

It's the Coupling That Counts

Analysis of Gas Emissions from Biomass during Thermal Processes

A new method of coupling thermogravimetry to GC automates the continuous or event-controlled characterization of gas emissions from biomass during thermal processes. Individual components in gas mixtures can thus be better qualified.

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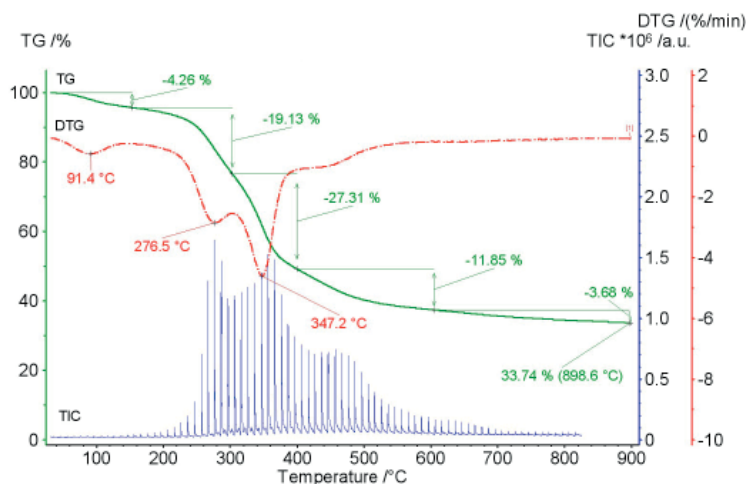
1 TG 209 F1 Libra® thermobalance with heated transfer line to the JAS valve box at the Agilent GC-MS

As a renewable and nearly CO₂-neutral energy source, biomass has become the subject of intensive analyses. Along with techniques for direct gas generation (biogas plants), many thermal treatment steps will be studied in order to produce high-energy solid fuels from biomass which can then be used as blending components in conventional fuels (coal) or as the single energy source in incineration plants. To achieve this, the volatiles must be thermally expelled in order to obtain fixed carbon, which is an effective energy source. For modeling the thermal treatment (combustion, pyrolysis) in the laboratory, thermal analysis offers well-established test methods:

Thermogravimetry (TG) serves for the precise recording of temperature-dependent mass changes, and differential scanning calorimetry (DSC) – often simultaneously applied – allows for the determination of energetic changes. In traditional instrument combinations, such as directly coupled mass spectrometers (MS) and infrared spectrometers (FT-IR), the gases evolving from the biomass are continuously recorded and analyzed, or they are all condensed into adsorption tubes, then thermally desorbed and subjected to a separate analysis.

The decomposition processes of the main biomass components (cellulose,

hemi-cellulose, lignin) overlap, so it is usually not possible to separate and identify individual components by means of directly coupled gas analysis systems. When analyzing products previously condensed in small adsorption tubes, on the other hand, the direct correlation with the temperature of the gas separation from the biomass is largely lost. Gas chromatography (GC) is a high-resolution method for separating volatile and semi-volatile compounds. The gas mixtures are separated on the basis of differences in component distribution between a stationary phase (e.g. inner coating of a capillary) and a mobile phase (e.g. helium as a purge gas). Since gas separation in the GC



2 19.79 mg of reed, pyrolysis in helium at 10 K/min, determination of residual moisture, volatiles and fixed carbon, with the profile of the total ion chromatogram (TIC) for volatiles.

separation column takes a certain amount of time – the duration depends on the sample properties, gas flow rate and length of the separation column as well as the type of stationary and mobile phases – direct coupling of a GC-MS to the TG with a continuous gas flow is not possible.

The new solution, however, is a direct coupling of TG/STA to a GC-MS (see figure 1), which is capable of implementing software-controlled gas sampling (sample loop in the heated valve block) as well as gas injection in a quasi-continuous operation mode, even at short intervals. Mass spectrometry is used as a detection system at the outlet of the GC separation column and records the time distribution of the separated gas components in the purge gas flow. This pre-separation of the gases by means of GC along with the high sensitivity and resolution of the MS allow structural information to be obtained, in turn enabling reliable identification of most of the evolved gas components.

