in Publication 2.

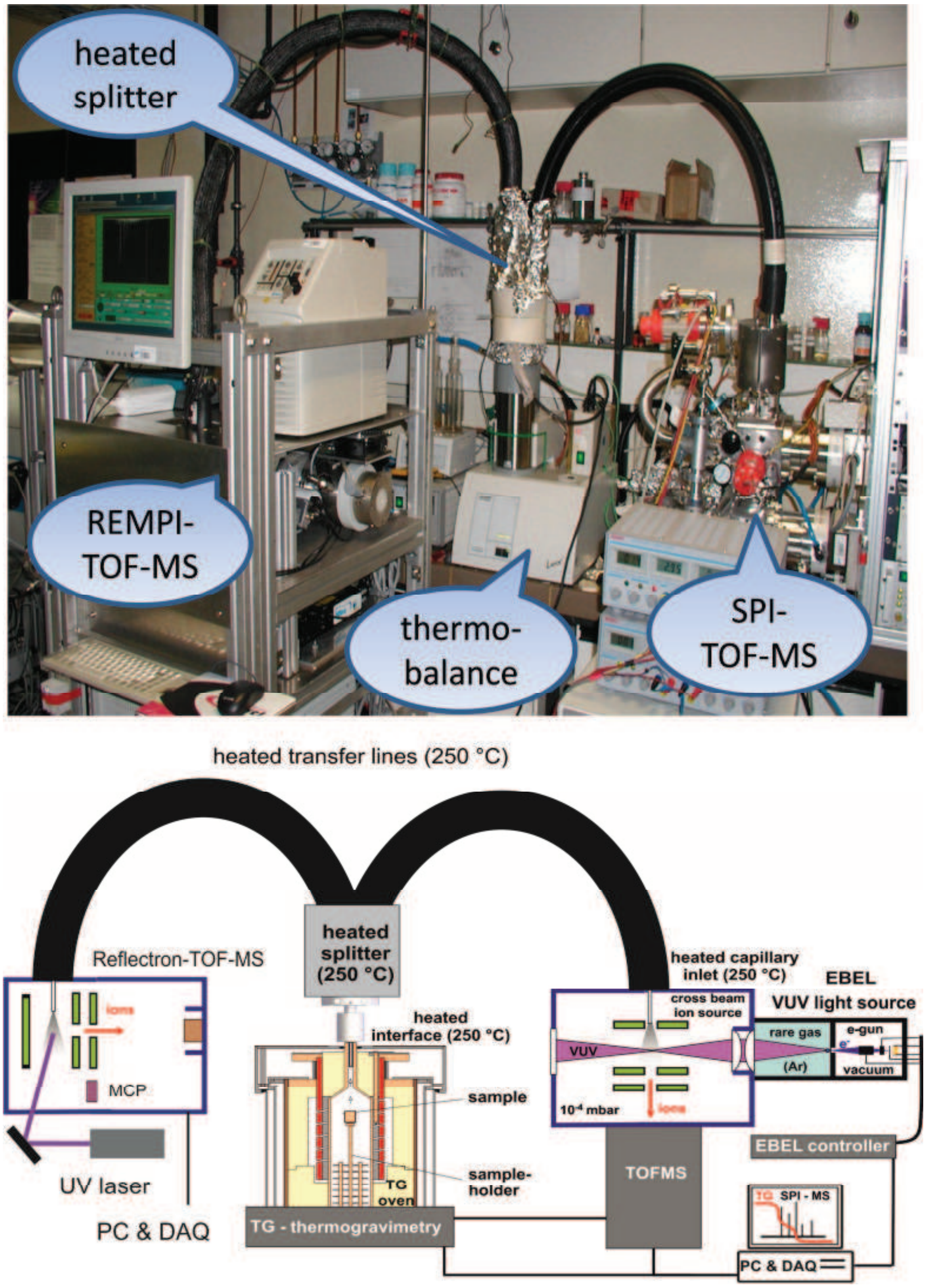

Figure 23: Picture and scheme of both photo ionization mass spectrometers coupled to the thermobalance (on the left the REMPI-TOF-MS, on the right the SPI-TOF-MS)

Both photo ionization mass spectrometers are hyphenated simultaneously to the thermobalance. The evolved gases arising at the thermal analysis provided information about the expected compounds at the KIT. In earlier measurements (see Publication 3) using the SPI-MS (right in the picture), the investigation of biomass and mineral oils had been achieved already.

In comparison with the technical flash pyrolysis process, the product pattern is significantly different for the same temperature in this case, in particular the occurrence of a multitude of polyaromatic hydrocarbons (PAHs) starting at around 450 °C, as depicted in Figure 24 (top right) using the example of wheat straw. However, the same key components could be found here at lower temperatures, as apparent from the evolved gases at 340 °C (top left) as well as from the summed up REMPI spectra of wheat bran and hay (see also Figure 18).

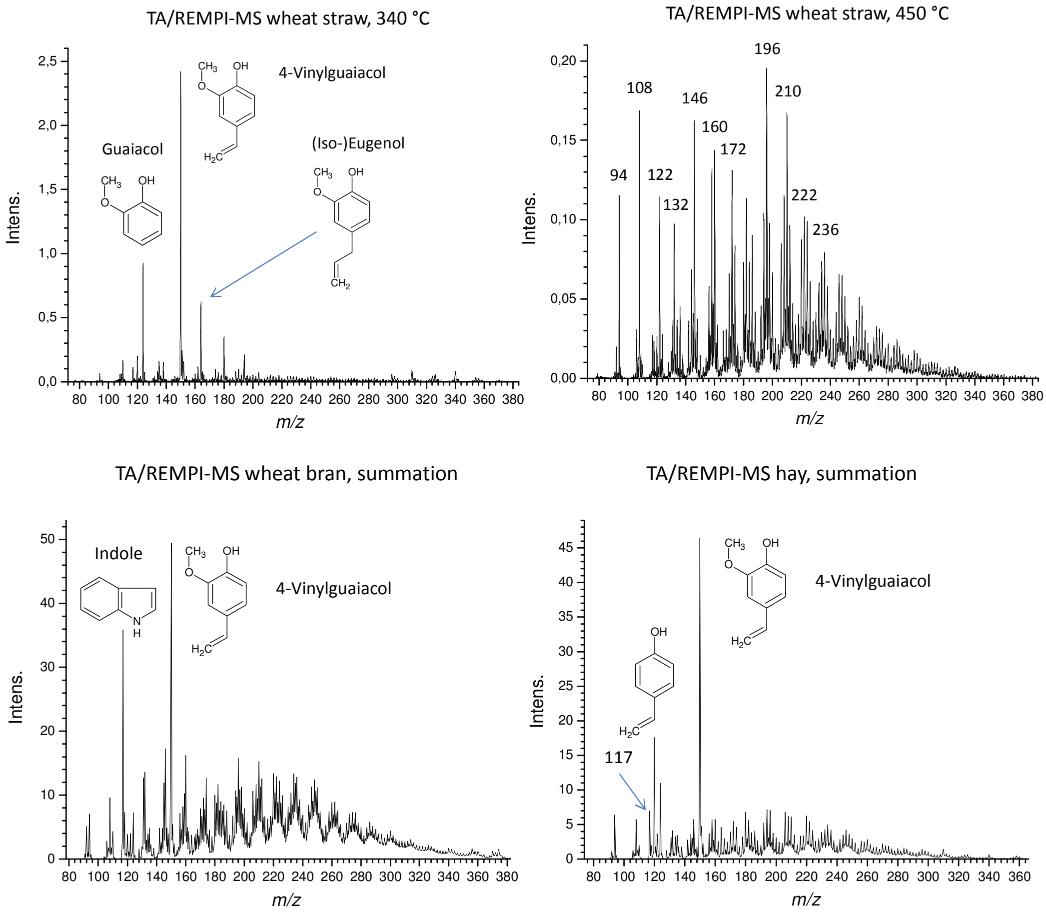

Figure 24: REMPI mass spectra of evolved gases of wheat straw at 340 °C and 450 °C during thermogravimetric analysis (TA) and summed up spectra of wheat bran and hay, showing lignin-based phenol derivatives as well as a multitude of PAHs

The employed biochars exhibit a desorption step first, which already starts below 100 °C, followed by a pyrolysis step at around 450 °C. In Figure 25, color-coded intensity plots of simultaneous SPI- and REMPI-MS measurements of wheat straw char are depicted. With SPI-MS, the smaller (and also non-aromatic) substances stick out especially in the first desorption step, whereas with REMPI-MS aromatic compounds are detected selectively and with high sensitivity in both steps.

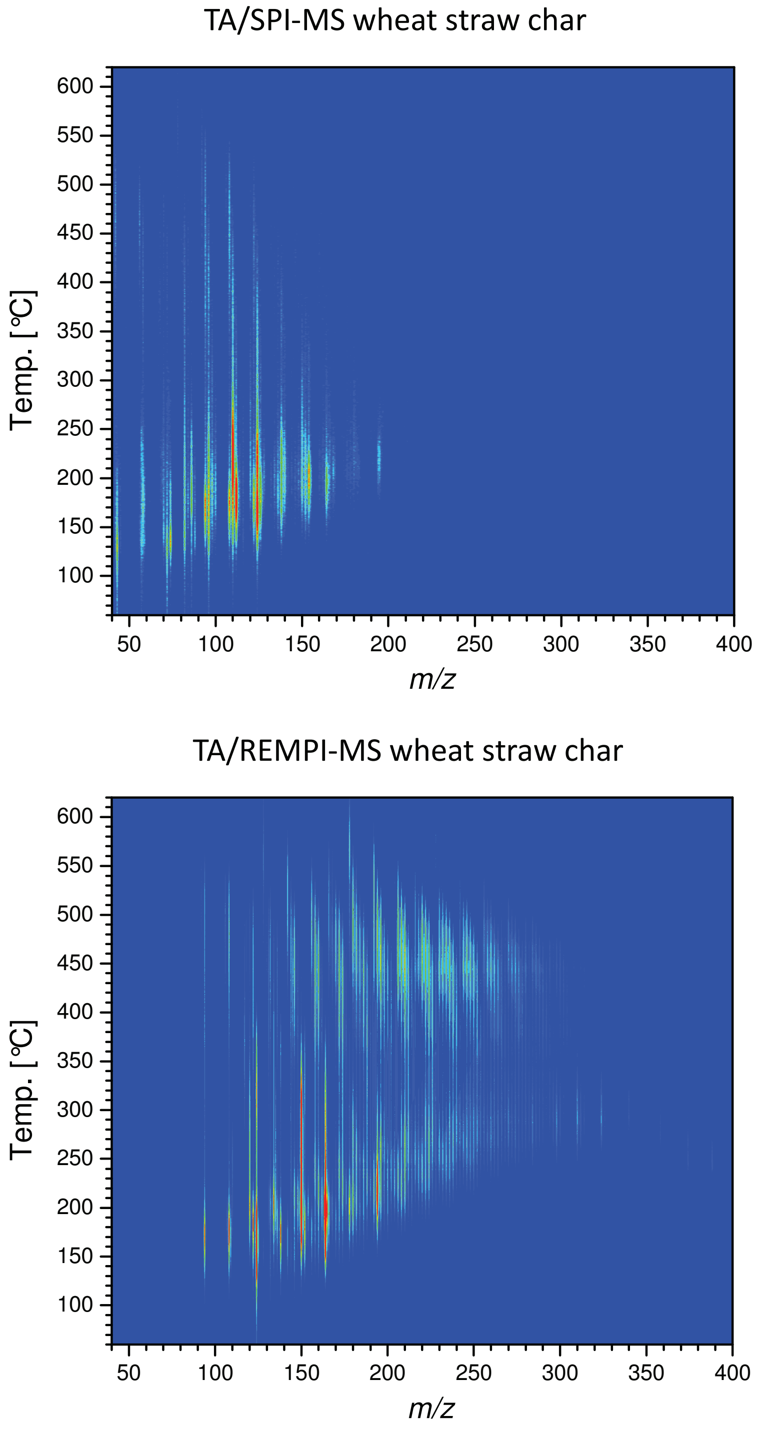

Figure 25: Color-coded intensity plots of the course of evolved gases from wheat straw char at thermogravimetric analysis using REMPI- and SPI-MS simultaneously

2.7 Laboratory oven pyrolysis

To point out the flash pyrolysis gas characteristics with regard to a wider temperature range compared to the measurements at the KIT, pyrolysis measurements have been conducted using a laboratory oven. The mobile SPI-MS is directly (without a filter) coupled thereto, as depicted in Figure 26. The setup and measurement details are explicated in Publication 4.

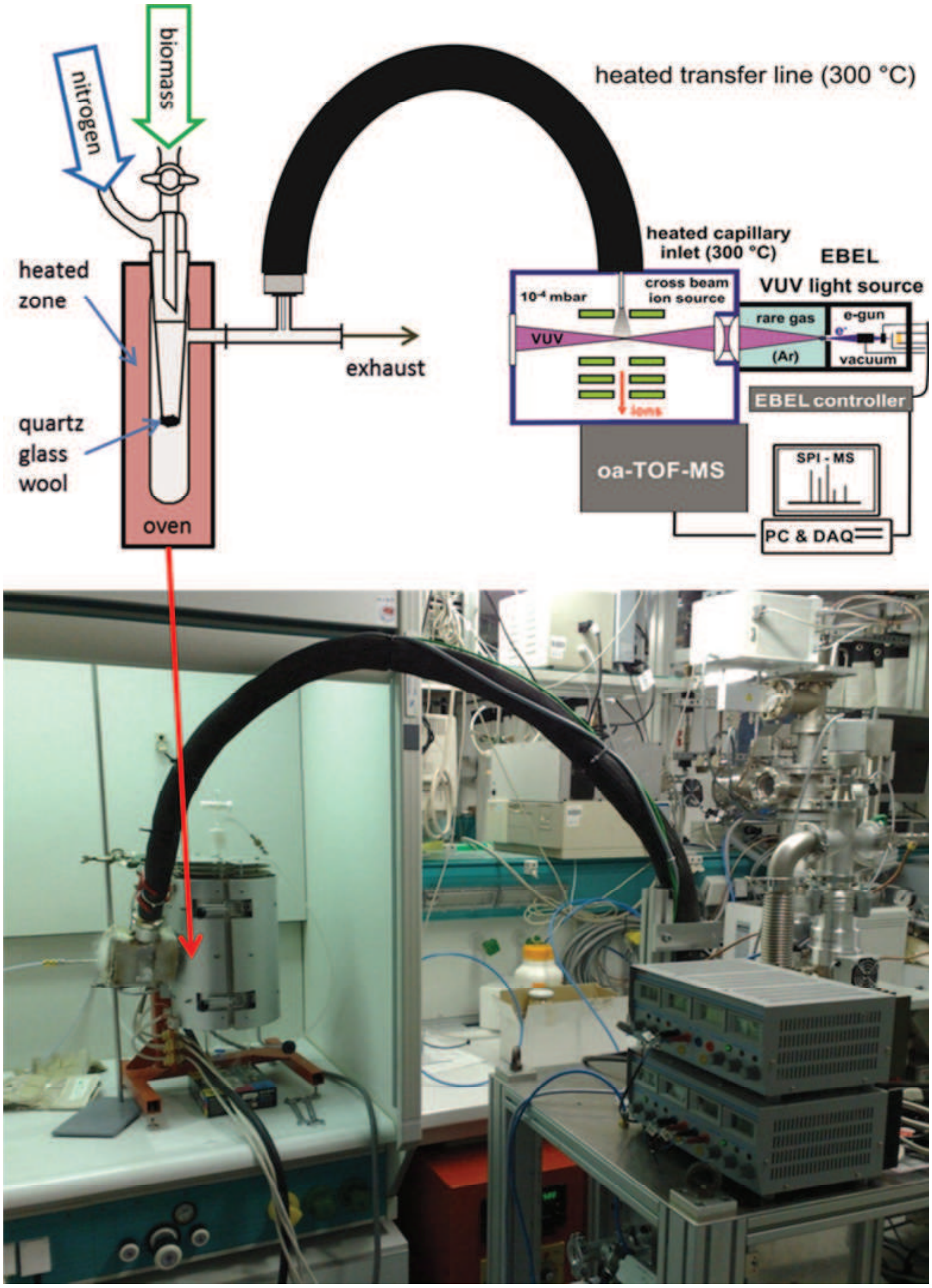

Figure 26: Scheme and picture of the direct coupling of the mobile SPI-TOF-MS to the laboratory pyrolysis oven (on the left)

Regarding the feedstock, the identical biomass samples and species already used at the KIT have been employed. In a similar way, certain biomasses are differentiated by their ratios of specific groups of lignin (phenolic) decomposition products, and Principal Component Analysis (PCA) is used to describe the varied pyrolysis gas composition for temperature variations and for different biomass species. The results basically agree with the measurements at the KIT, proving the here employed method to be a good bench-scale model for simulations of parameters in this process. Ranking lists of the compounds with the highest variance in terms of temperature variations and different biomass species have been generated, in addition.

Furthermore, pyrolysis gases of biomass structural units (lignin, cellulose, and xylan and galactan as hemicellulose model compounds) are investigated to reveal the respective key components. Moreover, time series of selected samples are shown (Figure 27) as proof of principle for the capability of the analytical technique for studies on thermal decomposition mechanisms and kinetic aspects in terms of biomass feedstock.

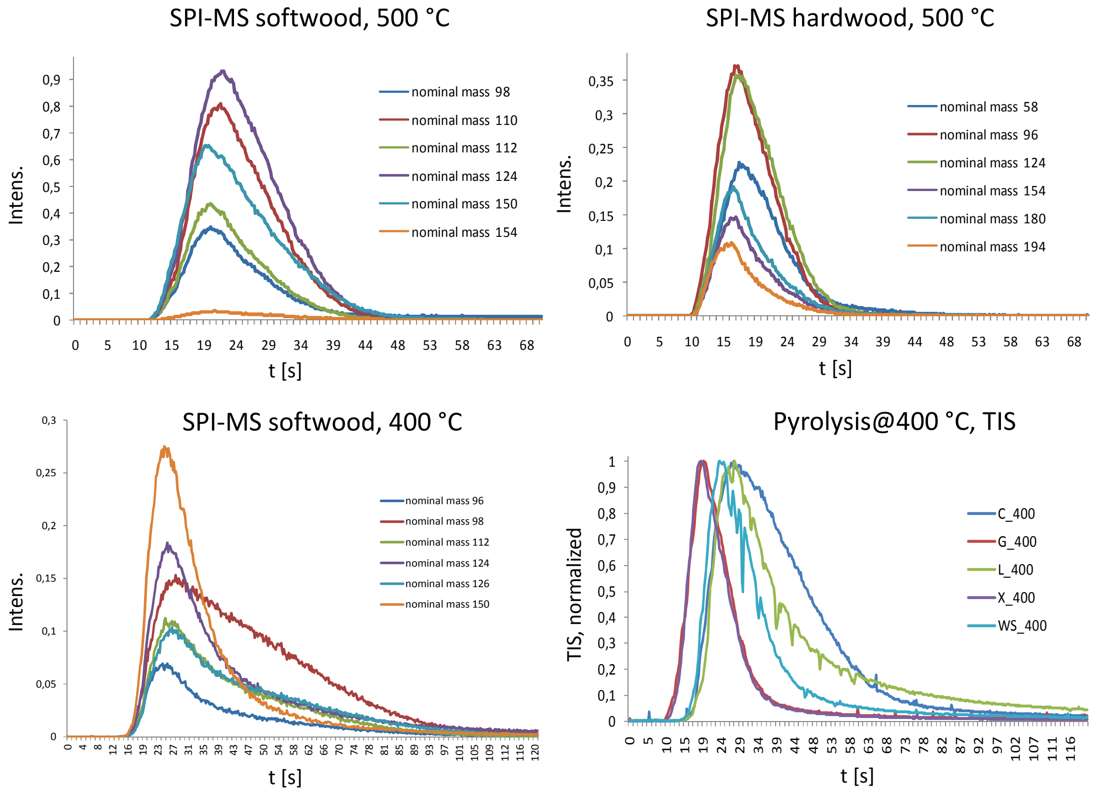

Figure 27: Time series of selected nominal masses of soft- and hardwood pyrolysis gases at 500 °C and 400 °C pyrolysis temperature; down right: total ion signal (TIS) of biomass components (C: cellulose, G: galactan, L: lignin, X: xylan) and wheat straw (WS)

3

Conclusion and Outlook

In this work, the application of soft photo ionization mass spectrometry is demonstrated for on-line and real-time measurements of biomass pyrolysis gases at a technical flash pyrolysis plant. In contrast, most studies on biomass pyrolysis focus on product identification as well as on elucidation of biomass structure and kinetic aspects. Here, the distinguishability of the employed biomass feeds is shown, using H/G/S ratios on the basis of selected mass spectra. Furthermore, Principal Component and Cluster Analysis point up the different pyrolysis gas composition for all employed biomasses and process variations. The applied analytical techniques implicate that the mass peaks cannot be clearly assigned to certain compounds. For this, literature studies as well as own Py-GC/MS measurements have been conducted. Furthermore, the selectivity of REMPI provided additional information for mass assignment. Moreover, laboratory (TA and oven) experiments have been carried out for comparison with the technical process.

With both photo ionization techniques shown here, fragmentation free mass spectra can be obtained, masking out the matrix gases, but then small molecules, which could be of interest, such as acetic acid or acetaldehyde, can also not be detected with the current measurement setup. However, with other rare gas (mixtures) in the VUV light source, higher photon energies are achievable. On the other hand, the high REMPI selectivity leads to clear mass spectra, therefore a process monitoring covering only 4 – 6 masses would be possible, particularly with regard to the good detectability of most of the key substances with REMPI, as illustrated in Table 2. For example, the nominal masses 117, 120, 124, 164 and 180 are sufficient for the differentiation of rape shred, wheat bran and hay. But due to the strongly differing ionization cross sections, it is difficult to compare the REMPI@266 nm spectra with others obtained at different wavelengths, or in general with other soft (photo) ionization techniques. Furthermore, this could distort the results of statistical analysis, especially the PCA. For the miscellaneous biomass feeds used, specific mass spectrometric patterns could be obtained, mainly exhibiting typical lignin and (hemi-)cellulose decomposition products, and nitrogen containing substances in some cases. The compounds have been arranged in groups for a first characterization, according to the biopolymer they are originating from. Particularly the S/G ratio is often used for differentiation of soft- and hardwood; with SPI-MS, this is well achievable, too.

Principal Component Analysis (PCA) was used for the differentiation of all employed biomass species. The Loadings plots point out the importance of the respective compounds in terms of the highest variance. Furthermore, the PCA-Loadings values open up a facile path for creating a ranking of the biomass pyrolysis products, and for reducing the number of variables. Additionally, the results of the PCA or the underlying data matrix of the SPI-MS spectra can be combined with other findings within the bioliq® process, viz. char yields, pyrolysis oil composition and biosyncrude consistency, respectively, that are important feedstock selection and process criterions and subject of current investigations. However, these correlations between the measured transient products and the composition of the obtained biooil as well as the biosyncrude will have to be investigated in more detail in the future, as a part of process optimization strategies in terms of the product quality of the successive process steps. For this purpose, the aforementioned parameters could be integrated in the data matrix as additional category variables, for example. Moreover, it's easily possible to add new samples to the matrix and conduct the PCA anew. Furthermore, the relative content of the three monomeric lignin precursor groups (H, G and S), the ratio or the percentage could be correlated with the properties of the biosyncrudes, what potentially could be achieved with TA of biochars, too. The employed hyphenation technique of Thermal Analysis with both soft photo ionization time-of-flight mass spectrometers using a heated splitter is a novel and well suited method for evolved gas analysis, as demonstrated for biomass and biochar samples. Again, the ratio of phenol derivatives varies for different temperatures and owing to different lignin structures of the miscellaneous biomasses. The biochars exhibit a desorption peak in the temperature profiles, in addition to specific pyrolytic decomposition products. What is more, both ionization methods allow detailed kinetic studies. That also applies for the laboratory oven measurements, using the SPI-TOF-MS. Thereby, the main issue was to point out the flash pyrolysis gas characteristics with regard to a wider temperature range compared to the measurements at the KIT. The data analysis has been carried out in a similar way, calculating

H/G/S ratios and applying PCA. Furthermore, pyrolysis gases of biomass structural units (lignin, cellulose and hemicellulose model compounds) are investigated to reveal the respective key components.

