Journal of Thermal Analysis and Calorimetry, Vol. 97 (2009) 2, 615–619

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

T. Streibel[1,2], *A. Fendt*[2,3], *R. Geißler*[1,2], *E. Kaisersberger*[5], *T. Denner*[5] *and R. Zimmermann*[1,2,4]*

[1]Helmholtz Zentrum München, 85764 Oberschleißheim, Germany
[2]Universität Rostock, Chair of Analytical Chemistry, 18059 Rostock, Germany
[3]University of Augsburg, Chair of Solid State Chemistry, 86159 Augsburg, Germany
[4]bifa-Umweltinstitut GmbH, 86167 Augsburg, Germany
[5]Netzsch-Gerätebau GmbH, 95100 Selb, Germany

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.

---

* Author for correspondence: ralf.zimmermann@uni-rostock.de

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

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.

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 $0.7 \cdot 0.7$ 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.

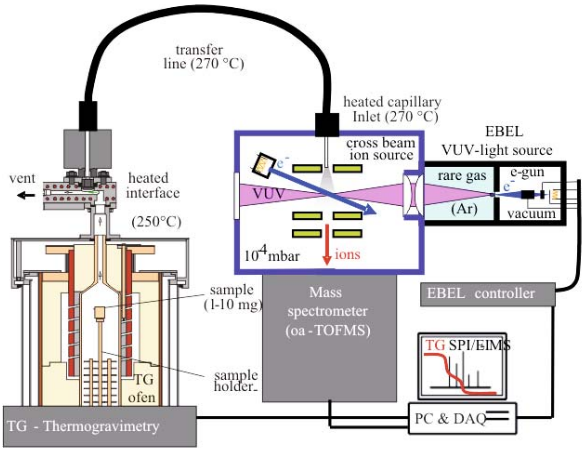

Fig. 1 Schematic representation of the TG-EBEL-SPI-oaTOFMS system

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.

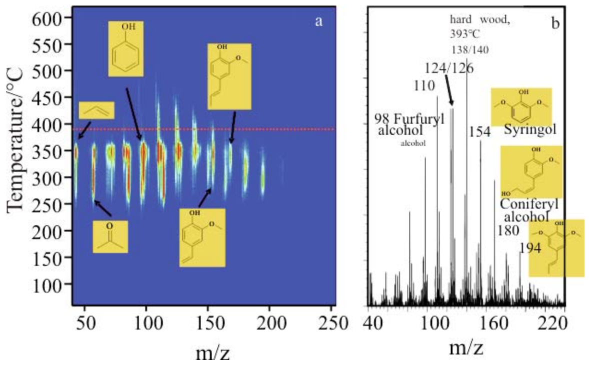

Fig. 2 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of beech wood, b – SPI-oaTOFMS spectrum from thermal analysis of beech wood at 393°C

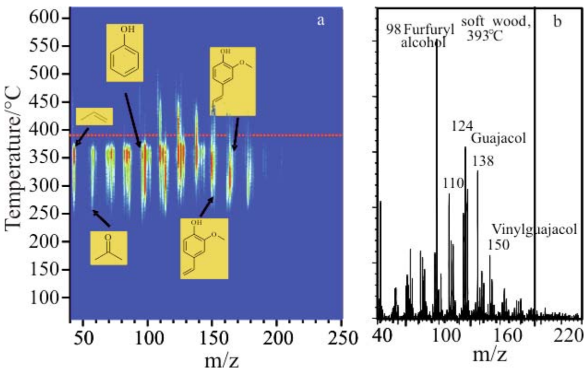

Fig. 3 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of a spruce/fir wood mixture, b – SPI-oaTOFMS spectrum from thermal analysis of a spruce/fir wood mixture at 393°C

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

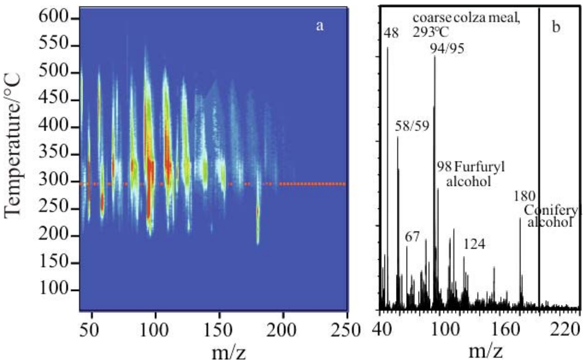

Fig. 4 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of coarse colza meal, b – SPI-oaTOFMS spectrum from thermal analysis of coarse colza meal at 293°C

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.

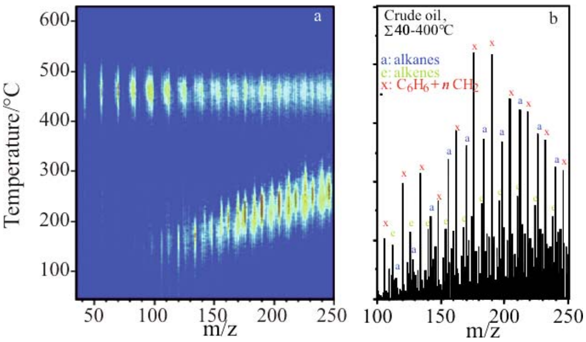

Fig. 5 a – Two-dimensional graph of TG-SPI-oaTOFMS measurement of Turkish crude oil, b – added up SPI-oaTOFMS spectrum from thermal analysis of Turkish crude oil in the temperature range between 40 and 400°C

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

Acknowledgements

Funding from the German Ministry of Education and Research (BMBF) and the Bavarian Science Foundation (Bayerische Forschungsstiftung, BFS) is gratefully acknowledged.

References

1 J. Chiu, Anal. Chem., 40 (1968) 1516.
2 K. G. H. Raemaekers and J. C. J. Bart, Thermochim. Acta, 295 (1997) 1.
3 L. Cao, F. Mühlberger, T. Adam, T. Streibel, H. Z. Wang, A. Kettrup and R. Zimmermann, Anal. Chem., 75 (2003) 5639.
4 T. Adam, T. Streibel, S. Mitschke, F. Mühlberger, R. R. Baker and R. Zimmermann, J. Anal. Appl. Pyrol., 74 (2005) 454.
5 D. L. Zoller and V. J. Murray, Energy Fuels, 13 (1999) 1097.
6 D. L. Bowman, C. J. Smith, B. R. Bombick, J. T. Avalos, R. A. Davis, W. T. Morgan and D. J. Doolittle, Mutation Research/Genetic Toxicology and Environmental Mutagenesis, 521 (2002) 137.
7 F. Mühlberger, T. Streibel, J. Wieser, A. Ulrich and R. Zimmermann, Anal. Chem., 77 (2005) 7408.
8 F. Mühlberger, J. Wieser, A. Morozov, A. Ulrich and R. Zimmermann, Anal. Chem., 77 (2005) 2218.
9 M. Saraji-Bozorgzad, R. Geißler, T. Streibel, F. Mühlberger, M. Sklorz, E. Kaisersberger, T. Denner and R. Zimmermann, Anal. Chem., 80 (2008) 3393.
10 J. Wieser, D. E. Murnick, A. Ulrich, H. A. Huggins, A. Liddle and W. L. Brown, Rev. Sci. Instr., 68 (1997) 1360.

ICTAC 2008

DOI: 10.1007/s10973-008-9769-5