The advantages of this new coupling are:

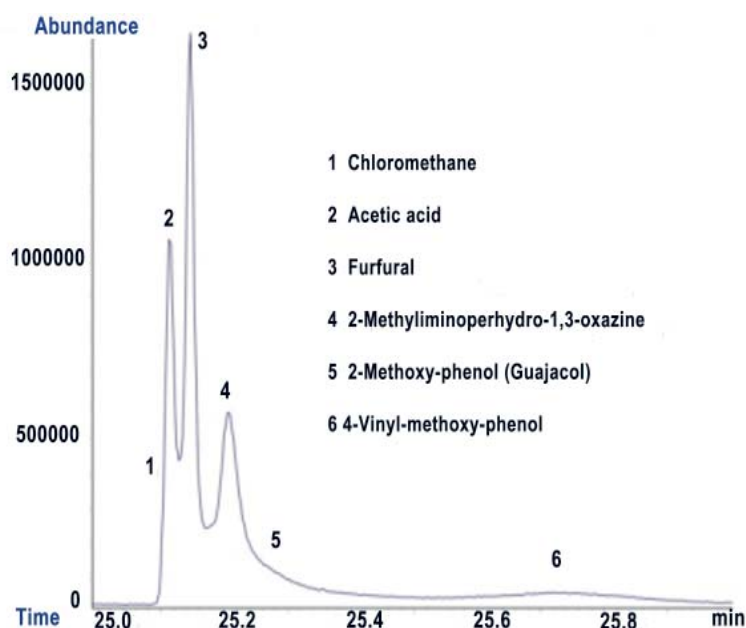
- TG/STA-GC-MS coupling with automatic, event-controlled or temperature-dependent GC-MS triggering.

- Completely heated gas transfer (300°C) from the TG/STA furnace outlet to the valve box and the injector at the GC-MS.
- Fast MS with a wide mass range for analysis of the gas chromatogram.
- The GC-MS can be used as a stand-alone application for liquid/gas injection at any time.

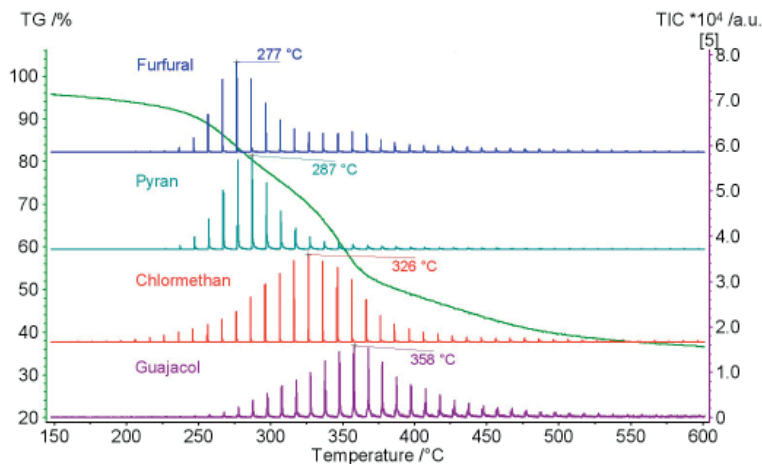
Sample and Results

As a representative of energy grasses, reed (*Phragmites australis*) was investigated in the continuous mode. Prior to the measurement, the dried grasses were chopped and ground for homogenization.

The heartwood of a domestic oak (*quercus robur*) in the form of fine sawdust was subjected to event-controlled TG-GC-MS analysis. For thermogravimetry with GC-MS coupling, sample masses of approx. 4 mg to 20 mg were inserted in small



3 Reed, section of the total ion chromatogram at 287°C (25 min) with indication of the main components identified in the pyrolysis gas.