In any case, the applied analytical techniques allow the characterization of the biomass pyrolysis gases and the differentiation of the employed feedstock on the basis of the mass spectrometric patterns. Beyond that, it could also be possible to select certain (groups of) substances, for example to direct the process in relation to reduction of oxygen-rich compounds, to obtain products with higher energy content.

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4

Publications

The results obtained within this work as well as contributions to other publications are listed below. A detailed description of the employed methods and the results can be found within the publications.

4.1 On-Line Process Analysis of Biomass Flash Pyrolysis Gases Enabled by Soft Photoionization Mass Spectrometry (Publication 1)

Published in: energy&fuels, Volume 26, 2012, Pages 701–711

By: Alois Fendt, Thorsten Streibel, Martin Sklorz, Daniel Richter, Nicolaus Dahmen and Ralf Zimmermann

Alois Fendt was strongly involved in preparation and accomplishment of the measurement campaigns. He carried out all measurements by himself as well as the data analysis, and he prepared the most part of the manuscript and contributed to discussions. The work of Alois Fendt to this publication accounts to approximately 70 %.

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On-Line Process Analysis of Biomass Flash Pyrolysis Gases Enabled by Soft Photoionization Mass Spectrometry

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Supporting Information

ABSTRACT: In the current discussion about future energy and fuel supply based on regenerative energy sources, the so-called second-generation biofuels represent a vitally important contribution for the provision of carbon-based fuels. In this framework, at the Karlsruhe Institute of Technology (KIT), the bioliq process has been developed, by which biomass is flash-pyrolyzed at 500 °C for the production of so-called biosyncrude, a suspension of the pyrolysis liquids and the remaining biochar. However, little is known about the composition of the pyrolysis gases in this process with regard to different biomass feedstock and process conditions, and the influence on the subsequent steps, namely, the gasification and subsequent production of biofuels or base materials. Time-of-flight mass spectrometry (TOFMS) with two soft (i.e., fragmentation free) photoionization techniques was for the first time applied for on-line monitoring of the signature organic compounds in highly complex pyrolysis gases at a technical pyrolysis pilot plant at the KIT. Resonance-enhanced multiphoton ionization with TOFMS using UV laser pulses was used for selective and sensitive detection of aromatic species. Furthermore, single-photon ionization using VUV light supplied by an electron beam-pumped excimer light source was used to comprehensively ionize (nearly) all organic molecules. For the miscellaneous biomass feeds used, distinguishable mass spectra with specific patterns could be obtained, mainly exhibiting typical pyrolytic decomposition products of (hemi)cellulose and lignin (phenol derivatives), and nitrogen-containing compounds in some cases. Certain biomasses are differentiated by their ratios of specific groups of phenolic decomposition products. Therefore, principal component and cluster analysis describes the varied pyrolysis gas composition for temperature variations and particularly for different biomass species. The results can be integrated in the optimization of the bioliq process.

■ INTRODUCTION

Given the background of diminishing or difficult-to-exploit fossil energy sources, new developments in the field of energy generation or production of chemicals have to focus more on the increased frequency of application of regenerative sources in the future. In addition, this would be a benefit in terms of reducing the emissions of the greenhouse gas carbon dioxide. Biomass is the only regenerative energy source containing carbon. However, an argument recently developed is related to the increased frequency of biomass utilization for energy production, because a conflict between "food and fuel" is feared, which could lead to a decrease in the harvest of edibles and rising food prices. Hence, in particular, the use of rest and waste biomass such as straw and urban waste wood has become of interest for the production of liquid fuels (so-called second-generation biofuels) and chemicals.

At the Karlsruhe Institute of Technology (KIT), North Campus, a process has been developed to achieve this generation of fuels and chemicals out of waste biomass. The first step in this "biomass to liquid" (bioliq or BTL in general) process[1−4] is a flash pyrolysis of biomass at 500 °C in a twin screw mixer with a heat transfer material such as hot sand. Subsequently, the evolving pyrolysis gases are condensed and immingled with the remaining char, providing the so-called biosyncrude or bioslurry, which can be pumped and stored. In this manner, the energy density of the often voluminous biomass is considerably increased. In a second step, synthesis gas is generated from the biosyncrude in a pressurized entrained flow gasifier.[5] After thorough purification, the tar free synthesis gas can be used directly for a variety of well-known processes such as the Fischer−Tropsch reaction[6−8] or the synthesis of methanol and higher alcohols[9] and dimethyl ether (DME),[10] which themselves could serve as fuels or as educts of other organic chemicals.

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However, relatively little is known about the primary products in the pyrolysis off-gas under these conditions or the mechanisms of the thermal decomposition of the biomass feedstock. The latter is complicated by the fact that preferably a large variety of different biomasses should be subjected to the process, each of them exhibiting distinct chemical compositions and thermal properties. This could in turn influence the composition of the biooils and the biosyncrude. Therefore, it is of interest to learn more about the intermediary gaseous products evolving directly from the pyrolyzed feedstock prior to condensation. For this, a direct on-line analysis of the evolved organic species is required.

Until now, products of biomass pyrolysis have been extensively investigated mainly by applying analytical (Curie-point) pyrolysis gas chromatography and mass spectrometry with electron ionization (Py-GC−MS), particularly for the structural elucidation of lignins. This technique was employed by Meier and co-workers[11−15] for studies of powdered wood and milled wood lignins (MWLs), by Pouwels et al.[16−18] for beech wood, derived fractions, and cellulose, by Kuroda et al.[19−21] for the analysis of softwoods (with classification) and lignins (including the effect of inorganic substances), by Hempfling and Schulten[22,23] for agricultural and forest soils, and by van der Hage et al.[24] for several lignins; additionally, they used resonance-enhanced multiphoton ionization (REMPI) and in-source pyrolysis mass spectrometry for the analysis of cottonwood MWL pyrolysates.[25] Genuit et al.[26] characterized beech MWL by pyrolysis gas chromatography in combination with photoionization MS using a rare gas glow discharge resonance lamp. In contrast, Evans et al.[27−29] used molecular beam sampling with quadrupole MS with low-energy electron ionization for the analysis of several wood samples and components thereof. The same technique was used by Sykes et al.[30] for studies of the within tree variability of lignin. However, EI ionization with a well-defined low electron energy is difficult to achieve,[25] and small variations in electron energy lead to large differences in mass spectra, resulting in poor reproducibility.[26] Additionally, off-line methods, e.g., GC−MS characterization of biomass-based pyrolysis oils[31,32] or off-line pyrolysis gas chromatography with flame ionization detection (Py-GC−FID),[13] have been applied. An overview of mass spectrometric investigations of lignins, including soft ionization techniques, is provided by Reale et al.[33] Generally, isolated lignins and cellulose, or pretreated biomass samples, in usually small batches, have been employed in most cases, which may lead to differences in the distribution of the pyrolysis products compared to the technical process. In particular, no reports of direct on-line measurements at technical or commercial pyrolysis plants could be found in the literature.

The aim of this paper is to point out the different flash pyrolysis gas characteristics for a variety of biomass feeds and, on a limited scale, for process variations. For this, time-of-flight mass spectrometry using soft photoionization methods for the investigation of organic intermediates in a technical flash pyrolysis pilot plant is used in real time. Photoionization allows the direct and on-line monitoring of the pyrolysis gases, whereas the customarily employed electron ionization (EI) would lead to fragmentation of the molecules and make an interpretation of the resulting mass spectra nearly impossible in this complex mixture. Ionization is conducted by single-photon ionization (SPI) with a continuous beam of VUV photons produced by an innovative electron beam-pumped excimer light source (EBEL)[34−37] as well as by REMPI[38,39] with laser-generated pulsed UV photons. Both techniques have been used previously to investigate pyrolysis and other thermal processes.[35,40−44] REMPI utilizes a two-photon absorption, whereby the one photon energy is in resonance with an excited electronic state, from which the absorption of the second photon can lead to ionization, if the combined energy of the two photons matches the ionization energy of the molecule. The applied wavelength strongly influences the ionizability of the investigated molecules;[25,45,46] in the 240−270 nm UV range, for example, this scheme is selective for (poly)aromatic compounds. In contrast, single-photon ionization is a more "universal" ionization technique, because all compounds whose ionization energies are below the energy of the applied VUV photon are ionized. Both REMPI and SPI lead to fragment free mass spectra, depicting only molecular ions and, furthermore, suppressing the matrix gas nitrogen and other highly concentrated small molecules. In any case, this allows the direct analysis of the whole width of organic compounds from the biomass pyrolysis process.

■ MATERIALS AND METHODS

Experiments were conducted at the technical flash pyrolysis pilot plant at KIT North Campus with a throughput of 10 kg/h, which consists of a twin screw mixer (Lurgi-Ruhrgas) and a two-stage biomass feeding. Thereby, chopped biomass is added to a storage tank, funneled in a nitrogen-purged reservoir, and conveyed to the reactor by a screw. Hot steel spheres are supplied as heat exchangers; in addition, metal-doped alumina spheres have been tested, too. The pyrolysis products arise via suction and are cooled in several stages, yielding char mainly in the first stage and pyrolysis oil in the following stages. The steel spheres are led back from the end of the mixer to the reactor via a heat exchanger (Figure 1).

For the on-line analysis of the primary organic biomass pyrolysis products at the technical pilot plant, a heated sampling train had to be conceived and developed. Thereby, the main challenge is the fact that the pyrolysis gas is very rich in both coarse and fine particles. These particles must be removed from the gas stream to prevent clogging of the last component of the sampling train, a deactivated quartz capillary with an inner diameter of 200 μm. For this purpose, a series of particle filter devices has been mounted. The sampling train begins directly at the exhaust of the pyrolysis reactor. The pyrolysis gas is immediately diluted by nitrogen, which acts as the carrier gas. This is followed by a cyclone for removing the coarse particles. After the cyclone, the sampling path is divided into two parallel lines, each containing a bag filter. If one of the filters is saturated, the gas stream could be switched to the parallel line, thus allowing the continuation of the sampling process. Then, there are two fine particle filters in line. Finally, the sampled gases reach the aforementioned capillary, which runs in a heated hose and serves as a restriction between the atmospheric-pressure conditions of the pyrolysis plant and the vacuum of the mass spectrometer (Figure 1). The ionizing photons hit the pyrolysis gases immediately underneath the inlet needle at the end of the capillary in the space of the ionization source of the mass spectrometer, where an effusive molecular beam is formed.[45] The whole sampling train is heated to not less than 300 °C.

For ionization with SPI, a home-built EBEL-VUV light source was utilized, whose main innovation is a 0.7 mm × 0.7 mm ceramic silicon nitride (SiNx) foil only 300 nm in thickness that separates the rare gas volume ($p > 1$ bar) from a vacuum chamber containing an electron gun. The latter generates a 12 keV electron beam that is directed into the rare gas through the SiNx foil with low-energy loss. The energetic electrons excite and ionize the rare gas atoms. In successive processes, excited diatomic rare gas molecules (excimers) are formed. Upon the radiative decay of these rare gas excimers, VUV radiation is emitted. As a result of the high gas pressure, excimer formation occurs in a small volume in the proximity of the electron entrance foil. The rare gas volume was filled with argon with an emission maximum at 126 nm

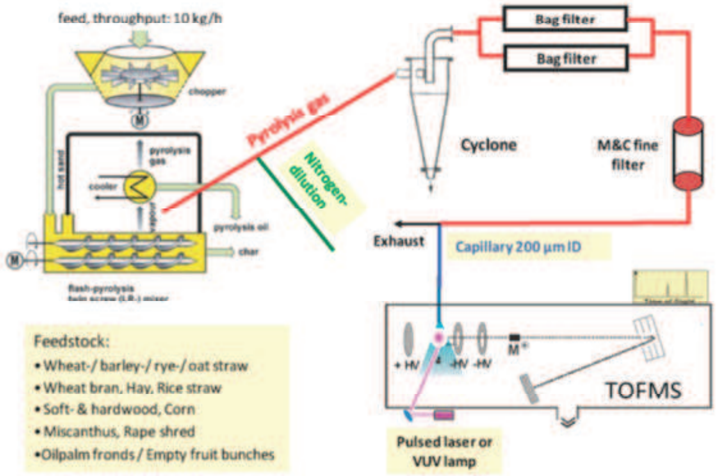

Figure 1. Scheme of the on-line pyrolysis gas analysis of biomass at the technical pyrolysis plant on KIT North Campus.

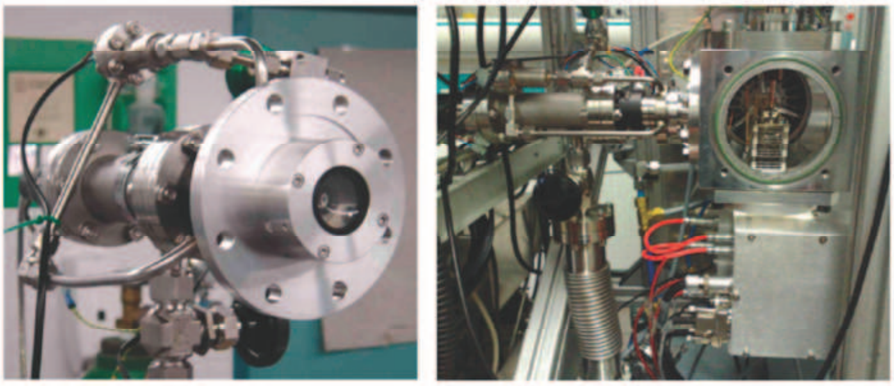

Figure 2. Photograph of the newly developed EBEL VUV lamp, which on the right is mounted on the SPI−MS system.

(9.8 eV center photon energy available for ionization). In principle, it is possible to vary the ionization energy by replacing the argon filling with other rare gases or rare gas mixtures, thus enhancing the selectivity of VUV ionization. For REMPI, a Nd:YAG laser (BIG SKY ULTRA, Quantel, Les Ulis Cedex, France) with two frequency doubling units at 266 nm, a 10 ns pulse width, and a 10 Hz repetition rate with a power density of approximately 7×10^6 W/cm^2 was employed. Despite the fact that this wavelength is highly selective for aromatic compounds, one has to take into account the fact that the ionization cross sections[47] of the compounds may differ greatly.

Because of the different nature of the ionizing photons and their generation, i.e., short laser pulses for REMPI and a continuous VUV beam for SPI, two different time-of-flight mass spectrometers (TOF-MSs) have been applied for the detection of the molecular ions. For the REMPI and the first SPI−MS measurements, a mass spectrometer (Reflectron CTF10, Kaesdorf Geräte für Forschung and Industrie, Munich, Germany) was employed that has been proven and tested in comparable measuring campaigns; for SPI, the EBEL VUV light source was used and an accessory HV pulser for the extractor plates had to be mounted. With the second measurement campaign as a starting point, the SPI−MS measurements were taken with a mobile orthogonal acceleration TOF-MS (C-TOF, TOFWERK AG, Thun, Switzerland), which is particularly suited for the use of continuous light sources such as the EBEL because of the special type of construction with pulsed (around 70000 Hz) orthogonal extractor plates.[34] During the course of the three measurement campaigns, the mass spectrometric systems were continuously optimized. In the third campaign, during which only SPI measurements were performed, a newly developed EBEL version (Figure 2) was employed, leading to the improved sensitivity of the C-TOF mass spectrometer (LOD, 10 ppb for toluene; S/N = 3). Data were acquired from the mass spectrometers with Acqiris AP240 (Agilent Technologies) averager cards and special software.

For the assignment of the mass spectrometric peaks, our laboratory conducted Py-GC−MS measurements with a double-shot pyrolysator (PY-2020iD, Frontier Laboratories). The detected pyrolysis decomposition products are consistent with the findings in the literature,[11−33,48,49] where a series of phenol derivatives from lignin and furan derivatives, ketones, and aldehydes from cellulose and other polysaccharides (hemicellulose) are described. Additionally,

Table 1. Mass Assignments of the Most Important Pyrolysis Products, Derivation from Structural Groups (tentative), and Significance for Certain Biomasses

mass	biomass pyrolysis products	group[a]	significant for biomass
42	propene		all
43	carbohydrate fragment $C_3H_7^+$, $C_2H_3O^+$[30,55]	C	all
48	methanethiol[41,55,57]	P	rape shred
56	butene	C	all
57	carbohydrate fragment[17,30]	C	all
58	acetone	C	all
67	pyrrole	P	rape shred
68	furan/isoprene	C	all
70	2-butenal	C	all
72	2-oxopropanal/2-butanone	C	all
74	hydroxypropanal/hydroxypropanone	C	all
81	methylpyrrole	P	rape shred
82	methylfuran/2-cyclopenten-1-one	C	all
84	furanone	C	all
86	2,3-butanedione/tetrahydrofuran-3-one	C	all
92	toluene	P	rape shred, wheat bran
94	phenol	H, P	EFB, OPF
95	pyridinol[54]	P	rape shred
96	furfural	C	all
98	dihydromethylfuranone/2-furanmethanol	C	all
100	2,3-pentanedione/tetrahydro-4-methyl-3-furanone	C	all
108	methylphenol (cresol)/anisole	H, P	all
109	methylpyridinol	P	rape shred
110	5-methylfurfural/catechol	C/H	all, rape shred
112	methyldihydropyranone/hydroxypyranone	C	all
117	indole	P	rape shred, wheat bran, hay
120	4-vinylphenol	H	corn, Miscanthus
122	dimethylphenol/ethylphenol/methylanisole	H	all
124	guaiacol	G	all
126	5-hydroxymethylfurfural/maltol/levoglucosenone	C	all
131	methylindole	P	rape shred
134	4-allylphenol/cinnamic alcohol	H	all
136	dimethylanisole/anisaldehyde		all
138	4-methylguaiacol	G	all
140	2,3-dihydroxyanisole		all, hardwood
148	cumarylaldehyde	H	all
150	4-vinylguaiacol	G	all, varying
152	vanillin/4-ethylguaiacol	G	all
154	syringol	S	hardwood, rape shred, EFB, OPF
162	methoxycinnamic aldehyde		all
164	(iso)eugenol (eugenic acid)	G	all, softwood
166	4-propylguaiacol/4-acetylguaiacol	G	all
168	methylsyringol	S	hardwood, rape shred, EFB, OPF
178	coniferyl aldehyde/methyleugenol	G	all, softwood
180	4-vinylsyringol/coniferyl alcohol/guaiacylacetone/propioguaiacone	S/G	varying, hardwood
182	syringaldehyde/trimethoxytoluene	S	all
194	allylsyringol	S	hardwood
196	acetosyringone/propylsyringol	S	hardwood
208	sinapaldehyde	S	hardwood
210	sinapyl alcohol/syringyl acetone	S	hardwood

[a] Abbreviations: P, proteins; C, cellulose/carbohydrates; H, hydroxybenzene; G, guaiacol; S, syringol.

the selectivity of the REMPI method was helpful for the mass assignment, too.

A large variety of biomass feedstocks have been investigated with the described experimental setup, comprising several kinds of straw and corn, soft- and hardwood, hay, wheat bran, rice straw (from Egypt), rape extraction residue (RES), oil palm residues (EFB and OPF), and Miscanthus. Straw (from wheat, barley, rye, and oat), hay, wood, RES, and bran were from the surrounding area of Karlsruhe, and corn cobs and corn stover were from South Africa. Normally, a pyrolysis temperature of 500 °C was applied. As process variations, temperatures have been changed to 450 and 550 °C. Furthermore, another heat exchanger material has been employed, consisting of doped alumina. The SPI mass spectra recorded during the third measuring campaign have been evaluated statistically by applying multivariate data analysis and, in some cases, by calculating the ratio of the different lignin components. The underlying data have been averaged over at least 15 min and range-normalized before application of principal component analysis (PCA) and cluster analysis [k-means algorithm, distance type (absolute) correlation], using The Unscrambler (CAMO Software AS, Oslo, Norway). PCA has been used to analyze the influence of the sampling train, too. For that purpose, the measurements of wheat straw and hardwood have been apportioned into 10 equal parts of 2 and 3 min, respectively. Furthermore, a ranking list of the biomass pyrolysis products (Table 2) was generated by adding the absolute Loadings values of the principal components (of all biomasses and process conditions), weighted by their explained variances (see lines below the graphs). This method was also used to reduce the involved masses in the PCA of the Poaceae, which imply hay, Miscanthus, and all kinds of straw and corn. The calculation has been conducted anew with the 30 key masses used in this study (Figure 8).

■ RESULTS

The mass spectra obtained by pyrolysis gas measurements at the technical pyrolysis pilot plant revealed a series of the typical pyrolysis products described in the literature; the most important ones are listed in Table 1, and only substances with ionization energies of <9.81 eV have been taken into account. For all employed biomass feedstocks, measurements under constant conditions could be achieved. Char yields have been determined for some biomasses at a pyrolysis temperature of 500 °C, ranging from 14% (softwood and corn cobs) to 26% for hay (see the Supporting Information). By closing and reopening the valve to the reactor, we could estimate a residence time of ~140 s in the sampling train (Figure 3), using the example of SPI−MS of wheat straw. The influence of the sampling train on the pyrolysis gas composition has been investigated by PCA (see below and the Supporting Information) and by laboratory oven experiments, too. Thereby, no significant changes could be observed. Further details as well as studies on the mechanisms leading to the important pyrolysis products arising from the decomposition of the various feedstocks will be discussed in a forthcoming publication. At this stage, it becomes apparent that the sampling system reacts comparatively fast to changes in the concentration and composition of the pyrolysis gas. For a first characterization of the pyrolysis products, they have been arranged in groups according to their derivation from either lignin or (hemi)cellulose, or from proteins in some cases (Table 1). Lignin in turn predominantly consists of three monomers, namely, *p*-coumaryl alcohol, coniferyl alcohol,

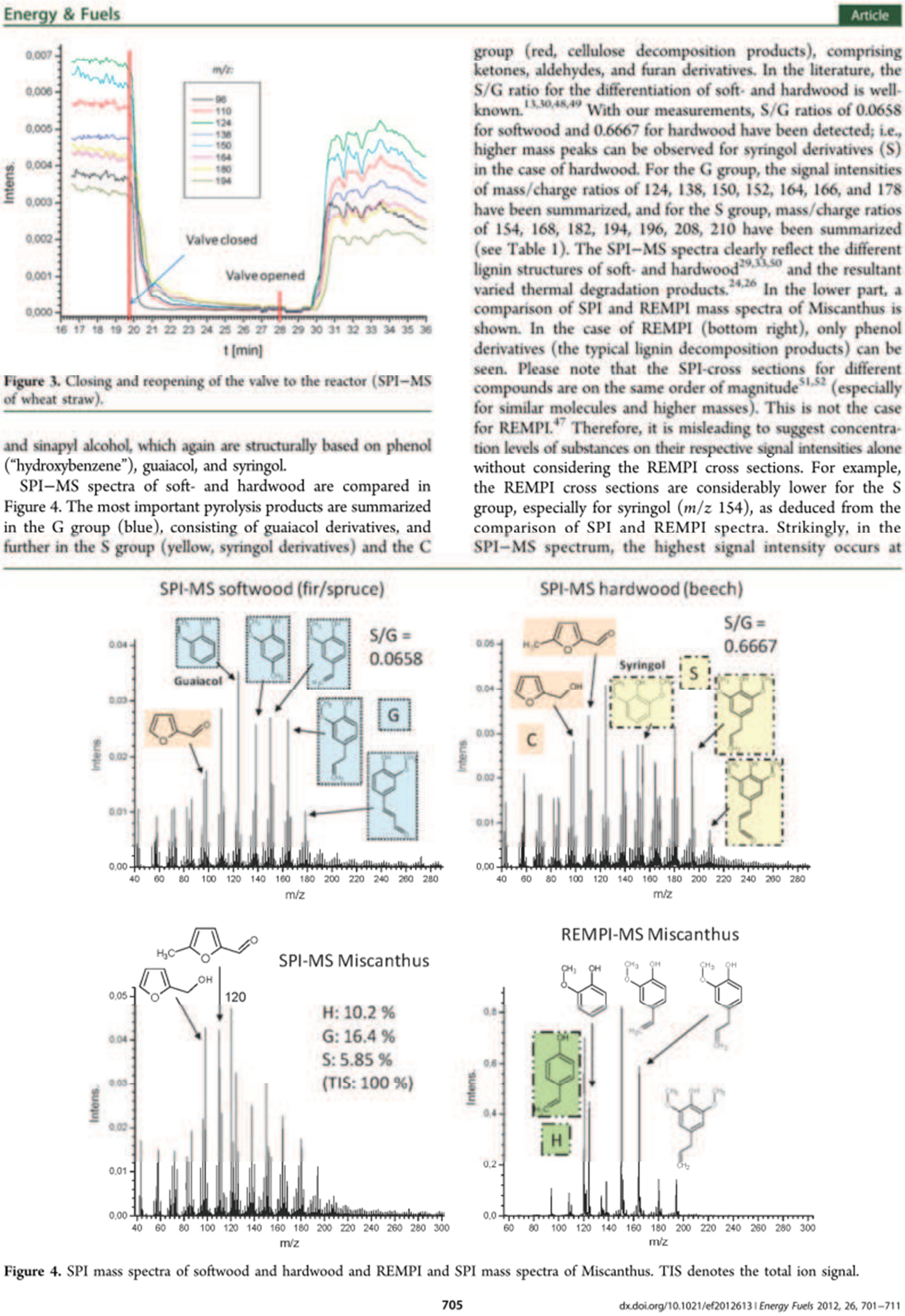

Figure 3. Closing and reopening of the valve to the reactor (SPI−MS of wheat straw).

and sinapyl alcohol, which again are structurally based on phenol ("hydroxybenzene"), guaiacol, and syringol.

SPI−MS spectra of soft- and hardwood are compared in Figure 4. The most important pyrolysis products are summarized in the G group (blue), consisting of guaiacol derivatives, and further in the S group (yellow, syringol derivatives) and the C group (red, cellulose decomposition products), comprising ketones, aldehydes, and furan derivatives. In the literature, the S/G ratio for the differentiation of soft- and hardwood is well-known.[13,30,48,49] With our measurements, S/G ratios of 0.0658 for softwood and 0.6667 for hardwood have been detected; i.e., higher mass peaks can be observed for syringol derivatives (S) in the case of hardwood. For the G group, the signal intensities of mass/charge ratios of 124, 138, 150, 152, 164, 166, and 178 have been summarized, and for the S group, mass/charge ratios of 154, 168, 182, 194, 196, 208, 210 have been summarized (see Table 1). The SPI−MS spectra clearly reflect the different lignin structures of soft- and hardwood[29,33,50] and the resultant varied thermal degradation products.[24,26] In the lower part, a comparison of SPI and REMPI mass spectra of Miscanthus is shown. In the case of REMPI (bottom right), only phenol derivatives (the typical lignin decomposition products) can be seen. Please note that the SPI-cross sections for different compounds are on the same order of magnitude[51,52] (especially for similar molecules and higher masses). This is not the case for REMPI.[47] Therefore, it is misleading to suggest concentration levels of substances on their respective signal intensities alone without considering the REMPI cross sections. For example, the REMPI cross sections are considerably lower for the S group, especially for syringol (*m/z* 154), as deduced from the comparison of SPI and REMPI spectra. Strikingly, in the SPI−MS spectrum, the highest signal intensity occurs at

Figure 4. SPI mass spectra of softwood and hardwood and REMPI and SPI mass spectra of Miscanthus. TIS denotes the total ion signal.

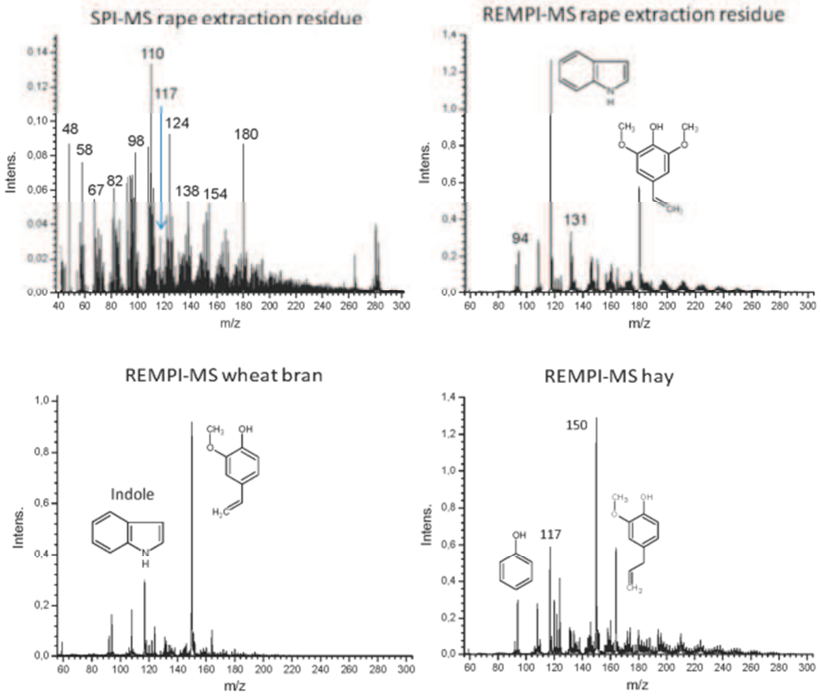

Figure 5. SPI and REMPI mass spectra of rape extraction residue and REMPI mass spectra of wheat bran and hay.

4-vinylphenol (m/z 120), a member of the H group (hydroxybenzene derivatives), as opposed to wood, where only marginal peaks appear at m/z 120. However, the other substances and groups depicted above are also present in both REMPI and SPI–TOF-MS spectra. The ratio of the H group, which includes the mass/charge ratios of 94, 108, 120, 122, 134, and 148, is calculated to be 10.2% relating to the sum of all mass peaks, the total ion signal (TIS); for G and S groups, the values are 16.4 and 5.8%, respectively. Accordingly, the S/G ratio of 0.3565 lies between soft- and hardwood, indicating a more heterogeneous lignin structure of the energy crop Miscanthus, which is characteristic of the Poaceae family.[53]

Interestingly, a completely different pattern arises in the case of rape extraction residue (Figure 5). In the very complex SPI spectrum, many new substances appear, most of which contain nitrogen, e.g., pyridinol[54] (m/z 95), pyrrole (m/z 67), indole[43] (m/z 117), ethylamine (m/z 45), and propylamine (m/z 59), and others such as methanethiol[39,55] that are likely be formed by the decomposition of proteins.[54,56] In the REMPI spectrum, indole is the highest peak because of the high selectivity of the method, whereas most of the other (protein) decomposition products do not appear. In the REMPI mass spectra of wheat bran and hay (bottom part), considerable indole peaks occur, too. In both graphs, the highest peak is observed for 4-vinylguaiacol (m/z 150), but they are well distinguished by the higher signal intensities of 4-vinylphenol, guaiacol, and (iso)eugenol in the case of hay.

To exemplify the course of pyrolysis gas measurements and the process variations, SPI–MS mass traces, recorded during a continuous run of the flash pyrolysis unit with subsequent introduction of Miscanthus, wheat straw, oil palm fronds (OPF), hay, and rice straw as feedstock at a pyrolysis temperature of 550 °C are shown in Figure 6. The selected nominal masses demonstrate the varied signal intensity ratios

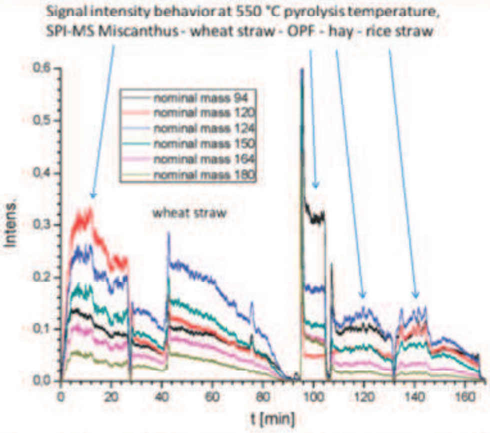

Figure 6. Course of pyrolysis gas SPI–MS measurements of Miscanthus, wheat straw, oil palm fronds (OPF), hay, and rice straw at a pyrolysis temperature of 550 °C.

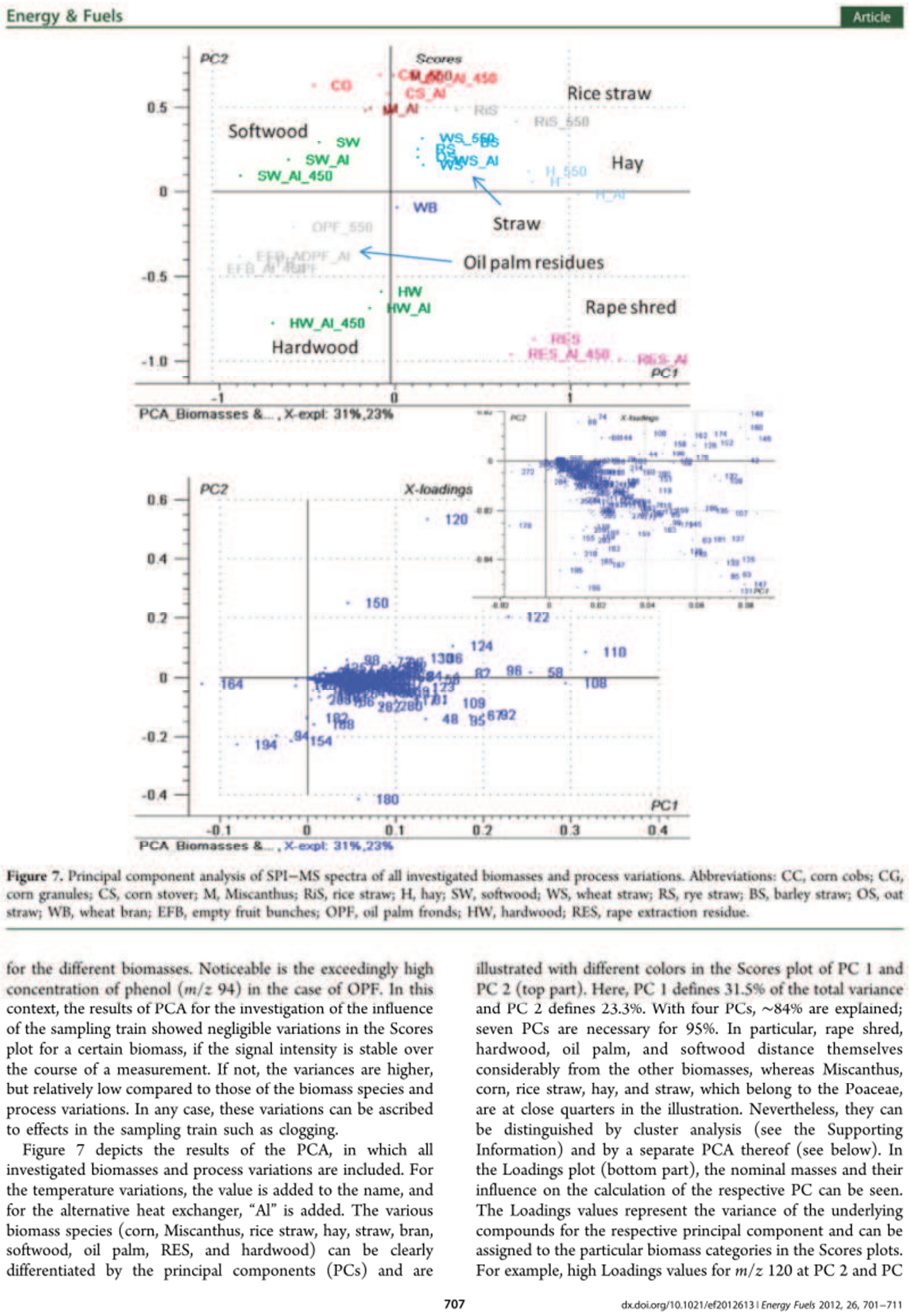

Figure 7. Principal component analysis of SPI−MS spectra of all investigated biomasses and process variations. Abbreviations: CC, corn cobs; CG, corn granules; CS, corn stover; M, Miscanthus; RiS, rice straw; H, hay; SW, softwood; WS, wheat straw; RS, rye straw; BS, barley straw; OS, oat straw; WB, wheat bran; EFB, empty fruit bunches; OPF, oil palm fronds; HW, hardwood; RES, rape extraction residue.

for the different biomasses. Noticeable is the exceedingly high concentration of phenol (m/z 94) in the case of OPF. In this context, the results of PCA for the investigation of the influence of the sampling train showed negligible variations in the Scores plot for a certain biomass, if the signal intensity is stable over the course of a measurement. If not, the variances are higher, but relatively low compared to those of the biomass species and process variations. In any case, these variations can be ascribed to effects in the sampling train such as clogging.

Figure 7 depicts the results of the PCA, in which all investigated biomasses and process variations are included. For the temperature variations, the value is added to the name, and for the alternative heat exchanger, "Al" is added. The various biomass species (corn, Miscanthus, rice straw, hay, straw, bran, softwood, oil palm, RES, and hardwood) can be clearly differentiated by the principal components (PCs) and are illustrated with different colors in the Scores plot of PC 1 and PC 2 (top part). Here, PC 1 defines 31.5% of the total variance and PC 2 defines 23.3%. With four PCs, ~84% are explained; seven PCs are necessary for 95%. In particular, rape shred, hardwood, oil palm, and softwood distance themselves considerably from the other biomasses, whereas Miscanthus, corn, rice straw, hay, and straw, which belong to the Poaceae, are at close quarters in the illustration. Nevertheless, they can be distinguished by cluster analysis (see the Supporting Information) and by a separate PCA thereof (see below). In the Loadings plot (bottom part), the nominal masses and their influence on the calculation of the respective PC can be seen. The Loadings values represent the variance of the underlying compounds for the respective principal component and can be assigned to the particular biomass categories in the Scores plots. For example, high Loadings values for m/z 120 at PC 2 and PC

4 (see the Supporting Information) correlate with corn and Miscanthus in the Scores plots (same position in the respective plot); in contrast, the *m*/*z* value of 164 has high negative values for PC 1 and PC 4, correlating with softwood. The most important pyrolysis products and their significance for certain biomasses are listed in Table 1. Additionally, a short ranking list (Table 2) represents their importance to the PCA calculation.

Table 2. Ranking List (PCS calculation) of the Biomass Pyrolysis Products with Nominal Masses and Detectability with REMPI at a Wavelength of 266 nm

priority	nominal mass	biomass pyrolysis products	ionization with REMPI at 266 nm[a]
1	120	4-vinylphenol	++
2	94	phenol	++
3	180	4-vinylsyringol/coniferyl alcohol/ guaiacylacetone/propioguaiacone	+++
4	194	allylsyringol	++
5	124	guaiacol	++
6	110	5-methylfurfural/catechol	−/+
7	164	(iso)eugenol	+++
8	122	xylenol/ethylphenol/methylanisole	++
9	150	4-vinylguaiacol	+++
10	108	methylphenol (cresol)/anisole	++
11	154	syringol	
12	92	toluene	++
13	95	pyridinol	
14	138	4-methylguaiacol	+
15	67	pyrrole	
16	58	acetone	
17	98	dihydromethylfuranone/2-furanmethanol	
18	48	methanethiol	
19	96	furfural	
20	168	methylsyringol	+

[a]Abbreviations: +, moderate; ++, good; +++, very good.

Furthermore, the Scores plots reveal a substantial influence in the pyrolysis temperature on the SPI−MS spectra, but the differences cannot be related to certain substances with regard to all biomasses. The alternative heat exchanger, on the other hand, leads to only marginal differences in the pyrolysis gas composition, which is confirmed by cluster analysis that precisely differentiates the 10 biomass species irrespective of the heat exchanger material (see the Supporting Information). In contrast, the differences for the temperature variations are too large and have not been taken into account. These results coincide with the colors in the Scores plot, which represent the biomass species. For instance, all kinds of straw are classified in one group, whereas Miscanthus and corn are separated, although they exhibit similar mass spectra. For further illustration, Figure 8 shows a PCA, where only the Poaceae (without wheat bran) at a pyrolysis temperature of 500 °C are included in the calculation. Here, the involved biomass species are clearly separated in the Scores plot. The most relevant substances for the distinguishability are 4-vinylphenol (*m*/*z* 120), relating to corn and Miscanthus, and other members of the H group (*m*/*z* 94, 108, and 122), which can be found in the top left part of the Loadings plot, as well as the protein decomposition products (*m*/*z* 67, 81, 92, 95, 109, and 117), whicht are correlated with hay in the Scores plot (see also Figure 5). In contrast, the G group compounds (*m*/*z* 124, 138, 150, 164, and 180) in the bottom part can be assigned to straw and Miscanthus (see also Figures 3 and 4). For the sake of clarity in the Loadings plot, the calculation was conducted with the 30 key masses. Therefore, nearly no difference appeared, compared to the PCA with all masses.

■ DISCUSSION

In this paper, the application of soft photoionization mass spectrometry for on-line measurements of biomass pyrolysis gases is demonstrated with regard to the optimization of the bioliq process. In this manner, these results (especially of the PCA) can be combined with other findings within the process, viz., char yields, pyrolysis oil compositions, and biosyncrude consistency, that are important feedstock selection and process criteria and the subject of current investigations. Compared to our work, most studies of biomass pyrolysis in the literature focus on the identification of the products thereof as well as the elucidation of the biomass structure and kinetic aspects. Here, the distinguishability of the employed biomass feeds is shown, using H/G/S ratios on the basis of selected mass spectra. Furthermore, PCA and cluster analysis yield the different pyrolysis gas compositions for all employed biomasses and process variations. The applied analytical techniques imply that the mass peaks cannot be clearly assigned to certain compounds. For this reason, laboratory Py-GC−MS measurements were taken, whereby the lignin decomposition products could be confirmed and, furthermore, constitutional isomers could be detected, for example, eugenol and isoeugenol at *m*/*z* 164 or coniferyl alcohol, 4-vinylsyringol, guaiacylacetone, and propioguaiacone at *m*/*z* 180. In the past, the investigation of biomass pyrolysis products was mainly conducted via analytical (Curie-point) Py-GC−MS, too. Altogether, these studies support and complement our mass assignments.

With both photoionization techniques shown here, fragmentation free mass spectra can be obtained, masking out the matrix gases, but then small molecules, which could be of interest, such as acetic acid or acetaldehyde, also cannot be detected with the current measurement setup. However, with other rare gas (mixtures) in the VUV light source, higher photon energies are achievable. On the other hand, the high REMPI selectivity leads to clear mass spectra; therefore, a process monitoring only four to six masses would be possible, particularly with regard to the good detectability of most of the key substances (see Table 2) with REMPI. For example, the nominal masses of *m*/*z* 117, 120, 124, 164, and 180 are sufficient for the differentiation of rape shred, wheat bran, and hay (see Figure 5).

Because of the strongly differing ionization cross sections, it is difficult to compare the REMPI spectra at 266 nm with others obtained at different wavelengths, or in general with other soft (photo) ionization techniques. Furthermore, this could distort the results of statistical analysis, especially the PCA. In any case, the selectivity of REMPI can provide additional information for mass assignment. For example, the peaks at *m*/*z* 280 and 282 appear in only the SPI−MS spectrum of rape extraction residue (Figure 5); therefore, nonaromatic compounds such as phytene and phytane are supposable.

With regard to the relative content of the three monomeric lignin precursor groups (H, G, and S), the ratio or the percentage could be correlated with the properties of the biosyncrudes. However, the S/G ratio of a certain biomass differs from that of lignins obtained in a different manner thereof and also depends on the analysis technique. For example, our calculated values for

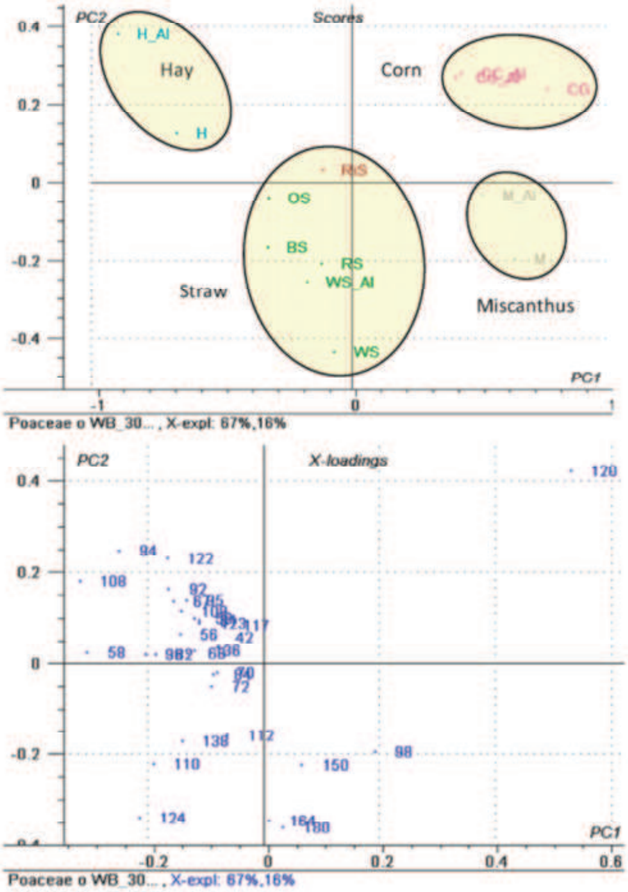

Figure 8. PCA of SPI−MS spectra of Poaceae at a pyrolysis temperature of 500 °C.

wood are comparable with FTIR analyses but smaller than that observed by Py-GC−FID measurements.[13,49] This may also be the result of excluding the mass of 180 from the calculations, which comprises S and G compounds, especially 4-vinylsyringol in the case of hardwood. Note that the PCA-ranking of the biomass pyrolysis products (Table 2) depends on the included feedstock. In general, the PCA Loadings values open up a facile path for creating such position tables and for reducing the number of variables; in our case, however, fewer nominal masses did not lead to better results, as tested with 20 and 50 variables (masses), and with 30 masses in the case of the Poaceae, but this enhances the clarity of the Loadings plot (see Figure 8). At the technical pyrolysis plant, only limited temperature variations have been feasible. To study the influence of temperature on the pyrolysis gases, further investigations are necessary. For this purpose and for comparison with the technical process, the results of measurements on a small laboratory pyrolysis oven without a filter line, including wider pyrolysis temperature variations, will be presented in a forthcoming publication. These data and the mass spectra from the flash pyrolysis plant could be the basis for further investigations of lignins, too, especially for the barely examined biomasses like Miscanthus or rape shred.