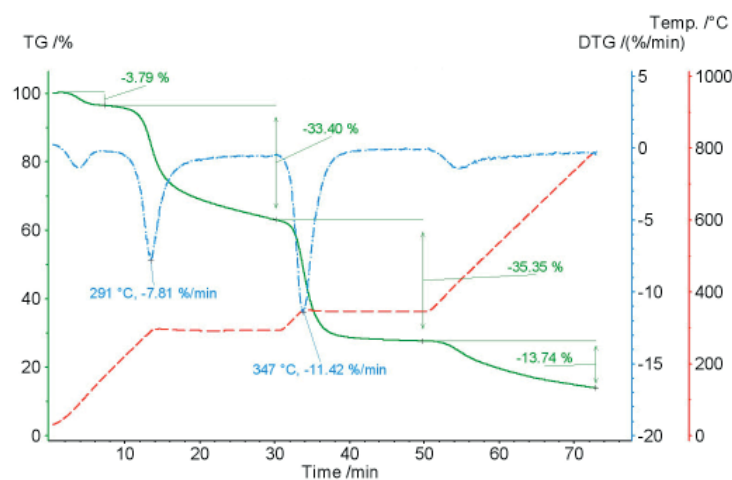
4 Temperature-dependence of selected pyrolysis products of reed with temperatures at maximum intensities (excerpt).

alumina crucibles. Helium and nitrogen, respectively, were selected as gas atmospheres in the sample chamber. The carrier gas for the GC was helium.

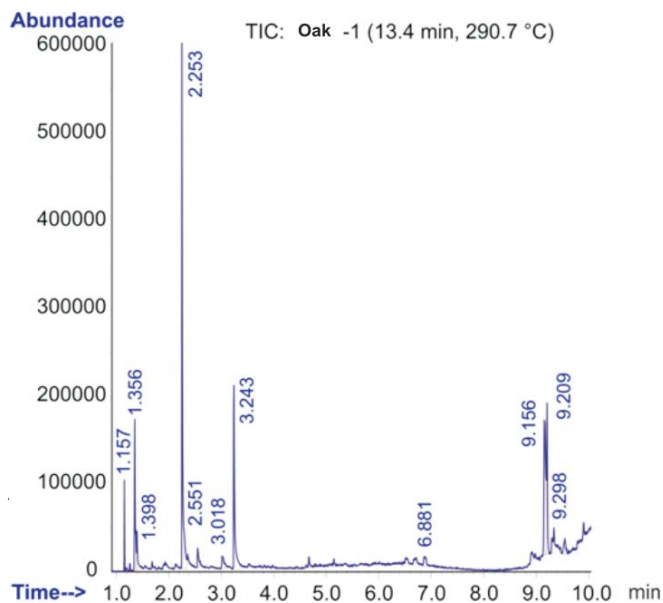
Heating of the reed in the thermo-balance resulted in the separation of residual moisture and volatiles in a multi-step process (see figure 2). The primary objective of the investigation was the analysis of organic components in the range from 200°C to 550°C; these are presented here by the total ion current curve at 1-min injection intervals and the mass spectrometer scan range of 45 u to 300 u, all highly analogous to the mass-change rate. The residual mass (here 33.74% evaluated at 899°C or, for more practical purposes, 37.42% at 600°C) is the measure for the fixed carbon (energy carrier) and the mineral content (ash). Further evaluation of the TIC curve – e.g., in the DTG peaks at 277°C and 347°C – also allows for good identification of the main components in the pyrolysis gas (see figure 3), even with the short 1-min intervals in the GC separation column (kept at a constant temperature of 250°C).

Variation of the injection intervals, the GC capillary temperature and the carrier gas flow rate offer the user great latitude, when necessary, for optimizing the separation of gas mixtures for this quasi-continuous operation mode of the TG-GC-MS coupling. In the process, the exact correlation with the gas separation temperature is preserved (see figure 4).