■ CONCLUSION

The employed soft photoionization techniques in combination with time-of-flight mass spectrometers have proven to be a suitable method for the on-line analysis of ultra-complex gas mixtures such as the biomass pyrolysis gases investigated here. These consist of (hemi)cellulose decomposition products (Table 1) and typical lignin decomposition products, mainly guaiacol, syringol, and their derivatives. The ratio of phenol derivatives varies with regard to different lignin structures of the miscellaneous biomasses. For certain biomass feedstocks, nitrogen-containing substances were also detected, especially N-heterocyclic compounds such as pyrrole or indole. In general, the mass spectra of the investigated pyrolysis gases show different patterns for the miscellaneous biomasses, which could be pointed out by means of PCA. With SPI, all organic

molecules with ionization energies of <9.81 eV can be ionized without fragmentation. With REMPI at 266 nm, the lignin-derived phenolic components (especially members of the G group) and indole can be detected selectively. The potential for process control monitoring as well as research and development applications is apparent, especially if selected target masses would be monitored to distinguish between different process conditions (e.g. feedstocks, temperatures, mechanical parameters such as the rotation frequency of the twin-screws, etc.) in real time. This finally should allow a fast prediction of the quality and properties of the condensed pyrolysis products as a function of process parameters. However, the correlations between the measured transient products and the composition of the obtained biooil need to be investigated in more detail in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional data and observations. This material is available free of charge via the Internet at http://pubs.acs.org.

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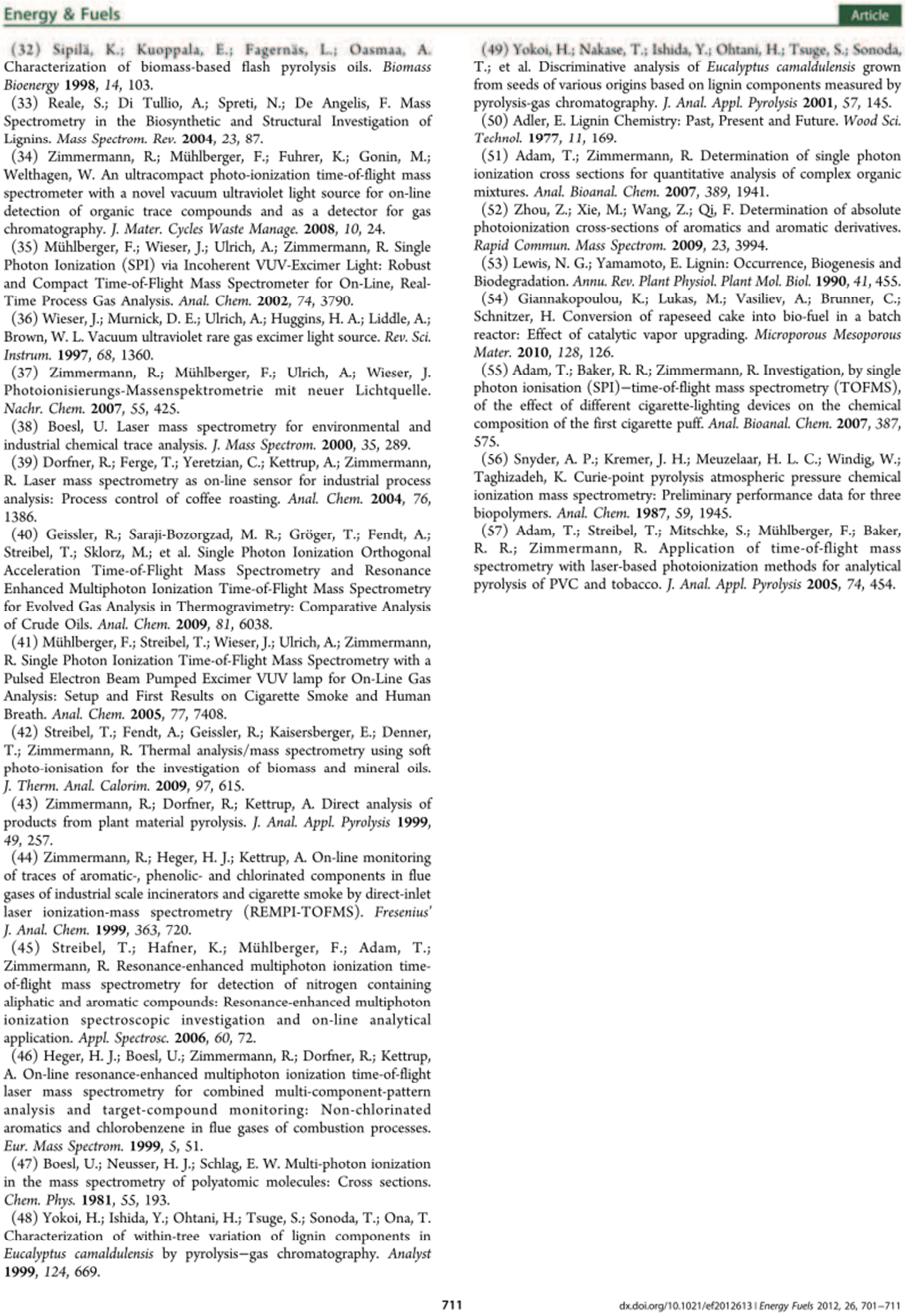

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4.2 Hyphenation of two simultaneously employed soft photo ionization mass spectrometers with Thermal Analysis of biomass and biochar (Publication 2)

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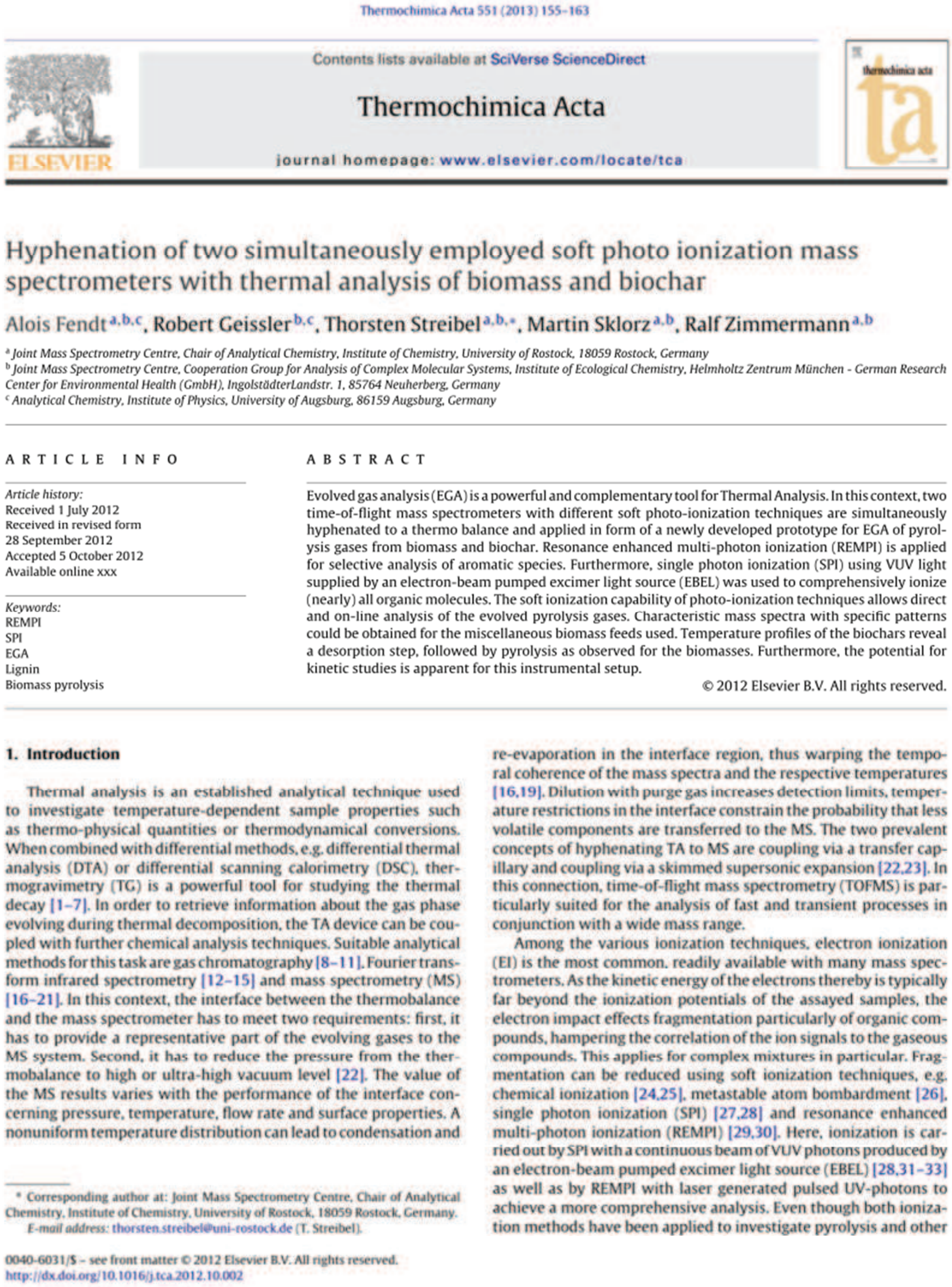
By: Alois Fendt, Robert Geissler, Thorsten Streibel, Martin Sklorz and Ralf Zimmermann

Alois Fendt was involved in development of the method and achieved a substantial part of the preparations and of the measurements. He accomplished the most part of data analysis and the manuscript and contributed to discussions. His own share accounts to approximately 60 %.



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Hyphenation of two simultaneously employed soft photo ionization mass spectrometers with thermal analysis of biomass and biochar

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ABSTRACT

Evolved gas analysis (EGA) is a powerful and complementary tool for Thermal Analysis. In this context, two time-of-flight mass spectrometers with different soft photo-ionization techniques are simultaneously hyphenated to a thermo balance and applied in form of a newly developed prototype for EGA of pyrolysis gases from biomass and biochar. Resonance enhanced multi-photon ionization (REMPI) is applied for selective analysis of aromatic species. Furthermore, single photon ionization (SPI) using VUV light supplied by an electron-beam pumped excimer light source (EBEL) was used to comprehensively ionize (nearly) all organic molecules. The soft ionization capability of photo-ionization techniques allows direct and on-line analysis of the evolved pyrolysis gases. Characteristic mass spectra with specific patterns could be obtained for the miscellaneous biomass feeds used. Temperature profiles of the biochars reveal a desorption step, followed by pyrolysis as observed for the biomasses. Furthermore, the potential for kinetic studies is apparent for this instrumental setup.

1. Introduction

Thermal analysis is an established analytical technique used to investigate temperature-dependent sample properties such as thermo-physical quantities or thermodynamical conversions. When combined with differential methods, e.g. differential thermal analysis (DTA) or differential scanning calorimetry (DSC), thermogravimetry (TG) is a powerful tool for studying the thermal decay [1–7]. In order to retrieve information about the gas phase evolving during thermal decomposition, the TA device can be coupled with further chemical analysis techniques. Suitable analytical methods for this task are gas chromatography [8–11], Fourier transform infrared spectrometry [12–15] and mass spectrometry (MS) [16–21]. In this context, the interface between the thermobalance and the mass spectrometer has to meet two requirements: first, it has to provide a representative part of the evolving gases to the MS system. Second, it has to reduce the pressure from the thermobalance to high or ultra-high vacuum level [22]. The value of the MS results varies with the performance of the interface concerning pressure, temperature, flow rate and surface properties. A nonuniform temperature distribution can lead to condensation and re-evaporation in the interface region, thus warping the temporal coherence of the mass spectra and the respective temperatures [16,19]. Dilution with purge gas increases detection limits, temperature restrictions in the interface constrain the probability that less volatile components are transferred to the MS. The two prevalent concepts of hyphenating TA to MS are coupling via a transfer capillary and coupling via a skimmed supersonic expansion [22,23]. In this connection, time-of-flight mass spectrometry (TOFMS) is particularly suited for the analysis of fast and transient processes in conjunction with a wide mass range.

Among the various ionization techniques, electron ionization (EI) is the most common, readily available with many mass spectrometers. As the kinetic energy of the electrons thereby is typically far beyond the ionization potentials of the assayed samples, the electron impact effects fragmentation particularly of organic compounds, hampering the correlation of the ion signals to the gaseous compounds. This applies for complex mixtures in particular. Fragmentation can be reduced using soft ionization techniques, e.g. chemical ionization [24,25], metastable atom bombardment [26], single photon ionization (SPI) [27,28] and resonance enhanced multi-photon ionization (REMPI) [29,30]. Here, ionization is carried out by SPI with a continuous beam of VUV photons produced by an electron-beam pumped excimer light source (EBEL) [28,31–33] as well as by REMPI with laser generated pulsed UV-photons to achieve a more comprehensive analysis. Even though both ionization methods have been applied to investigate pyrolysis and other

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thermal processes before [16,31,34–40], the simultaneous hyphenation, in particular to Thermal Analysis, is novel. REMPI utilizes a two photon absorption, whereby the one photon energy is in resonance with an excited electronic state, from which the absorption of the second photon can lead to ionization, if the combined energy of the two photons matches the ionization potential of the molecule. The applied wavelength strongly influences the ionizability of the investigated molecules [30,41–43]; in the UV range, for example, this scheme is selective for (poly)aromatic compounds. In contrast, single photon ionization is a more "universal", semi-selective ionization technique, since all compounds are ionized whose ionization potentials are below the energy of the applied VUV photon. Both – REMPI and SPI – lead to soft mass spectra depicting in many cases only molecular ions and, moreover, masking out omnipresent small matrix molecules, particularly nitrogen and carbon dioxide.

Up to now, thermal analysis has been employed for a plethora of applications. Measurements related to this work have been conducted by, e.g. Müller-Hagedorn et al. [44,45] for the studies on different wood species and other biomasses. Pyrolysis of biomass and their major components has been investigated by Gani et al. [46] as well as by Várhegyi et al. [47,48] using a thermogravimetric analyzer. The effect of heating rate on the pyrolysis yields of rapeseed [49] was tested by Haykiri-Acma et al. A detailed kinetic modeling of thermal degradation of biomasses [50] is described by Frassoldati et al. However, most experiments do not employ and focus on EGA, respectively.

The aim of this paper is to point out the simultaneous coupling of two soft photo ionization mass spectrometers as a proof of principle and to illustrate the respective evolved pyrolysis gas characteristics for different biomass and biochar samples. The quality of biochar is a major process and, with regard to the biomasses, feedstock selection criterion in the production of biofuels. Furthermore, as inartificial samples may show irreproducible results, it suggests itself to conduct relevant measurements in one go. Photo ionization in combination with time-of-flight mass spectrometry allows fast, direct and on-line measuring of the pyrolysis gases, whereas the customarily employed electron ionization (EI) would lead to fragmentation of the molecules and make an interpretation of the resulting mass spectra in this complex mixture nearly impossible.

In this connection, on-line measurements at a flash pyrolysis pilot plant at the Karlsruhe Institute of Technology (KIT), North Campus, have been presented recently [51]. There, a process has been developed to achieve the so-called second generation of fuels and chemicals out of waste biomass. The first step in this "biomass to liquid" (bioliq® or BTL in general) process [52–55] is a flash-pyrolysis of biomass at 500 °C in a twin screw mixer with a heat transfer material such as hot sand. Subsequently, the evolving pyrolysis gases are condensed and immingled with the remaining char, providing the so-called biosyncrude or bioslurry, which is pump- and storable. At this juncture, the characterization of the biochars could be of note for the optimization of this process.

2. Materials and methods

In the context of this work, a STA 409 PG Luxx thermobalance (Netzsch Gerätebau GmbH, Selb, Germany) has been used. The samples have been processed with a heating rate of 10 K/min from 40 °C to 800 °C in an aluminum oxide crucible (6 mm in diameter) in nitrogen atmosphere. The nitrogen flow through the sample chamber was set to 60 ml/min with 20 ml/min protection gas and 40 ml/min purge gas. For the parallel sampling of the evolved gases, a splitter in the form of a heatable aluminum casing, that allows the lead-through of two capillaries into the sampling region over the crucible has been coupled to the TAfor simultaneous gas analysis with the SPI- and REMPI-TOF mass spectrometers. At the TA end, an ad hoc designed heatable aluminum adapter with a tubular copper core [19] encloses the capillary. This configuration has shown its suitability even with tailing-prone substances like heptadecane [19]. The coupling of the mass spectrometric systems to the thermobalance was carried out via deactivated 250 °C heated fused silica capillaries with a length of 2.1 m and inner diameters of 150 μm and 200 μm, respectively, which proceed in heating hoses from the heated aluminum casing to the inlet system of the ionization source of the mass spectrometers.

The instrumental setup is shown in Fig. 1. The mobile REMPI mass spectrometer on the left side consists of a laser cabinet containing a Nd:YAG laser with two frequency-doubling units for the generation of $\lambda = 266$ nm (BIG SKY ULTRA, Quantel, Les UlisCedex, France), and the ion source with the mass spectrometer (ReflectronCTF10,KaesdorfGerätefürForschung und Industrie, Munich, Germany), which are both evacuated by turbo molecular pumps. Furthermore, several electronic devices for instrument control and data acquisition are mounted in 19-in. racks (vacuum and heat control units, DAQ computer, high-voltage supplies for the mass spectrometer). Every 5 s a mass spectrum has been obtained, using a laser repetition rate of 10 Hz and a averaging of 50 single spectra. To the right of the thermobalance (in the middle), the SPI-MS system is arranged, that consists of an orthogonal acceleration TOF-MS (C-TOF, TOFWERK AG, Thun, Switzerland), which is particularly suited for the use of continuous light sources like the EBEL due to the special type of construction with pulsed (around 70 kHz) orthogonal extractor plates [28,56]. This allows for an acceleration

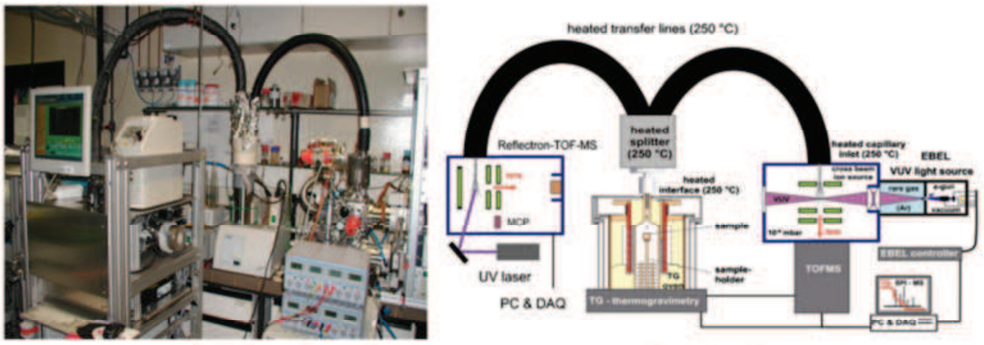

Fig. 1. Picture and scheme of both photoionization mass spectrometers coupled to the thermobalance.

Table 1
Mass assignment of the most important biomass pyrolysis products and detectability with REMPI at 266 nm wavelength (+ moderate, ++ good, +++ very good).

Nominal mass	Biomass pyrolysis products	Ionization with REMPI@266 nm
42	Propene	
48	Methanethiol	
58	Acetone	
67	Pyrrole	
68	Furan/isoprene	
72	2-oxo-Propanal/2-butanone	
74	Hydroxy-propanal/-propanone	
82	Methylfuran/2-cyclopenten-1-one	
86	23-Butanedione/tetrahydrofuran-3-one	
92	Toluene	++
94	Phenol	++
95	Pyridinol/dialkylpyrroles	
96	Furfural	
98	Dihydro-methyl-furanone/2-furanmethanol	
108	Methylphenol(cresol)/anisole	++
110	5-Methylfurfural/catechol	-/+
112	Methyl-dihydro-pyranone/hydroxy-pyranone	
117	Indole	+++
120	4-Vinylphenol	++
122	Dimethylphenol/ethylphenol/methylanisole	++
124	Guaiacol	++
126	5-Hydroxymethylfurfural/maltol/levoglucosenone	
131	Methyl-indole	++
138	4-Methylguaiacol	+
140	23-Dihydroxyanisole	
150	4-Vinylguaiacol	+++
152	Vanillin/4-ethylguaiacol	+
154	Syringol	
164	(Iso-)Eugenol(eugenicacid)	+++
166	4-Propylguaiacol/4-acetylguaiacol	+
168	Methylsyringol	+
178	Coniferylaldehyde/methyleugenol	+
180	4-Vinylsyringol/coniferylalcohol/guaiacylacetone/propioguaiacone	+++
182	Syringaldehyde/trimethoxytoluene	+
194	Allylsyringol	++

trajectory component that is linearly independent from the inherent spatial distribution of the ions after the extraction from the continuous ion source which would affect the mass resolution and accuracy in non-orthogonal TOF builds. The acquisition unit is of similar construction as for the REMPI-TOF. An Acqiris AP 240 card (Agilent Technologies, Plan-les-Ouates, Switzerland, 1–2 GS/s) is used to average and record the spectra gained from the TOF-MS. For an increased dynamic range of the ion signal strength, the card features two input channels. 62,500 spectra are collected and averaged, resulting in around one recorded spectrum per second. This speed allows for a mass range width up to *m*/*z* 410.

For single photon ionization a home-made EBEL-VUV light source was used whose main innovation is a 0.7 mm × 0.7 mm ceramic silicon nitride (SiNx) foil of only 300-nm thickness that separates the rare gas volume ($p > 1$ bar) from a vacuum chamber containing an electron gun. The latter generates a 12 keV electron beam which penetrates into the rare gas through the SiNx foil with low-energy loss. The energetic electrons excite and ionize the rare gas atoms. In successive processes excited diatomic rare gas molecules (excimers) are formed. Upon the radiative decay of these rare gas excimers VUV-radiation is emitted. As a result of the high gas pressure the excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The rare gas volume was filled with argon with an emission maximum at 126 nm (9.8 Ev centre photon energy available for ionization). In principles it is possible to vary the ionization energy by replacing the argon filling with other rare gases or rare gas mixtures thus enhancing the selectivity of VUV ionization. The decay of heavier noble gas excimers yields photons of lower energies than the decay of lighter noble gas excimers. The emitted light is first collimated and then focused on the effusive gas inlet with two MgF_2 lenses (Korth Kristalle GmbH Altenholz (Kiel), Germany). The EBEL was filled with argon of purity 5.0 and was purified over the complete measurement period using a heated gas getter (SAES Getters S.p.A. Lainate (MI), Italy). The Nd:YAG laser for REMPI@266 nm features 10 ns pulse width and approximately 7E+06 W/cm^2 power density. Despite this wavelength being highly selective for a romatic compounds one has to take into account that the ionization cross sections [57] of the compounds may differ widely. The investigated samples – wheat straw (9.5 mg weighted sample) soft- and hardwood (12.0 and 24.7 mg) rape extraction residue (49.7 mg) as well as chars of pyrolyzed wheat straw (22.1 mg) and soft- and hardwood (45.2 and 44.3 mg) – have been employed and produced respectively in the above mentioned technical pyrolysis plant at the KIT.

3. Results and discussion

The mass spectra obtained by the evolved pyrolysis gas measurements revealed a series of pyrolysis products; the most important ones are listed in Table 1 at which only substances with ionization energies below 9.81 eV have been taken into account. Polyaromatic hydrocarbons appearing at higher temperatures are not listed here (see [39]). As a matter of course most of the mass spectrometric peaks comprise several compounds due to structural isomers and nominal mass processing. The assignment of the mass peaks was carried out by literature studies as well as by own Py-GC/MS measurements with a double-shot pyrolyzer [51]. In literature [58–62] pyrolysis decomposition products of laboratory works have been characterized showing a series of furan derivatives ketones and aldehydes from cellulose and other polysaccharides (hemicellulose) as well as phenol derivatives from lignin decomposition such as guaiacol and syringol and their derivatives.

In Fig. 2, REMPI and SPI mass spectra of wheat straw are depicted by comparison. In the color-coded intensity plots (upper part) it becomes apparent that REMPI-MSis particularly suited for higher masses (see also Table 1), whereas SPI covers the lower mass range, too. Furthermore, this kind of plot provides first information about the relevant pyrolysis temperature range. Hereunder, the respective mass spectra at 300 °C are presented. Thereby, high mass peaks can be seen for the aforementioned phenol derivatives

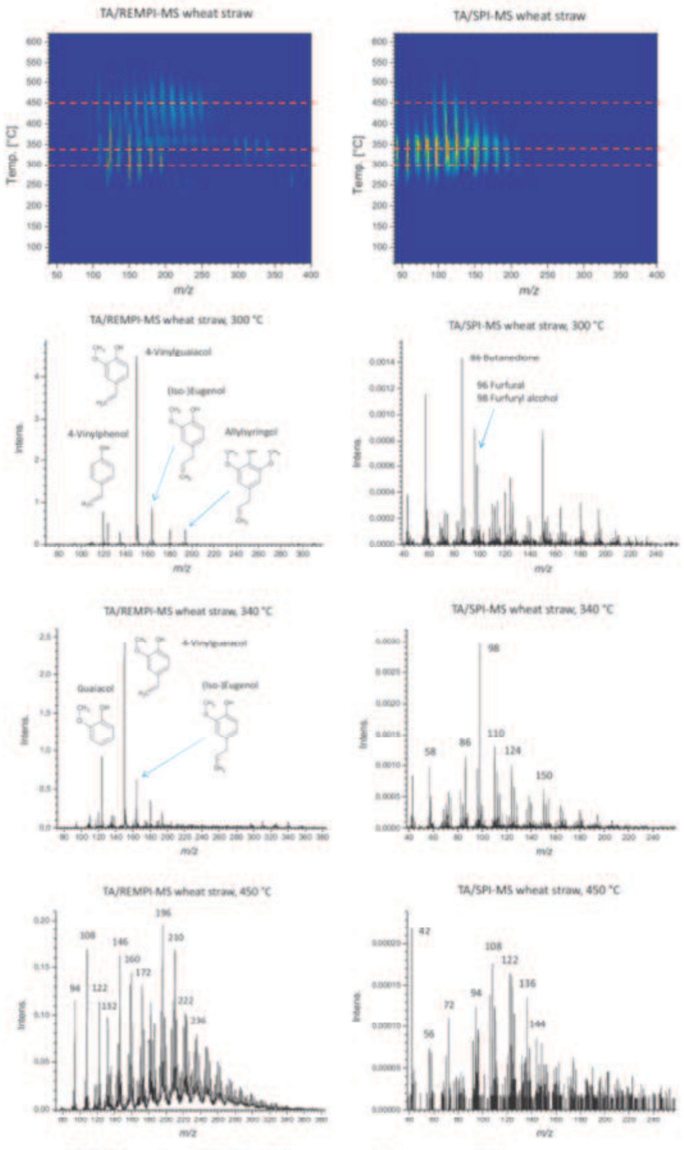

Fig. 2. Comparison of REMPI and SPI mass spectra of wheat straw at different temperatures.

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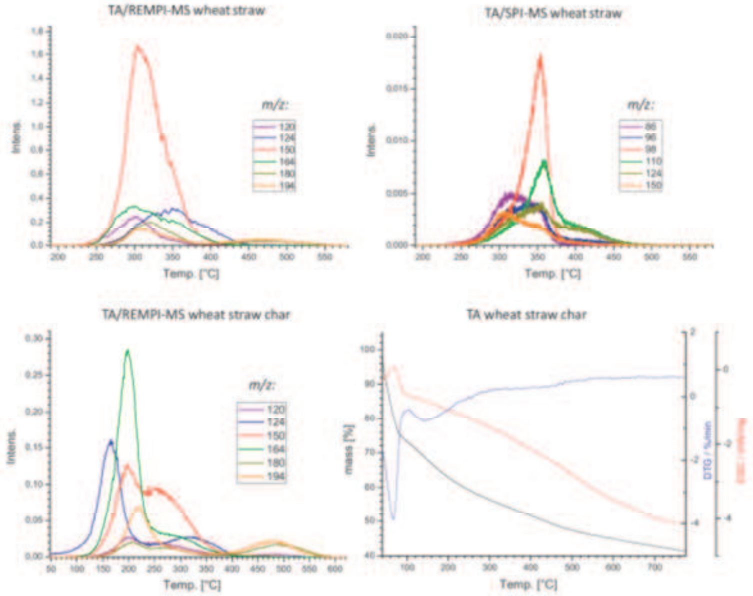


Fig. 3. Temperature profiles of wheat straw (char) and thermoanalytical plot.

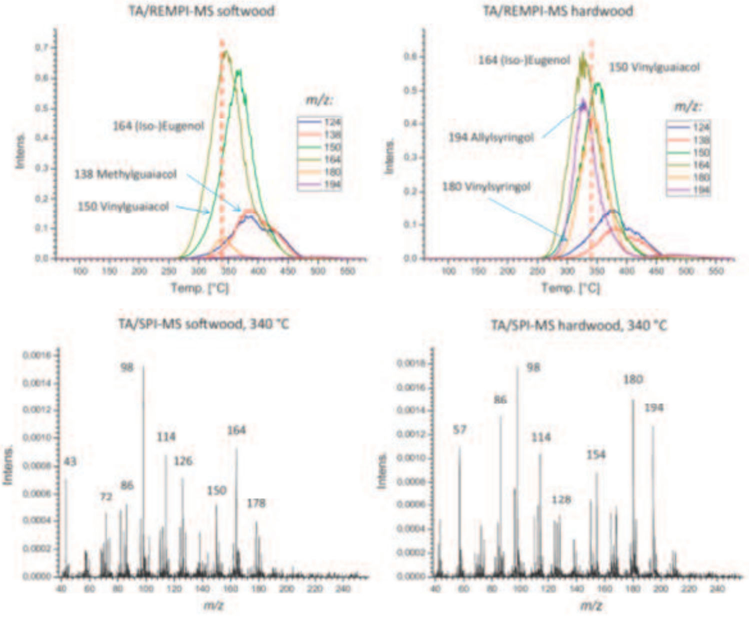


Fig. 4. Temperature profiles of soft- and hardwood and the respective SPI mass spectra at 340 °C.

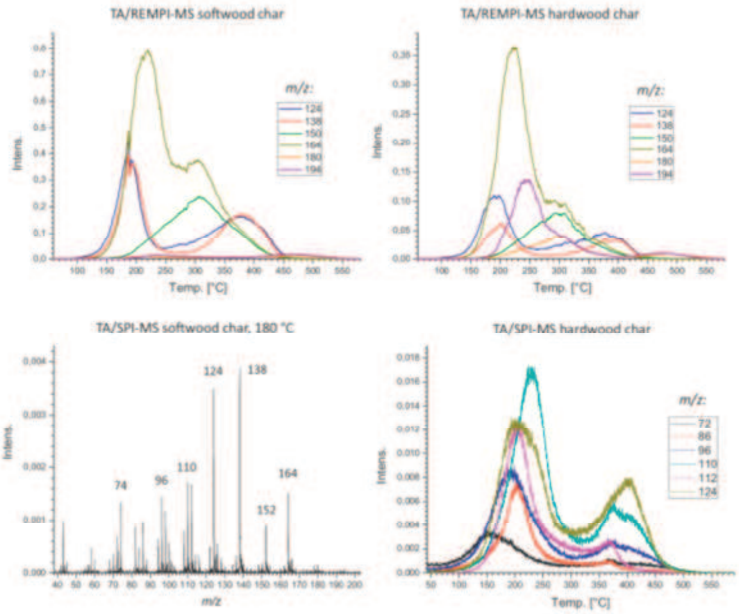


Fig. 5. Temperature profiles of soft- and hardwood chars and the respective SPI mass spectrum at 180 °C.

in case of REMPI ionization (left side). For SPI (right side), additionally the polysaccharide-derived compounds appear. Please note that the cross sections for SPI are within the same order of magnitude [63,64] (especially for similar molecules and higher masses), but not in case of REMPI [57]. Therefore it is deceivable to suggest concentration levels of substances on their respective signal intensities alone without considering the REMPI ionization cross sections. The REMPI and SPI mass spectra obtained at subsequent temperatures are shown in the lower part. Thereby, in the REMPI spectrum particularly the signal intensity ratio of 4-vinylphenol and guaiacol changes from 300 °C to 340 °C. Whereas only the lignin decomposition products can be seen here, mainly (hemi-)cellulose decomposition products appear in the SPI spectrum, particularly nominal masses 58, 86, 96, 98, 110 and 112. Their ratio also changes with increasing temperature. At even higher temperatures (around 450 °C), a completely different pattern with a wide variety of (poly-)aromatics arises (see also Sharma et al. [65]), albeit at low intensity level). By all means, REMPI is particularly suited for highly sensitive detection of polyaromatic compounds. In the SPI spectrum, propene (*m*/*z* 42) as predominant peak, as well as other small molecules can be seen in addition.

In the (REMPI and SPI) temperature profiles of wheat straw (Fig. 3, upper part), signal intensities of certain compounds show different maxima for the respective masses, starting from around 300 °C up to 360 °C. Interestingly, especially nominal mass 98 (a furan derivative and typical cellulose decomposition product) in the SPI-MS spectrum demonstrates the higher temperature stability as well as the faster decay of cellulose [66,67], compared to lignin as exhibited in the REMPI-MS spectrum. There, the signal intensity maxima emerge at significantly lower temperatures. Additionally, slight differences can be seen within the respective group. In general, these plots depict the different decomposition behavior of the biomass basic constituents and allow a valuation of their composition. In the lower part, the REMPI plot of wheat straw char shows signal intensity maxima at considerably lower temperatures in most cases, indicating a desorption step of pyrolysis products. A second maximum occurs in some cases, relating to the pyrolysis step, and the formation of polyaromatics at higher temperatures, respectively. Generally, the maxima and the signal intensity ratios completely differ from that of wheat straw. For comparison, the thermoanalytical plot of wheat straw char is displayed on the right side with the mass signal in black, its first derivative in blue and the DSC (differential scanning calorimetry) signal in red. In the shown plot, two extrema occur in the first derivative of the TG-signal at 67 °C and at 143 °C. The first and more distinct mass loss maximum coincides with an endothermic transition, whereas the second mass loss maximum features no such distinct DSC peak. The plot shows a two-step thermal decay of wheat straw char: The first, endothermic reaction with fast mass loss of ~25% occurs till 80 °C with its maximum at 67 °C, without much doubt caused by water. A more continuous and slower mass loss of another ~35% then occurs with its maximum at 143 °C, presumably effected by small organic molecules, that cannot be detected with our photo ionization methods. In contrast, the signal intensity maxima in the REMPI plot are different for every compound. Therefore, more detailed kinetic investigations are possible with the evolved gas analysis.

In Fig. 4 (upper part), temperature profiles of soft- and hardwood are shown. Thereby, the REMPI-MS data are chosen due to a better depiction compared to SPI, owing to greater differences in signal intensities by reason of highly varying cross sections of the underlying molecules. The respective SPI-MS spectra at 340 °C are listed in the lower part. The temperature profiles as well as the mass spectra clearly reflect the different lignin structures of soft- and hardwood [68–70] and the resultant varied thermal degradation products [61,71]. Especially the mass to charge ratios 86, 180 and 194 are substantially higher for hardwood, whereas *m*/*z* 126 and

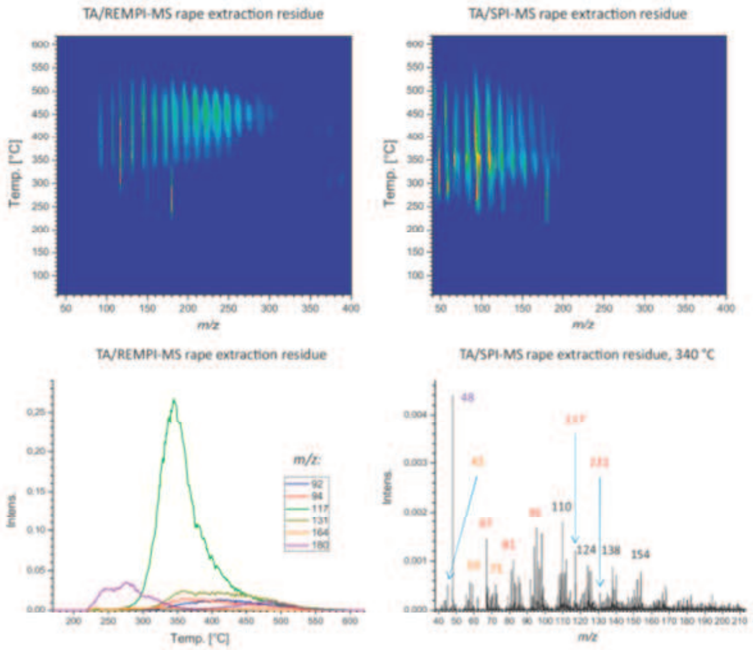


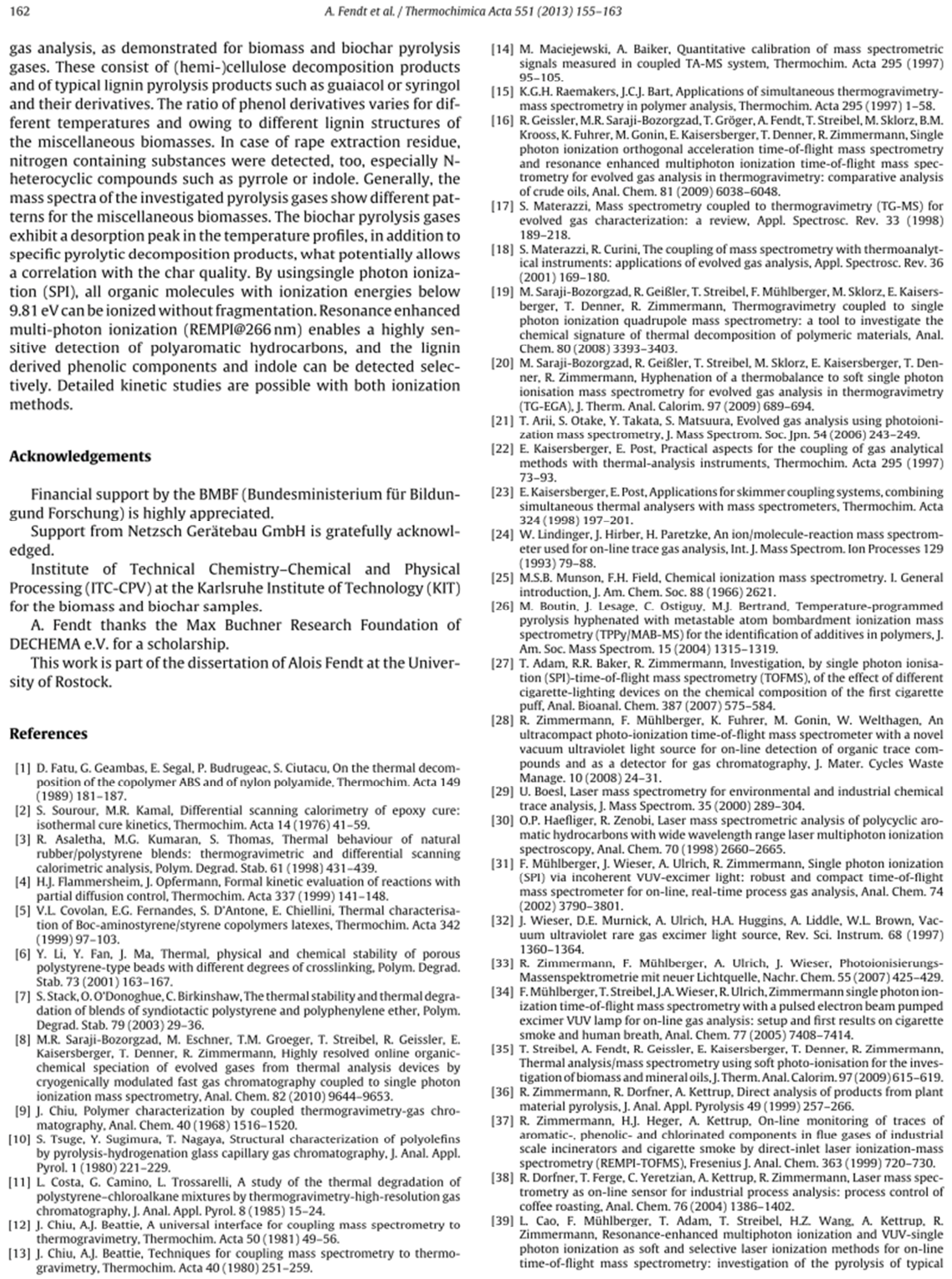
Fig. 6. REMPI and SPI temperature profiles/mass spectra of rape extraction residue.

178 are higher in case of softwood. Nominal masses 43 and 57 are thermal fragments of cellulose decomposition [27]. Strikingly, the signal intensity maxima altogether occur at higher temperatures compared to wheat straw due to the lower ash content [44,45]. REMPI-MS temperature profiles of soft- and hardwood chars are correspondingly shown in Fig. 5 (upper part), including the same major lignin decomposition products. The main differences of the two kinds of wood chars result from nominal masses 180 and 194 as well. Moreover, two maxima appear for most of the detected substances just as in case of wheat straw char. There, the signal intensities of those two masses lie in between soft- and hardwood. In the lower part, a SPI-MS spectrum of softwood char represents the evolved gas composition of the desorption step with maxima at around 180 °C, in principle depending on the molecular weight as a matter of course. That is also clearly apparent in the SPI-MS temperature profile to the right, as depicted by the curves, which are mainly representing polysaccharide decomposition products in this case. In this connection, an estimation of the adsorbed material compared to the net amount of char is possible with the applied analysis method, what could be an important criterion for subsequent use, e.g. in the production of biofuels.

Completely different compound classes arise in case of rape extraction residue (Fig. 6). In the REMPI-MS temperature profile (thereunder), indole (m/z 117) is the highest peak owing to the high selectivity of the method. Moreover, the signal intensity onset of mass to charge ratio 180 at already a temperature of approximately 220 °C and the occurrence of two or three peaks in the temperature profile indicates the existence of isomers at this nominal mass and possibly of an unknown substance. With our Py-GC/MS measurements, 4-vinylsyringol has been identified as main compound. A lot of new substances appear in the very complex SPI mass spectrum, most of which are formed by the decomposition of proteins [72,73]. Above all, nitrogen-containing compounds are very characteristic, e.g. ethyl- and higher substituted amines (orange marked) as well as pyrrole, pyridinol [72] and indole [36] (red font color). Interestingly, methane thiol [27] (purple) shows the highest signal intensity at 340 °C. Anyway, the REMPI- and SPI-MS spectra here again reflect the different characteristics of these ionization methods. The latter depict the whole width of organic pyrolysis products, whereas REMPI (at 266 nm) is highly selective for aromatic compounds, in part also for nitrogen-containing. Admittedly, the ionization efficiency is strongly varying, even for similar compound classes. Beyond that, a comparison of pyrolysis gases obtained at Thermal Analysis and flash pyrolysis processes is possible only to a certain extent due to distinct thermal decay mechanisms at TA and flash pyrolysis, respectively. In this context, the TA heating rate has an important influence on thermal decomposition [47,49,74,75], too. By all means, the mass spectrometric patterns of the major compounds are similar for both processes, but at around 340 °C in the course of the TA measurements, compared to flash pyrolysis at 500 °C. Considerably higher amounts of PAHs arise in case of Thermal Analysis at 500 °C and even earlier. The effect of different temperatures at flash pyrolysis conditions on biomass and components thereof will be presented in a forthcoming publication.

4. Conclusion

The employed hyphenation technique of Thermal Analysis with two soft photo ionization time-of-flight mass spectrometers using a heated splitter is a novel and well suited method for evolved



gas analysis, as demonstrated for biomass and biochar pyrolysis gases. These consist of (hemi-)cellulose decomposition products and of typical lignin pyrolysis products such as guaiacol or syringol and their derivatives. The ratio of phenol derivatives varies for different temperatures and owing to different lignin structures of the miscellaneous biomasses. In case of rape extraction residue, nitrogen containing substances were detected, too, especially N-heterocyclic compounds such as pyrrole or indole. Generally, the mass spectra of the investigated pyrolysis gases show different patterns for the miscellaneous biomasses. The biochar pyrolysis gases exhibit a desorption peak in the temperature profiles, in addition to specific pyrolytic decomposition products, what potentially allows a correlation with the char quality. By usingsingle photon ionization (SPI), all organic molecules with ionization energies below 9.81 eV can be ionized without fragmentation. Resonance enhanced multi-photon ionization (REMPI@266 nm) enables a highly sensitive detection of polyaromatic hydrocarbons, and the lignin derived phenolic components and indole can be detected selectively. Detailed kinetic studies are possible with both ionization methods.