By triggering the GC-MS analysis via the Proteus software and importing the data into the TG evaluation, the relationship between the mass change of the reed sample and the temperature profile of the selected molecule ions for furfural (m/z 96), substituted pyran (m/z 114), chloromethane (m/z 50) and guaiacol (m/z 124) can be presented very clearly. Due to the lack of a direct temperature measurement at the sample, the pyrolysis GC-MS – otherwise useful – cannot offer the advantage of a reliable identification of overlapping gas separations including the precise temperature ($\leq +0.5^\circ\text{C}$) and time correlation ($\leq +0.1$ min) with the underlying mass loss in the temperature-controlled TG measurement. The novel TG-GC-MS coupling additionally offers automatic recognition of mass losses with direct triggering of the GC-MS analysis (event-controlled mode). The oak wood sample was heated in a nitrogen atmosphere at 20 K/min until the preset threshold of a mass-loss rate of 7.8%/min was first reached (see figure 5). At that moment, the heating



5 Event-controlled TG-GC-MS experiment on oak wood (4.37 mg) with two automatically detected mass-loss steps, stop of the heating with simultaneous start of the GC-MS analysis.



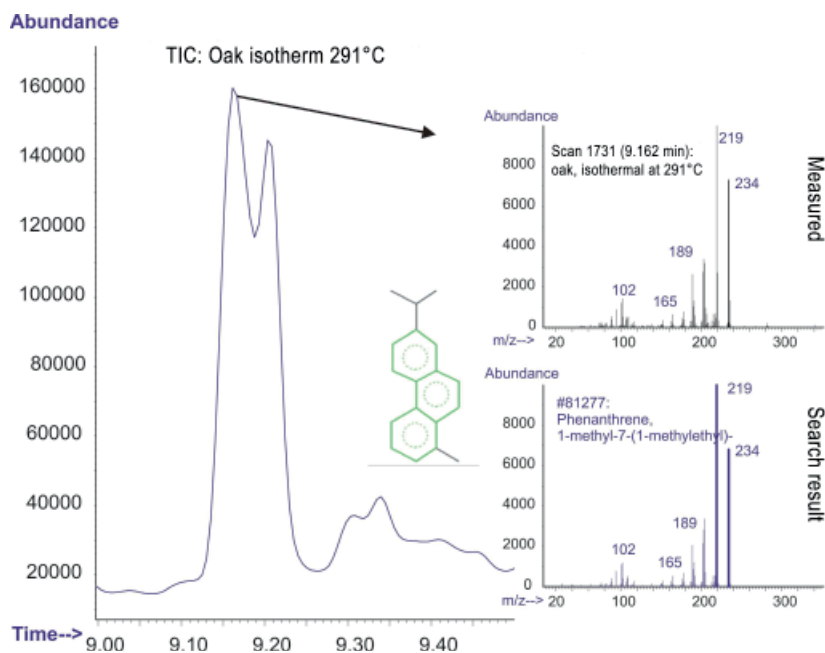
6 TIC chromatogram for oak wood at 291°C with indication of the retention times for the main peaks.

open the spectrum as recorded by the mass spectrometer at that point in time. Another click on the spectrum yields suggestions from the spectra library, sorted according to the quality of agreement with the measured spectrum. In the present case for the oak wood investigated, the substituted phenanthrene could clearly be identified. For quantifying the identified gases, both thermoanalytical and GC-MS possibilities are available. Determination of the area by means of the total ion chromatogram (yielded by the GC-MS software) is a simple method and correlates with the corresponding mass changes (yielded by the TG software).

was held (isotherm at 291°C) and a part of the content of the sample loop was injected into the GC separation capillary (split 10:1). With the GC furnace program (e.g., 0.5 min 60°C isothermal, heating 25 K/min to 310°C, duration approximately 10 min), a nearly complete separation of the gas mixture which is released at 291°C was achieved (see figure 6).

Analysis of the individual peaks in the registered TIC chromatogram and identification of the various components can be carried out automatically via the library search (integrated NIST 08 MS spectra library); here, for polycyclic aromatics, for example, the proof of substituted phenanthrene is presented (see figure 7).

A click on the peak in the TIC chromatogram at 9.156 min will



7 Identification of 1-methyl-7-(1-methylethylene)-phenanthrene during the pyrolysis of oak wood at 291°C at the TIC peak at 9.156 min; shown is the measured spectrum and the very good agreement (99%) with the NIST library spectrum for the substituted phenanthrene.