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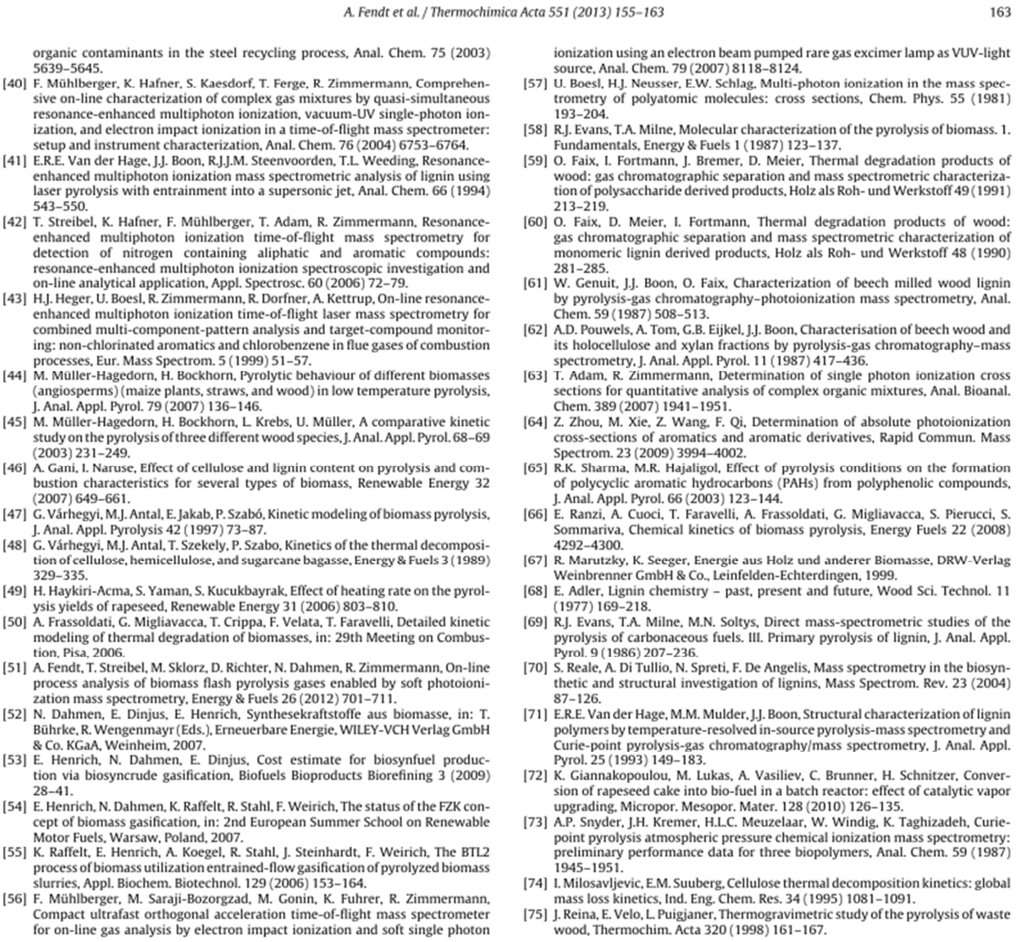

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4.3 Thermal analysis/mass spectrometry using soft photo-ionisation for the investigation of biomass and mineral oils (Publication 3)

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THERMAL ANALYSIS/MASS SPECTROMETRY USING SOFT PHOTO-IONISATION FOR THE INVESTIGATION OF BIOMASS AND MINERAL OILS

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The combined analytical methods of thermal analysis and mass spectrometry have been applied in form of a newly developed prototype of a thermogravimetry – single photon ionisation time-of-flight mass spectrometer coupling (TG-SPI-TOFMS) to investigate the molecular patterns of evolved gases from several biomass samples as well as a crude oil sample. Single photon ionization (SPI) was conducted by means of a novel electron beam pumped argon excimer lamp (EBEL) as photon source. With SPI-TOFMS various lignin decomposition products such as guaiacol, syringol and coniferyl alcohol could be monitored. Furthermore, SPI allows the detection of aliphatic hydrocarbons, mainly alkenes, carbonylic compounds such as acetone, and furan derivatives such as furfuryl alcohol and hydroxymethylfurfural. More alkaline biomass such as coarse colza meal show intense signals from nitrogen containing substances such as (iso-)propylamine and pyrrole. Thermal degradation of crude oil takes place in two steps, evaporation of volatile components and pyrolysis of larger molecular structures at higher temperatures. Due to the soft ionisation, homologue rows of alkanes and alkenes could be detected on basis of their molecular ions.

The obtained information from the thermal analysis/photo ionisation mass spectrometry experiments can be drawn on in comparison to the investigation of the primary products from flash pyrolysis of biomass for production of biofuels and chemicals.

Keywords: *biomass, crude oil, mass spectrometry, photo-ionisation, thermal analysis*

Introduction

In the vein of a sustainable energy and raw materials production, biomass may serve as the source for oil/coke slurries for the fabrication of synthesis gas as the first step of a process chain for the production of chemicals such as methanol and synthetic fuels. However, relatively little is known about the primary products in the pyrolysis off-gas or the mechanisms of the thermal decomposition of the various feedstock. In the framework of a joint project funded by the German ministry for education and research organic components of the flash pyrolysis off-gas from biomass produced by a flash pyrolysis experimental plant at Research Center Karlsruhe, Germany (throughput 10 kg h^{-1}) are currently investigated. As a preparatory study for this, the thermal decomposition of a large variety of vegetable educts has been investigated by means of thermal analysis/mass spectrometry.

For this purpose, a chemical analysis of the evolved gases is required, i.e. the thermogravimetry (TG) device has to be coupled to either a sequentially working analytical device such as gas chromatography/mass spectrometry (TG-GC/MS) [1] or an on-line real-time analytical technology. In the latter case Fourier-transform infrared spectrometry (FTIR) and mass spectrometry (MS) [2] may be applied. The coupling between the TG oven and the mass spectrometer is realised either via a transfer capillary or a skimmed supersonic expansion. However, the predominantly used mass spectrometric ionisation technique in this respect, electron ionisation (EI) exhibits some drawbacks when samples with larger complexity have to be investigated. This is mainly owed to the fact that the electrons used for ionisation are accelerated to energies of 70 eV, which exceeds the typical ionisation potentials of organic molecules (7–12 eV) to a great extent. As a consequence, the molecular ions are heavily fragmented upon ionisation. Since biomass material produces dozens of compounds at the same time when it is thermally decomposed, EI mass spectra tend to become very difficult to interpret.

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Soft photo ionisation utilizing UV or VUV photons for the production of molecular ions can serve as an alternative to overcome this disadvantage, since the photon energies are in the same region as the ionisation potentials of organic species. First thermal desorption studies, pyrolysis studies [3, 4] as well as TG studies using laser based soft ionisation mass spectrometry as detector [5] revealed that highly valuable information on the molecular signature of the thermal decomposition processes can be achieved. In this respect, a newly developed prototype of a TG-single photon ionisation time-of-flight mass spectrometer coupling (TG-SPI-TOFMS) is applied in this study. A novel electron beam pumped rare gas excimer VUV-lamp (EBEL) is used as a VUV photon source [6–8]. Such a device has recently been applied successfully in a TG-QMS coupling [9] for the investigation of thermal degradation of various polymers such as polyethylene and ABS.

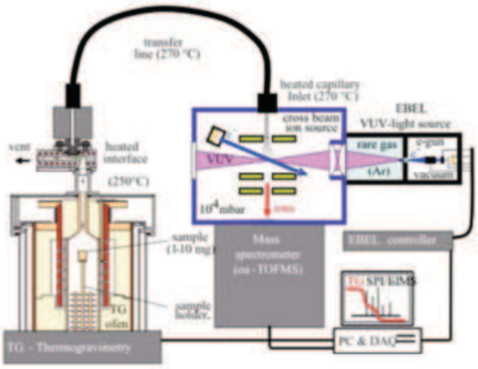


Fig. 1 Schematic representation of the TG-EBEL-SPI-oaTOFMS system

Experimental

The working principles of the EBEL [10] were described previously in the literature [7, 8] as well as the fundamentals on the coupling of the thermogravimetric analyzer to SPI mass spectrometric devices [9]. Briefly, a homebuilt EBEL-VUV light source was used for single photon ionisation in an orthogonal-accelerator (oa-)TOFMS system (C-TOF, Tofwerk, Thun, Switzerland). The main innovation of the novel EBEL-VUV light source is a 0.7·0.7 mm^2 ceramic silicon nitride (SiNx) foil of only 300 nm thickness that separates the rare gas volume (p>1 bar) from a vacuum chamber containing an electron gun (EG). The EG generates a 13-keV electron beam which is shot into the rare gas through the SiNx foil with low-energy loss. The energetic electrons excite and ionise the rare gas atoms. In successive processes, excited diatomic rare gas molecules (excimers) are formed. Upon the radiative decay of these rare gas excimers, VUV-radiation is emitted. As a result of the high gas pressure, the excimer formation occurs in a small volume in the close proximity of the electron entrance foil. The rare gas volume was filled with argon (emission maximum: 126 nm, 9.8 eV centre photon energy available for ionisation). The formed ions are drawn into the mass spectrometer and accelerated orthogonally to their original direction of movement into the filed free drift tube of the reflectron. The obtained single mass spectra are buffered on an Acqiris AP240 averager card. Each second, 62500 spectra are sent to the card and averaged. The averaged spectra, one per second, are stored on the HDD of the controlling computer. The available mass range with this acquisition rate is m/z=0…410, however, in this investigation the presented mass range is limited to 250 Dalton. The mass resolution with the used parameters is R=1000 according to the FWHM method.

The gas inlet of the oa-TOFMS was coupled via a heated transfer line (150 µm i.d.) to the TG system (Typ STA 409, Netzsch Gerätebau, Selb, Germany). A special heated adapter and deactivated transfer line (270°C) were developed for the TG-system to avoid memory effects from less volatile compounds. A scheme of the whole setup of the measurement device is shown in Fig. 1. Several biomass samples (beech wood (hard wood), a mixture of spruce and fir wood (soft wood), and coarse colza meal) were investigated. For comparison purposes, a fossil fuel (crude oil) was also studied under the same experimental conditions. All experiments were performed under nitrogen atmosphere with a heating rate of 10 K min^{-1}.

Results and discussion

The results of the TG/SPI-MS investigations of the various samples are presented in the following way: To get a comprehensive overview of the whole measurement, the data is depicted in a two-dimensional contour plot. The y-axis shows the temperature, while along the x-axis the m/z value is plotted. In this way the mass spectrometric signal recorded at the corresponding oven temperature can be seen at one glance for the complete thermal degradation. The respective intensity of the mass signal is depicted as false colour display. In addition to the two-dimensional plot, a profile at a certain temperature is shown as an example of a single mass spectrum. In principle at every temperature such a mass spectrum can be derived, the here presented spectra serve as an exemplary case to demonstrate the possibilities of the data acquisition routines. Please note that this paper focuses solely on the mass spectrometric results of the combined TG/MS approach, therefore, no TG or DSC curves are presented. This data will be discussed in a forthcoming publication, where the TG results of various samples such as crude oils, biomass, coal and plastics will be compared.

In Fig. 2 the accordant spectra of the hard wood sample are depicted. From the two-dimensional plot it can be seen that at a temperature of approximately 250°C first volatile organic compounds are evolving from the wood, which could be assigned amongst others to unsaturated hydrocarbons such as propene (*m/z* 42), carbonyls such as acetone (*m/z* 58), and aromatics such as phenol (*m/z* 94). The latter is a typical decomposition product of lignin, which itself mainly consists of ether bridged phenolic units. Other lignin derived products are dominating the mass spectrum in the *m/z* range above 100. This is entailing compounds such as guaiacol (*m/z* 124), methylguaiacol (*m/z* 138), vinylguaiacol (*m/z* 150), syringol (*m/z* 154), eugenol (*m/z* 164), coniferyl alcohol (*m/z* 180), and propenylsyringol (*m/z* 194). The detection of both derivatives from coniferyl alcohol and synapyl alcohol reflects the composition of hard wood lignin, which is assembled of phenolic units originating from these two basic structures. In addition to the lignin derived species, some decomposition products from cellulose could also be identified, namely furfuryl alcohol (*m/z* 98) and hydroxymethylfurfural (*m/z* 126). Above a temperature of 500°C, no evolving wood components could be detected anymore with the utilized measurement technique.

Figure 3 depicts the similar graphs for the soft wood sample. At first glance, the two-dimensional contour plot looks almost identical as the one derived from the hard wood sample. The temperature range where compounds can be detected also is located between 250 and 500°C. Typical lignin decomposition products such as guaiacol and vinylguaiacol are present as are smaller compounds such as propene and acetone. However, if a closer look is undertaken some differences become apparent. This is better seen in the single mass spectrum taken at 393°C, the same temperature as the profile in the previous figure. The first striking distinction is the higher signal of furfuryl alcohol and the lower signals of guaiacol and methylguaiacol. Moreover, syringol and other derivatives of synapyl alcohol are almost completely missing. This is explained by the well-known fact, that soft wood lignin is almost completely structured of coniferyl alcohol based units excluding synapyl alcohol derived parts. Thus the applied method allows a relatively quick differentiation of soft and hard wood which may be of importance for the characterisation of scrap wood feedstock of unknown origin prior to its usage for thermal treatment in order to produce biofuels.

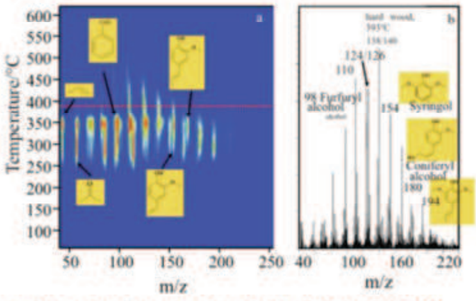


Fig. 2 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of beech wood, b – SPI-oaTOFMS spectrum from thermal analysis of beech wood at 393°C

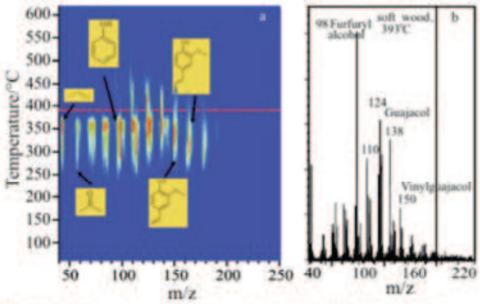


Fig. 3 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of a spruce/fir wood mixture, b – SPI-oaTOFMS spectrum from thermal analysis of a spruce/fir wood mixture at 393°C

In addition to wood and straw other biomass waste products are considered as feedstock for the future regenerative production of fuel and chemicals. Besides hay and wheat bran, coarse colza meal as a residue of the rape seed oil extraction is a possible educt in this respect. Therefore, a coarse colza meal was also investigated in the same manner as the previous described wood sample. From the obtained two-dimensional depiction (Fig. 4) it can be seen, that the onset of volatilized species is already beginning at a temperature of approximately 180°C (coniferyl alcohol) reflecting the different biomatrix coarse colza meal represents in contrast to wood leading to a dissimilar thermal behaviour. In addition to that a variety of distinct decomposition compounds could be detected which were not present in the spectra derived from the wood samples. This is due to the different chemical composition of coarse colza meal

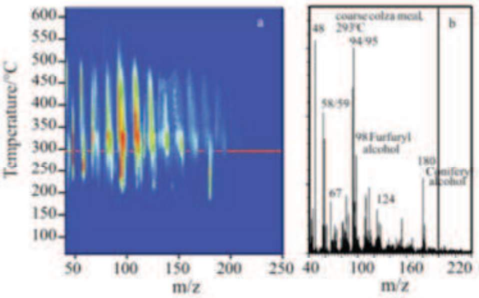


Fig. 4 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of coarse colza meal, b – SPI-oaTOFMS spectrum from thermal analysis of coarse colza meal at 293°C

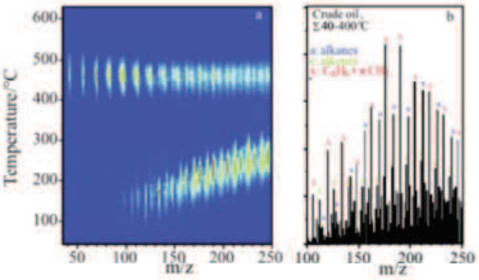


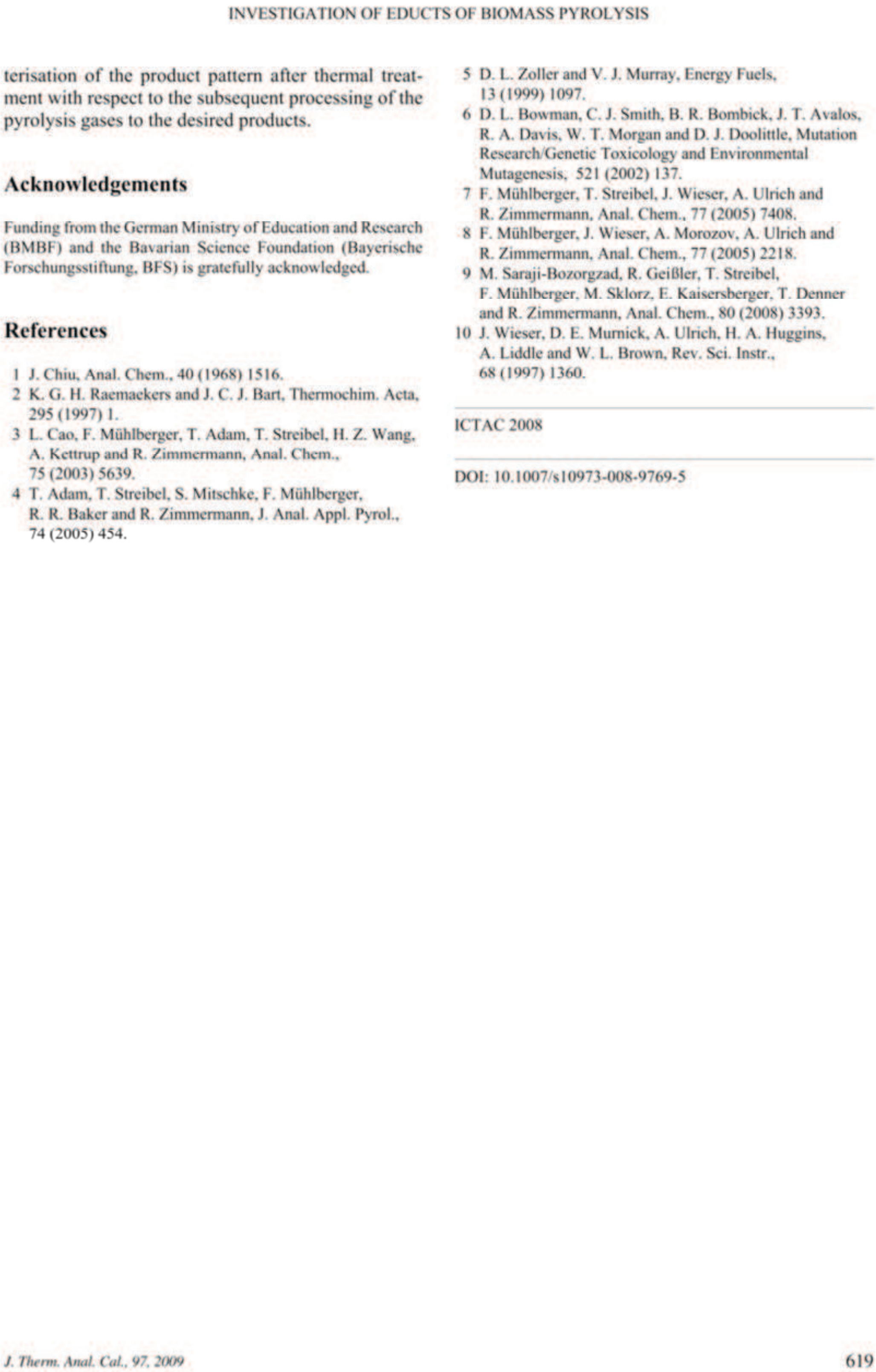
Fig. 5 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of Turkish crude oil, b – added up SPI-oaTOFMS spectrum from thermal analysis of Turkish crude oil in the temperature range between 40 and 400°C

which exhibits a high nitrogen content (up to 25 mass%) and a not to be neglected fraction of sulphur. As a consequence, the mass spectrometric profile extracted at 293°C shows high signals of methanethiol (*m/z* 48), propaneamine/isopropylamine (*m/z* 59), pyrrole (*m/z* 67), and dialkylpyrroles (*m/z* 95). Besides these compounds some well known lignin and cellulose decomposition products are also present, namely acetone (*m/z* 58), phenol (*m/z* 94), furfuryl alcohol (*m/z* 98), guaiacol (*m/z* 124), and the aforementioned coniferyl alcohol (*m/z* 180). However, these compound classes show comparable weak signals and a reduced variety of representatives.

The overall objective of the thermal decomposition studies of biomass material is the extraction of fuels and chemicals from the condensed oil derived from its pyrolysis or thermal degradation products. On this account a comparison study of the thermal decomposition from mineral oil samples has been undertaken, from which an exemplary outcome is shown in Fig. 5 for a crude oil sample from Turkey. The figure depicts a respective two-dimensional graph (temperature *vs.* *m/z* with mass signal intensity as false colours) as well as an added up mass spectrum, which summarizes the whole detectable organic content in the temperature range between 40 and 400°C. The mass loss of the relatively viscous Turkish crude oil is separated into two distinct steps. The first step is a quasi-continuous evaporation process which ends at a temperature of about 300°C. The second step starting at a temperature of 400°C is the release of products of a pyrolytic decomposition of non-volatile compounds. Above 500°C no more evolving species could be detected. The evaporation phase features the appearance of substances according to their volatility. It resembles a boiling point separation of the elevated compounds. With increasing temperature components with higher molecular masses can be detected, leading to a shift in the molecular pattern to higher *m/z* values. During the pyrolysis phase between 400 and 500°C, fragments of high molecular compounds over the complete observable *m/z* region are released. The summed up mass spectrum on the right hand side of the figure shows distinct homologue rows of alkanes, alkenes and alkylated benzenes, which account for the most important substance classes present in crude oil. The mass spectra from thermal analysis of crude oil display the advantage of soft photo ionisation for the characterisation of the evolving gases. Since fragmentation does not occur, each hydrocarbon may be identified according to its molecular ion peak. The utilization of EI would lead to intense fragmentation of the molecules to the respective same fragment ions making identification of distinct compounds very difficult if not impossible.

Conclusions

The potential of hyphenating thermogravimetry and soft photo ionisation mass spectrometry using VUV excimer lamps (EBEL-SPI-MS) for material analysis in the field of regenerative and fossile fuels was demonstrated. SPI-MS is capable of recording the molecular organic signature of the evolved gases from the thermal decomposition of biomass such as wood or coarse colza meal as well as crude oil. This includes a large variety of typical aromatic (lignin and cellulose derived components) and aliphatic substances, whereby the latter are difficult to detect by means of conventional TG mass spectrometric methods using electron ionisation (EI). Distinct molecular signatures could be elaborated for the different biomass samples providing a possible method for identification of a given biomass sort in an unknown mixture. Future applications could comprise charac-



terisation of the product pattern after thermal treatment with respect to the subsequent processing of the pyrolysis gases to the desired products.

Acknowledgements

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4.4 On-line and Real-time Analysis of Biomass Pyrolysis Gases by Single Photon Ionization Mass Spectrometry (Publication 4)

Submitted

By: Alois Fendt, Thorsten Streibel, Martin Sklorz and Ralf Zimmermann

Alois Fendt conducted all measurements including the data analysis, and he performed the predominant part of the measurement preparations as well as the writing of the manuscript. The work of Alois Fendt to this publication accounts to approximately 80 %.

On-line and Real-time Analysis of Biomass Pyrolysis Gases by Single Photon Ionization Mass Spectrometry

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Abstract:

Single photon ionization time-of-flight mass spectrometry (SPI-TOFMS) is applied for on-line and real-time analysis of signature organic compounds in complex pyrolysis gases at around 500 °C in a laboratory pyrolysis oven. VUV light supplied by an electron-beam pumped excimer light source (EBEL) was used for fragmentation free and comprehensive ionization of (nearly) all organic molecules. For the miscellaneous biomass feeds used, distinguishable mass spectra with specific patterns could be obtained, mainly exhibiting typical pyrolytic decomposition products of lignin and (hemi-)cellulose, and nitrogen containing compounds in some cases. Certain biomasses are differentiated by their ratios of specific groups of lignin (phenolic) decomposition products. Anymore, Principal Component Analysis describes the varied pyrolysis gas composition for temperature variations and for different biomass species. The results basically agree with measurements at a technical pyrolysis pilot plant at the Karlsruhe Institute of Technology (KIT). In addition, pyrolysis gases of the biomass components cellulose and lignin, as well as xylan and galactan as model compounds for hemicellulose, have been investigated. Moreover, time series are depicted for selected samples, demonstrating the potential for kinetic studies.

Keywords: Biomass pyrolysis, single photon ionization, cellulose, lignin

Introduction:

Analytical pyrolysis of biomasses and their basic components lignin and (hemi-)cellulose is an established technique for the investigation of the respective structural compositions and is extensively described in literature [1-18], including chemical, mechanistic and kinetic investigations. Moreover, it's still a matter of ongoing research [19-24]. On the one hand, thermogravimetric analysis can be utilized [21, 25-38]; however, the evolved gas characteristics and kinetics strongly depend on the employed heating rates and on experimental conditions [39, 40] in general, and mostly differ from fast and flash pyrolysis [41], respectively. On the other hand, products arising at high heating rates have been investigated by using fluidized bed systems [42-44], and mainly by applying analytical (Curie-point) pyrolysis-gas chromatography / mass spectrometry with electron ionization (Py-GC/MS). Miscellaneous varieties of this method have already been mentioned in a previous publication [45]. There, on-line measurements at a flash pyrolysis pilot plant at the Karlsruhe Institute of Technology (KIT), North Campus, have been presented. At the KIT, a process has been developed to achieve the so called second generation of biofuels and chemicals out of waste biomass. The first step in this "biomass to liquid" (bioliq® or BTL in general) process [46-49] is a flash-pyrolysis of biomass at 500 °C in a twin screw mixer with a heat transfer material such as hot sand. Subsequently, the evolving pyrolysis gases are condensed and immingled with the remaining char, providing the so-called biosyncrude or bioslurry, which is pump- and storable. In this manner, the energy density of the often voluminous biomass is considerably increased. In a second step, synthesis gas is generated from the biosyncrude in a pressurized entrained flow gasifier [50]. After thorough purification, the tar free synthesis gas can be used directly for a variety of well-known processes such as the Fischer-Tropsch reaction [51-53] or the synthesis of methanol and higher alcohols [54] and dimethyl ether (DME) [55], respectively, which themselves could serve as fuels or educts of other organic chemicals. The biosyncrude consistency – and the synthesis gas quality, accordingly – is strongly associated with the employed feedstock as well as the pyrolysis temperature. However, only limited temperature variations have turned out to be technically feasible at the pilot plant. Hence, it was not possible to reveal the principal substances that are accountable for the variations occurring at different pyrolysis temperatures. In this connection, the main issue of this paper is to point out the flash pyrolysis gas characteristics with regard to a wider temperature range compared to the measurements at the KIT, on the basis of biomass species already used there. Furthermore, pyrolysis gases of biomass structural units (lignin, cellulose and hemicellulose model compounds) are investigated to reveal the respective key components. In addition, time series of selected samples are shown as proof of principle for the capability of the analytical technique for studies on thermal decomposition mechanisms and kinetic aspects in terms of biomass feedstock.

For this, time-of-flight mass spectrometry using single photon ionization (SPI) with a continuous beam of VUV photons is applied for on-line and real-time analysis of organic decomposition products formed in a laboratory flash pyrolysis oven. SPI yields almost fragment free mass spectra, containing mostly molecular ions; furthermore, the matrix gas nitrogen and other highly concentrated small molecules are suppressed. In contrast, the customarily employed electron ionization (EI) would lead to fragmentation of the molecules and make an interpretation of the resulting mass spectra nearly impossible in this complex mixture. With SPI, all compounds are ionized whose ionization potentials are below the energy of the applied VUV photons, which are produced by an innovative electron-beam pumped excimer light source (EBEL) [56-59]. In this context, the photoionization cross-sections of the particular substances play an important role. The respective characteristics for a number of compounds have been published recently [60-66]. The analytical technique shown here has been applied to investigate pyrolysis and other thermal processes before [57, 67-71]. It allows the fast and direct analysis of the whole width of organic compounds from the biomass pyrolysis process, by contrast with common methods such as GC/MS, which are less suitable for the study of transient processes.

Materials and methods:

Experiments have been accomplished at a laboratory tube furnace (RoK/A 3/30S, Heraeus Holding GmbH, Hanau, Germany) (Figure 1), enclosing a home-made quartz tube with quartz glass wool placed in the middle of the oven, serving as pyrolysis reaction zone. The so called VCI-oven was originally developed for combustion experiments and is described in detail elsewhere [72, 73].

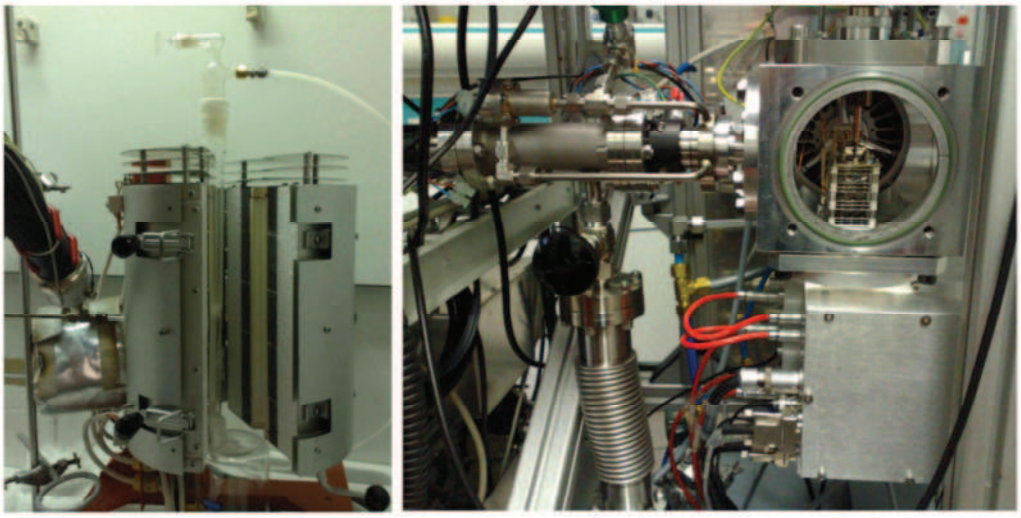


Figure 1: Photograph of the laboratory pyrolysis oven, on the right the SPI-MS system with the EBEL VUV-lamp

Generally, 20 mg of chopped biomasses are filled in a small glass scoop in the head end of the quartz tube. By turning the scoop, the sample falls onto the glass wool. The evolving products are directed to the outlet by a nitrogen flow of 100 ml/min, yielding a residence time of around 24 s downstream the reaction zone. Subsequently, the pyrolysis gases are sampled directly – without a filter line – by a capillary that runs in a heated hose (300 °C) and serves as a restriction between the atmospheric pressure conditions in the pyrolysis oven and the vacuum of the mass spectrometer. In the ion source of the mass spectrometer, the VUV photons hit the pyrolysis gases immediately underneath the inlet needle at the end of the capillary, where an effusive molecular beam is formed [74]. For ionization with SPI, a newly developed, homebuilt EBEL-VUV light source was employed (q.v. Figure 1). Great efforts have been made by joint work to achieve improved sensitivity (LOD: 1 ppm for toluene, S/N = 3, 1 s average) and higher stability than earlier models, as well as easy adaptability to different focusing systems. By the use of mirror modules [75], significantly higher sensitivity is obtainable compared to the here employed lenses. The basic principle of the EBEL is described in several publications [45, 56, 76, 77]. In brief, upon radiative decay of rare gas excimers, VUV-radiation is emitted. The emitted light is first collimated and then focused on the effusive gas using two MgF_2 lenses (Korth Kristalle GmbH, Altenholz (Kiel), Germany). The rare gas volume was filled with argon (6.0) and purified continuously using a heated gas getter (SAES Getters S.p.A., Lainate (MI), Italy), yielding an emission maximum at 126 nm (9.8 eV center photon energy available for ionization). The SPI-MS measurements were achieved using a mobile orthogonal acceleration TOF-MS (C-TOF, TOFWERK AG, Thun, Switzerland), which is particularly suited for the use of continuous light sources such as the EBEL due to the special type of construction with pulsed (around 70 kHz at a mass range up to m/z = 425) orthogonal extractor plates [56], enabling a very high time resolution. The data acquisition from the mass spectrometer was carried out by an Acqiris AP240 (Agilent Technologies, Plan-les-Ouates, Switzerland, 1 to 2 GS/s) averager card and the TofDaq_Acqiris software (TOFWERK AG). 16666 singular spectra have been averaged to obtain a stored mass spectrum, resulting in a measurement frequency of around 4 Hz. For the assignment of the mass spectrometric peaks, literature studies [3, 4, 6, 7, 12, 13, 16, 17, 24, 78-93] as well as own laboratory Py-GC/MS measurements [45] have been consulted. The most important pyrolysis products (with ionization energies below 9.81 eV) are listed in Table 1.

A large variety of biomass feedstock has been investigated with the described experimental setup, comprising two kinds of straw, corn, soft- and hardwood, hay, wheat bran, rice straw (from Egypt), rape extraction residue (RES), oil palm residues (EFB) and Miscanthus. Straw (from wheat and oat), hay, wood, RES and bran stem from the surrounding area of Karlsruhe. The samples are in a range of sizes between 1 and 3 mm and identical with those used at the KIT pyrolysis plant [45]. In addition, commercially available ground cellulose and lignin, as well as xylan (from beech wood) and galactan as model compounds for hemicellulose have been deployed. The applied temperatures range from 400 to 600 °C in steps of 50 °C. Experiments have been conducted with three replicates for every feedstock. The resulting mass spectra have been averaged and evaluated statistically by calculating the ratio of the different lignin components for soft- and hardwood and Miscanthus, and by applying multivariate data analysis. Thereby, the underlying data have been range normalized before applying Principal Component Analysis (PCA), using the program *The Unscrambler* (CAMO Software AS, Oslo, Norway). Moreover, a ranking of the biomass pyrolysis products was carried out by adding the absolute Loadings values of Principal Components 1 and 2 (priority numbers in Table 1), in order to take account of the temperature variations as well as of the biomass species in equal measure. Total ion signals (TIS) are calculated as sum of the signal intensities for *m/z* = 40 – 400. As to the time series of the biomass components and wheat straw, the TIS of single measurements are normalized and plotted against time. Concerning the chronological sequences of soft- and hardwood, the signal intensities of selected nominal masses are compared at 400 °C pyrolysis temperature.

Results and Discussion:

1) *Classification of lignin and protein degradation products*

The products obtained by the pyrolysis gas measurements have been arranged in groups for a first characterization, according to their derivation from either lignin or (hemi-)cellulose, or from proteins in some cases (q.v. Table 1). Lignin in turn predominantly consists of three monomers, namely p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which again are structurally based on hydroxyphenyl (H), guaiacyl (G) and syringyl (S) moieties[94]. SPI-MS spectra of soft- and hardwood are compared in Figure 2 (upper part).

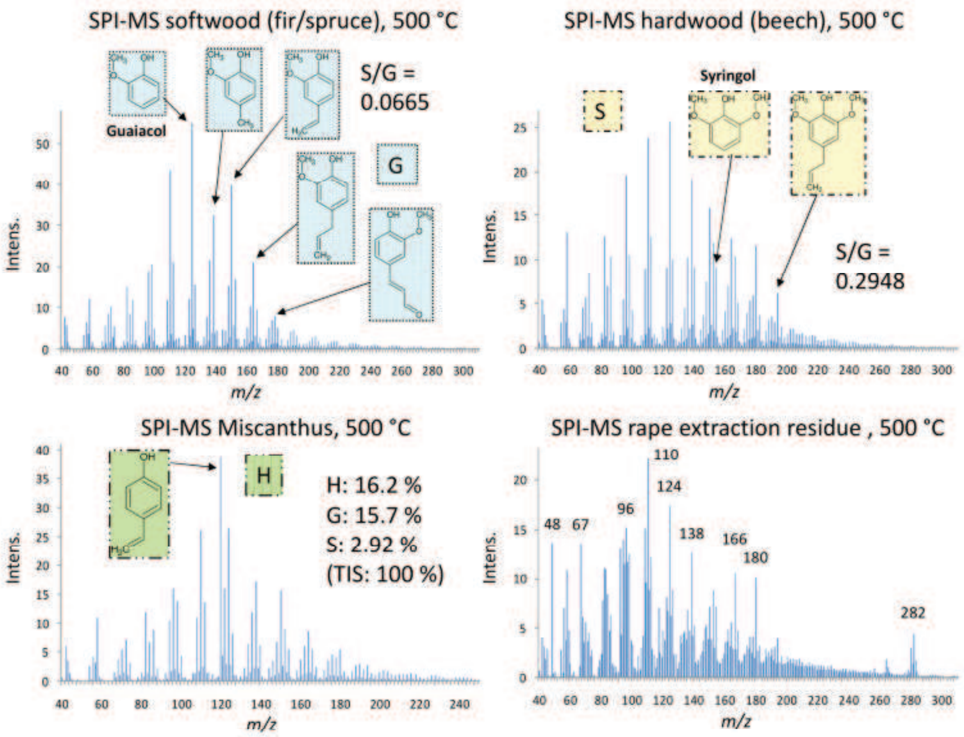


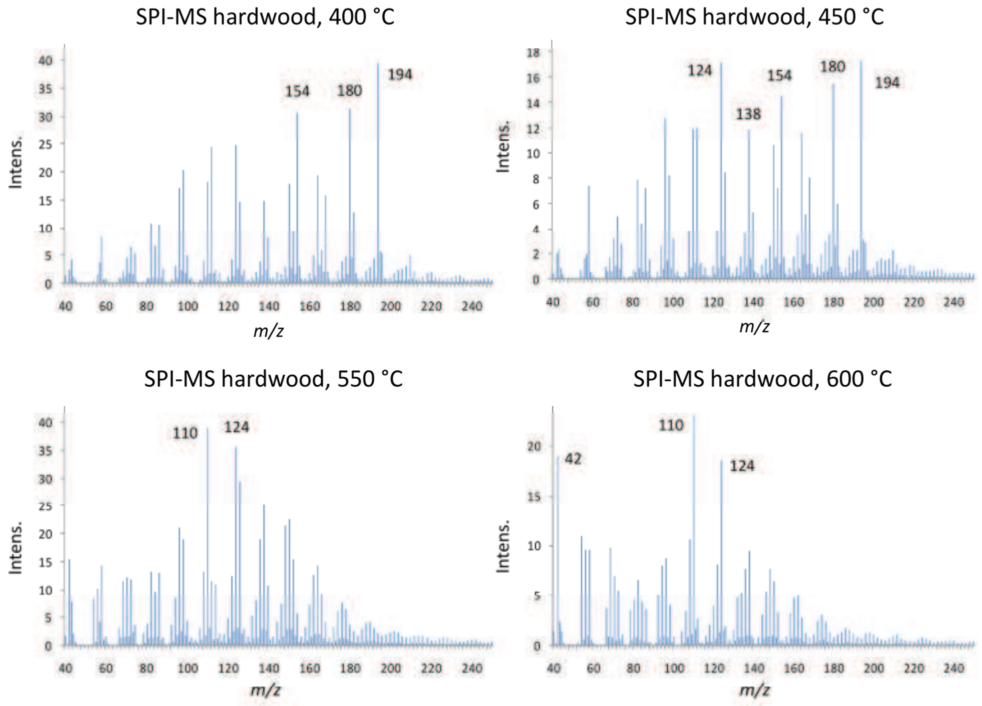
Figure 2: Comparison of SPI mass spectra of different biomasses at 500 °C pyrolysis temperature

The most important pyrolysis products are summarized in the "G"-group (blue), consisting of guaiacol derivatives, furthermore in the "S"-group (yellow, syringol derivatives), and in the "C"-group (not shown, cellulose decomposition products), comprising ketones, aldehydes and furan derivatives. In literature, the S to G ratio for the differentiation of soft- and hardwood is well known [4, 17, 24, 85]. With our measurements, S/G values of 0.0665 for softwood and 0.2948 for hardwood have been detected, i.e. higher mass peaks can be observed for syringol derivatives (S) in case of hardwood. For the G group, the signal intensities of the mass to charge ratios 124, 138, 150, 152, 164, 166 and 178 have been summarized, and for the S group the mass to charge ratios 154, 168, 182, 194, 196, 208, 210 (see Table 1). The SPI-MS spectra clearly reflect the different lignin structures of soft- and hardwood [13, 80, 95] and the resultant varied thermal degradation products [6, 16]. In the mass spectrum of Miscanthus (lower part), 4-vinylphenol (*m/z* = 120) – a member of the "H" group (hydroxybenzene derivatives) – exhibits the highest signal intensity, in contrast to wood, where only marginal peaks appear at *m/z* = 120. However, the other substances and groups depicted above are also present. The ratio of the H group, that includes the mass to charge ratios 94, 108, 120, 122, 134 and 148, is calculated to be 16.2 % relating to the sum of all mass peaks, the total ion signal (TIS); for G and S it is 15.7 % and 2.92 %, respectively. In the pyrolysis gas of rape extraction residue a lot of additional substances appear, most of which are nitrogen-containing, e.g. pyridinol [96] (*m/z* = 95), pyrrole (*m/z* = 67), indole [70] (*m/z* = 117), ethylamine (*m/z* = 45) and propylamine (*m/z* = 59), and others such as methanethiol [60, 97] that are formed by the decomposition of proteins [96, 98]. Many of these compounds can also be found in the mass spectra of wheat bran (not shown here), in particular propylamine (*m/z* = 59) and pyrrole (*m/z* = 67).

By comparison, the measurements at the technical flash pyrolysis plant in Karlsruhe show similar spectra pattern and significant nominal masses. Interestingly, the here obtained S/G value of softwood is nearly identical with that obtained at the KIT (S/G = 0.0658), whereas the S/G value of hardwood is considerably lower now (0.2948; KIT: S/G = 0.6667). This could be due to higher heating and heat transfer rates, respectively, in the laboratory oven, resulting in a more effective cracking of the bigger "S" molecules. In case of Miscanthus, the S/G value of 0.1855 again lies in between soft- and hardwood (KIT: S/G = 0.3565). Moreover, the mass spectrometric patterns of Miscanthus as well as of rape extraction residue are nearly identical in both cases. Furthermore, these results confirm that the influence of the sampling train used at the pyrolysis plant in Karlsruhe on the pyrolysis gas composition is negligible [45].

2) Temperature and feedstock dependence

The variations in the mass spectra for different pyrolysis temperatures are illustrated in Figure 3, using the example of hardwood. Thereby, a clear shift can be observed from higher to lower masses with increasing temperature. At 400 and 450 °C, allylsyringol (*m/z* = 194) shows the highest signal intensity, whereas nominal mass 110 (5-methylfurfural and catechol, respectively) is the major peak at 550 and 600 °C.


SPI-MS hardwood, 400 °C

SPI-MS hardwood, 450 °C

SPI-MS hardwood, 550 °C

SPI-MS hardwood, 600 °C

Figure 3: SPI mass spectra of hardwood at different pyrolysis temperatures

Remarkably, propene (potentially also ketene, *m/z* = 42) shows a very high peak at 600 °C, mainly originating from (hemi-)cellulose decomposition. In between, guaiacol (*m/z* = 124) is of great significance, particularly at 500 °C (see Figure 2). The temperature range applied is limited due to the focus on flash pyrolysis. At lower temperatures, the pyrolysis is too slow, and at higher temperatures, a variety of PAHs start to arise, what would lead to distortion of the results, especially in case of the Principal Component Analysis, which is depicted in Figure 4, including all investigated biomasses and temperature variations.

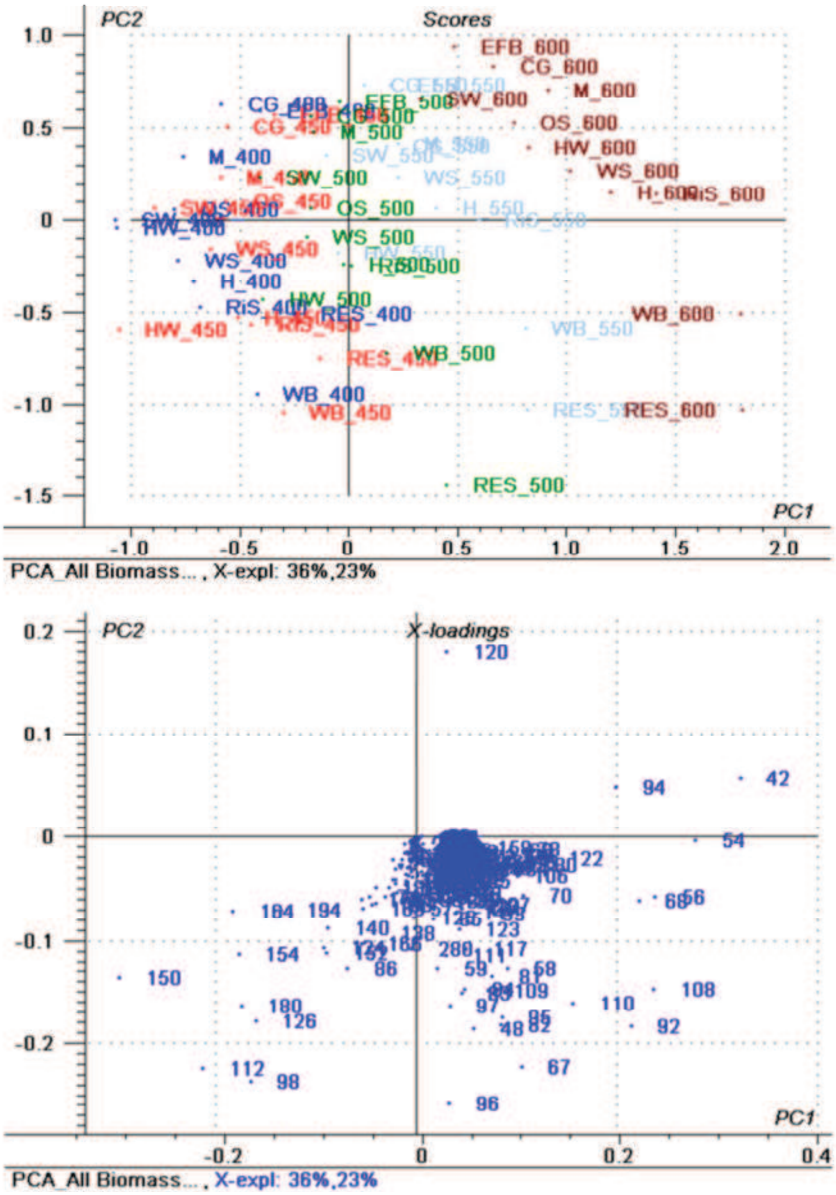
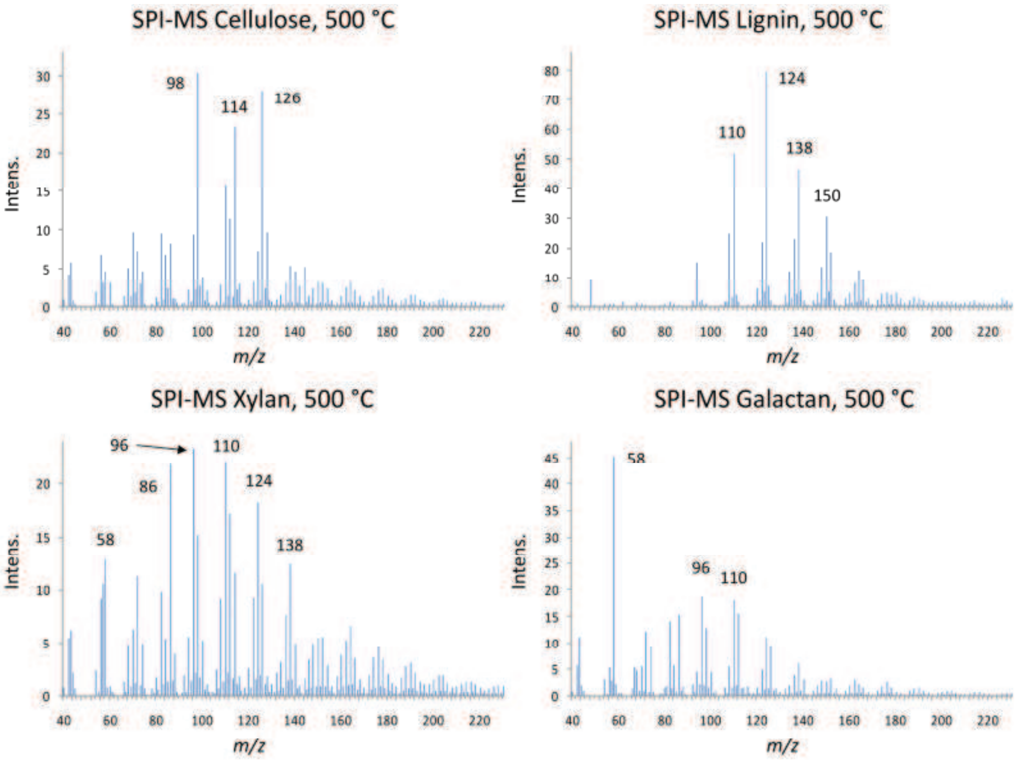


Figure 4: Principal Component Analysis (PCA) of SPI-MS spectra of all investigated biomasses and temperature variations. Abbreviations: CG: Corn granules, M: Miscanthus, RiS: Rice straw, H: Hay, SW: Softwood, WS: Wheat straw, OS: Oat straw, WB: Wheat bran, EFB: Empty fruit bunches, HW: Hardwood, RES: Rape extraction residue

The latter are indicated by the respective numbers and by different colors in the Scores plot of PC 1 and PC 2 (upper part). The different temperatures are distinguished by Principal Component (PC) 1, based on the highest variances of the underlying nominal mass peaks. This applies for 600 °C in particular. The various biomass species (corn, Miscanthus, rice straw, hay, straw, bran, softwood, oil palm, rape shred (RES) and hardwood) are separated by PC 2. Together, PC 1 & 2 already explain 59 % of the total variance, and 80 % are explained with four PCs. In the Loadings plot (lower part), the nominal masses and their influence on the calculation of the respective PC can be seen. The Loadings values represent the variance of the underlying compounds for the respective Principal Component and interrelate to the respective position in the Scores plot. Strikingly, the nominal masses 42, 150, 54, 56, 108 and 68 (for corresponding pyrolysis products see Table 1) are of the highest importance in terms of the temperature variations, whereas the masses 96, 98, 112, 67 and 48 have the highest priority for the distinction of the employed biomass feeds. The most important pyrolysis products and their priority number, representing the importance to the calculation, are shown in Table 1. Combined, the ranking order of the masses based on PC 1 and 2 is 112, 150, 98, 92, 108, 42, 180, 126, 67 and 110. PC 3 & 4 (not shown here) also reflect the responsible masses for the temperature and species variations, in particular for certain biomasses; notably, nominal mass 94 is mainly related to empty fruit bunches (EFB), whereas *m/z* = 124, 138, 148, 164 and 194 strongly correlate with both kinds of wood, and *m/z* = 48, 95 and 67 with rape extraction residue (RES).

3) Characteristic products of cellulose and other reference materials

The pyrolysis gas mass spectra at 500 °C of the major biomass components cellulose and lignin as well as of the hemicellulose model compounds xylan and galactan are shown in Figure 5. Here, the origin of specific compounds becomes apparent. In case of cellulose, the four major peaks are caused by 2-furanmethanol / methylfuranone (*m/z* = 98), 5-hydroxymethylfurfural / maltol / levoglucosenone (*m/z* = 126), 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one (*m/z* = 114) and 5-methylfurfural (*m/z* = 110). Interestingly, the signal intensity of levoglucosan (*m/z* = 162) – often described as a major pyrolysis product of cellulose – is very low, according to Broido et al. [99, 100]. Similarly, Evans et al. [101] mention significant decomposition products at *m/z* = 144 and 126, which appear here with medium and high abundance, respectively. Furthermore, a potentially low ionization cross-section of levoglucosan should be considered, too. In contrast, the key compounds in lignin pyrolysis gas are guaiacol (*m/z* = 124), catechol (*m/z* = 110), 4-methylguaiacol (*m/z* = 138) and 4-vinylguaiacol (*m/z* = 150). For xylan, the masses 96, 86 and 110 are most significant, and for galactan, *m/z* = 58 is the most prominent peak, followed by *m/z* = 96 and 110; however, the mass spectrum is less complex than that of xylan. A look back at the PCA can yield a hint, which biomasses are most related to the key masses of hemicellulose pyrolysis (*m/z* = 58, 96 and 110), for example. In the Loadings plot of PC 1 & 2, these masses can be found in the lower right quadrant, pointing to wheat bran and rape shred. Beyond that, a remarkable peak at *m/z* = 124 appears for all components, indicating a non-phenol derived compound, probably dimethylfurfural, originating from (hemi-)cellulose decomposition, in addition to Guaiacol (from lignin). In case of xylan, possibly lignin derived substances can be seen in addition, because the xylan is obtained from beech wood. With respect to the other temperatures, the same trend can be observed as already shown for hardwood; the higher the temperature, the smaller are the fragments of the respective biomass components.


SPI-MS Cellulose, 500 °C

SPI-MS Lignin, 500 °C

SPI-MS Xylan, 500 °C

SPI-MS Galactan, 500 °C

Figure 5: Pyrolysis gas mass spectra at 500 °C of the major biomass components cellulose and lignin, and of the hemicellulose model compounds xylan and galactan

4) Kinetic pyrolysis aspects

Figure 6 illustrates time series of the pyrolysis gas measurements. Thereby, only one measurement each has been employed due to non isochronous starting times of the MS measurements, as observable by shifts in the plots. However, the shape and width of the curves can be considered. In the upper part, total ion signals (TIS) of the biomass components and wheat straw are plotted versus time at 400 and 500 °C. Calculation of the full width at half maximum (FWHM) of the peaks at 400 °C provides a value of 11 s for xylan and galactan, 14 s for wheat straw, 17 s for lignin and 26 s for cellulose, corroborating it to be the most heat resistant component. At 500 °C, the differences in the FWHM values are negligible yet, indicating a real flash pyrolysis. To achieve this, a temperature of 450 °C (not shown here) is not sufficient yet; the FWHM values are still differing. In the lower part, time series of soft- and hardwood pyrolysis at 400 °C are shown, represented by selected key substances of (hemi-)cellulose (*m/z* = 96, 98, 112, 126) and lignin (*m/z* = 124 and 150). Strikingly, the pyrolysis behavior is different for both kinds of wood. In case of softwood (and similar for Miscanthus, not shown), the cellulose decomposition – mainly represented by nominal mass 98 – is remarkably delayed, in contrast to hardwood. These characteristics are comparable to Thermal Analysis, exhibiting wider hemicellulose and cellulose zones for softwood [27], too. However, the decomposition starts at lower temperatures there (see also [102]).

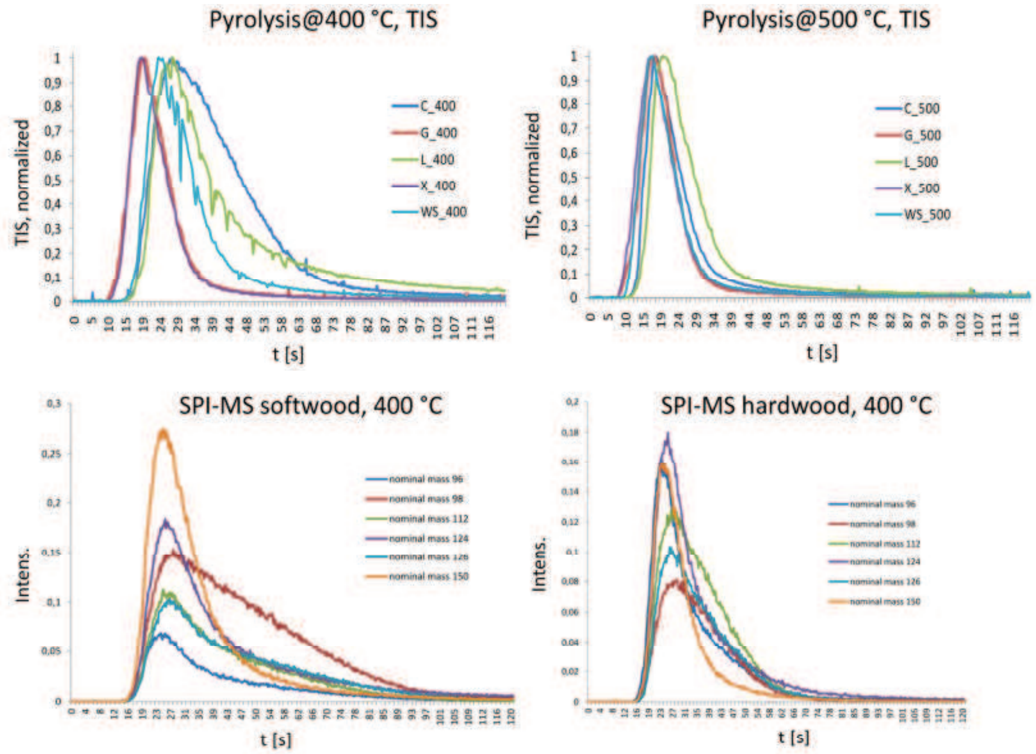


Figure 6: Time series of pyrolysis gas measurements. Abbreviations: C: Cellulose, G: Galactan, L: Lignin, X: Xylan, WS: Wheat straw, at 400 and 500 °C pyrolysis temperature, respectively

Conclusion:

Single photon ionization (SPI) using an electron-beam pumped rare gas excimer light source as soft photo ionization technique in combination with time-of-flight mass spectrometry has proven to be a suitable method for the analysis of complex pyrolysis gas mixtures, since all molecules with ionization energies <9.81 eV (nearly all organic substances) can be ionized without fragmentation. Here, the investigated biomass pyrolysis gases consist of typical (hemi-)cellulose and lignin decomposition products (q.v. table 1). The ratio of phenol derivatives varies with regard to different lignin structures of the miscellaneous biomasses. For certain biomass feedstocks nitrogen containing substances were detected, too, especially N-heterocyclic compounds such as pyrrole or indole. Generally, the mass spectra of the investigated pyrolysis gases show different patterns for the miscellaneous biomasses. The distinguishability of the employed biomass feeds is shown by using H/G/S ratios on the basis of selected mass spectra. Furthermore, Principal Component Analysis points up the different pyrolysis gas composition for all employed biomass species and temperature variations. The PCA-Loadings values open up a facile path for creating priority lists, and for reducing the number of variables. Additionally, the results of the PCA or the underlying data matrix of the SPI-MS spectra can be combined with other findings within the process. However, these correlations between the measured transient products and the composition of the obtained biooil as well as the biosyncrude will have to be investigated in more detail in the future. The pyrolysis gases of the biomass structural units revealed the respective significant decomposition products. Strikingly, nominal masses 42 and 124 could be mainly and also, respectively, assigned to (hemi-)cellulose.

In this paper, the application of SPI-MS for on-line measurements of biomass pyrolysis gases is demonstrated with focus on temperature variations and regard to the optimization of the bioliq® process. The similarity of the pyrolysis gas patterns and the significant nominal masses compared to the technical pyrolysis plant prove the here employed method to be a good bench-scale model for simulations of parameters in this process. In contrast to our work, most studies about biomass pyrolysis focus on the identification of the products thereof as well as on the elucidation of the biomass structure and kinetic aspects. However, it was not possible to discuss the kinetics appropriately due to the depth of topic coverage and the large variety of biomass samples dealt with. For this, thermogravimetric analysis is another possibility and has already been shown in a previous publication [102]. However, the decomposition mechanisms can be different from flash pyrolysis, hampering a comparability of both methods. For example, PAH formation appears much earlier in case of TA (at around 450 °C), whereas it cannot be observed here even at 600 °C. Generally, pyrolysis of biomass and their basic components is widely investigated and understood, even by the use of similar analytical methods (for example by Brown et al. [103], applying laser-SPI-TOFMS), but not for such a variety of different biomasses as here, to our knowledge, and against the background of producing biofuels thereof. In any case, the here presented method is a fast and easy way to investigate temperature dependencies as demonstrated for different biomass species and components thereof, and offers the potential to investigate other materials, and to focus on particular compounds beyond that.

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Tables

Table 1: Mass assignment of the most important pyrolysis products, derivation from structural groups (P: Proteins, C: Cellulose/Carbohydrates, H: Hydroxybenzene, G: Guaiacol, S: Syringol), and priority according to PC1+2

Nominal mass	Biomass pyrolysis products	Group	Priority PC1+2
42	Propene / Ketene	C	6
48	Methanethiol [60, 97, 104]	P	20
54	Butadiene	C	15
56	Butene	C	11
58	Acetone	C	22
59	Propylamine	P	36
67	Pyrrole	P	9
68	Furan / Isoprene	C	14
70	2-Butenal	C	33
74	Hydroxy-Propanal / -Propanone	C	55
81	Methylpyrrole	P	23
82	Methylfuran / 2-Cyclopenten-1-one	C	16
84	Furanone	C	31
86	2,3-Butanedione / Tetrahydrofuran-3-one	C	30
92	Toluene	P	4
94	Phenol	H, P	19
95	Pyridinol [96]	P	17
96	Furfural	C	12
98	2-Furanmethanol / Methylfuranone	C	3
100	2-Methyldihydrofuran-3(2H)-one / 2,3-Pentanedione	C	50
106	Ethylbenzene / Benzaldehyde		43
108	Methylphenol (Cresol) / Anisole	H, P	5
109	Methylpyridinol	P	21
110	5-Methylfurfural / Catechol	C / H	10
112	Methyl-dihydro-pyranone / Hydroxy-pyranone	C	1
114	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one	C	54
117	Indole	P	34
120	4-Vinylphenol	H	24
122	Dimethylphenol / Ethylphenol / Methylanisole	H	37
124	Guaiacol / Dimethylfurfural	G / C	27
126	5-Hydroxymethylfurfural / Maltol / Levoglucosenone	C	8
131	Methyl-Indole	P	47
134	4-Allylphenol / Cinnamic alcohol	H	57
136	Dimethylanisole / Anisaldehyde		59
138	4-Methylguaiacol	G	40
140	2,3-Dihydroxyanisole		32
148	Cumarylaldehyde	H	64
150	4-Vinylguaiacol	G	2
152	Vanillin / 4-Ethylguaiacol	G	26
154	Syringol	S	13
164	(Iso-)Eugenol (Eugenic acid)	G	18
166	4-Propylguaiacol / 4-Acetylguaiacol	G	35
168	Methylsyringol	S	44
178	Coniferyl aldehyde / Methyleugenol	G	46
180	4-Vinylsyringol / Coniferyl alcohol / Guaiacylacetone / Propioguaiacone	S / G	7
182	Syringaldehyde / Trimethoxytoluene	S	62
194	Allylsyringol	S	25
196	Acetosyringone / Propylsyringol	S	
208	Sinapaldehyde	S	
210	Sinapyl alcohol / Syringyl acetone	S	

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4.5 Contributions to other publications

4.5.1 Single Photon Ionization Orthogonal Acceleration Time-of-Flight Mass Spectrometry and Resonance Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometry for Evolved Gas Analysis in Thermogravimetry: Comparative Analysis of Crude Oils

Published in: *Analytical Chemistry* **2009,** 81, (15), 6038-6048

By: Geissler, R.; Saraji-Bozorgzad, M. R.; Gröger, T.; Fendt, A.; Streibel, T.; Sklorz, M.; Krooss, B. M.; Fuhrer, K.; Gonin, M.; Kaisersberger, E.; Denner, T.; Zimmermann, R.

Alois Fendt was partly involved in the preparation of the measurements.

4.5.2 Impact of grassland burning on soil organic matter as revealed by a synchrotron- and pyrolysis–mass spectrometry-based multi-methodological approach

Published in: *Organic Geochemistry* **2012,** 44, 8-20

By: Kiersch, K.; Kruse, J.; Eckhardt, K.-U.; Fendt, A.; Streibel, T.; Zimmermann, R.; Broll, G.; Leinweber, P.

Alois Fendt accomplished the SPI-MS measurements and the preparations therefor.

5

Annex

List of Abbreviations

BtL	biomass to liquid
C	cellulose (decomposition products)
DBD	dielectric-barrier discharge
EBEL	electron-beam pumped excimer light source
EFB	empty fruit bunches
EI	electron ionization
FAME	fatty acid methyl ester
G	guaiacol (decomposition products) / galactan
GC	gas chromatography
H	hydroxybenzene (decomposition products)
IP	ionization potential
KIT	Karlsruhe Institute of Technology
LOD	limit of detection
MS	mass spectrometry
m/z	mass-to-charge ratio
OPF	oil palm fronds
P	protein (decomposition products)
PCA	Principal Component Analysis
PI	photo ionization
PJ	petajoule
Py	pyrolysis
REMPI	resonance enhanced multiphoton ionization
RES	rape extraction residue
S	syringol (decomposition products)
SPI	single photon ionization
TA	thermal / thermogravimetric analysis
TIS	total ion signal
TOF	time-of-flight
(V)UV	(vacuum) ultraviolet (light)
WS	wheat straw
X	xylan

List of Figures

Table of pyrolysis products

Nominal mass	Biomass pyrolysis products
42	Propene / Ketene
48	Methanethiol
54	Butadiene
56	Butene
58	Acetone
59	Propylamine
67	Pyrrole
68	Furan / Isoprene
70	2-Butenal
74	Hydroxy-Propanal / -Propanone
81	Methylpyrrole
82	Methylfuran / 2-Cyclopenten-1-one
84	Furanone
86	2,3-Butanedione / Tetrahydrofuran-3-one
92	Toluene
94	Phenol
95	Pyridinol
96	Furfural
98	2-Furanmethanol / Methylfuranone
100	2-Methyldihydrofuran-3(2H)-one / 2,3-Pentanedione
106	Ethylbenzene / Benzaldehyde
108	Methylphenol (Cresol) / Anisole
109	Methylpyridinol
110	5-Methylfurfural / Catechol
112	Methyl-dihydro-pyranone / Hydroxy-pyranone
114	4-Hydroxy-5,6-dihydro-(2H)-pyran-2-one
117	Indole
120	4-Vinylphenol
122	Dimethylphenol / Ethylphenol / Methylanisole
124	Guaiacol / Dimethylfurfural
126	5-Hydroxymethylfurfural / Maltol / Levoglucosenone
131	Methyl-Indole
134	4-Allylphenol / Cinnamic alcohol
136	Dimethylanisole / Anisaldehyde
138	4-Methylguaiacol
140	2,3-Dihydroxyanisole
148	Cumarylaldehyde
150	4-Vinylguaiacol
152	Vanillin / 4-Ethylguaiacol
154	Syringol
164	(Iso-)Eugenol (Eugenic acid)
166	4-Propylguaiacol / 4-Acetylguaiacol
168	Methylsyringol
178	Coniferyl aldehyde / Methyleugenol
180	4-Vinylsyringol / Coniferyl alcohol / Guaiacylacetone / Propioguaiacone
182	Syringaldehyde / Trimethoxytoluene
194	Allylsyringol
196	Acetosyringone / Propylsyringol
208	Sinapaldehyde
210	Sinapyl alcohol / Syringyl acetone

List of Publications and Presentations

I. Peer-reviewed scientific articles

- Fendt, A.; Streibel, T.; Sklorz, M.; Richter, D.; Dahmen, N.; Zimmermann, R., On-Line Process Analysis of Biomass Flash Pyrolysis Gases Enabled by Soft Photoionization Mass Spectrometry. *Energy & Fuels* **2012,** 26, (1), 701-711.
- Fendt, A.; Geissler, R.; Streibel, T.; Sklorz, M.; Zimmermann, R., Hyphenation of two simultaneously employed soft photo ionization mass spectrometers with thermal analysis of biomass and biochar. *Thermochimica Acta* **2013,** 551, 155-163.
- Fendt, A.; Streibel, T.; Sklorz, M.; Zimmermann, R., On-line and Real-time Analysis of Biomass Pyrolysis Gases by Single Photon Ionization Mass Spectrometry. Submitted to Analytica Chimica Acta
- Streibel, T.; Fendt, A.; Geissler, R.; Kaisersberger, E.; Denner, T.; Zimmermann , R., Thermal analysis/mass spectrometry using soft photo-ionisation for the investigation of biomass and mineral oils. *Journal of Thermal Analysis and Calorimetry* **2009,** 97, (2), 615-619.
- Kiersch, K.; Kruse, J.; Eckhardt, K.-U.; Fendt, A.; Streibel, T.; Zimmermann, R.; Broll, G.; Leinweber, P., Impact of grassland burning on soil organic matter as revealed by a synchrotron- and pyrolysis–mass spectrometry-based multi-methodological approach. *Organic Geochemistry* **2012,** 44, 8-20.
- Geissler, R.; Saraji-Bozorgzad, M. R.; Gröger, T.; Fendt, A.; Streibel, T.; Sklorz, M.; Krooss, B. M.; Fuhrer, K.; Gonin, M.; Kaisersberger, E.; Denner, T.; Zimmermann, R., Single Photon Ionization Orthogonal Acceleration Time-of-Flight Mass Spectrometry and Resonance Enhanced Multiphoton Ionization Time-of-Flight Mass Spectrometry for Evolved Gas Analysis in Thermogravimetry: Comparative Analysis of Crude Oils. *Analytical Chemistry* **2009,** 81, (15), 6038-6048.

II. Oral presentations at conferences

- Fendt, T. Streibel, M. Sklorz, R. Geißler, R. Zimmermann, Soft Photo-Ionization Mass Spectrometry for the Analysis of Pyrolysis Gases from Biomass within the Karlsruhe Bioliq – Biomass to Liquid- Project, Pittcon 2009, Chicago, USA, 10.03.2009
- Fendt, T. Streibel, M. Sklorz, R. Zimmermann, Soft photo ionization mass spectrometry for the analysis of biomass flash pyrolysis gases within the Karlsruhe bioliq® - Biomass to Liquid – Project, Spectroscopy-Conference, Rostock, 17.06.2011

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Curriculum Vitae

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Helmholtz Zentrum München	05.2007 – 06.2008
Promotion zum Thema „Analyse von Biomasse-Pyrolysegasen mit Photoionisations-Massenspektrometrie“	
Universität zu Köln	
Wissenschaftliche Mitarbeit im Institut für Physikalische Chemie: Herstellung und Charakterisierung von Membranen	02.2005 – 11.2006
Studentische Hilfskraft in der Zentralen Koordinations-Stelle des Zentrums für Molekulare Medizin (ZMMK)	04.2002 – 05.2004
Studium der Chemie mit Abschluss Diplom	04.2002 – 12.2004
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Universität Würzburg	
Studium der Chemie	11.1999 – 03.2002
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Studium Chemieingenieurwesen / Maschinenwesen	10.1996 – 10.1999