

Simultaneous STA-FT-IR on Biomass Straw

Dr. Alexander Schindler

Introduction

Straw is a generic term for threshed, dried grain stalks and the leaves of plants used to produce oils and fibers. In addition to its use in agriculture, straw also has the potential to become important as a CO₂-neutral energy carrier in the future. It is an excellent form of biomass because it is a by-product of arable farming. Unlike other biofuels, no special measures or additional land is required to grow it. The fly-ash from the burning process can furthermore be used as soil fertilizers for local farms.

Thermogravimetric analysis (TGA) or simultaneous thermal analysis (STA) which refers to simultaneous TGA and differential scanning calorimetry (DSC) are particularly suited for the investigation of pyrolysis or combustion processes. Information about the thermal stability of mostly solid fuels in term of reaction temperatures as well as combustion kinetics can quickly be obtained. Furthermore, the mass loss during pyrolysis or combustion and the ash content can be quantified.

The measurement described herein examines the decomposition behavior of straw [1]. The gases evolved during decomposition are identified by means of FT-IR spectroscopy using the fully integrated STA-FT-IR coupling system NETZSCH *Perseus* STA 449 (see figure 1).

Measurement Results

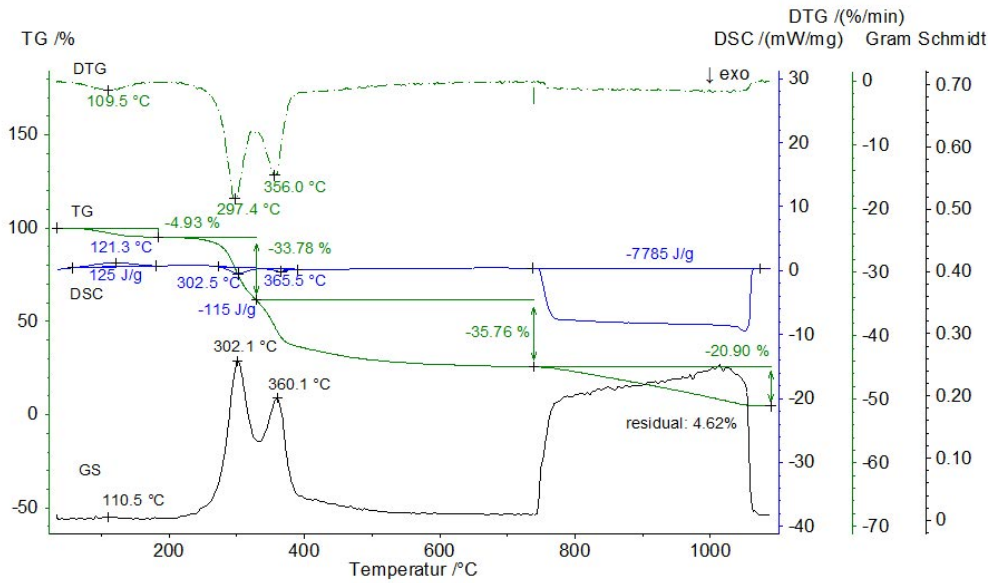
A powdered straw sample of unknown origin with an initial mass of 28.64 mg was measured in a Pt crucible with pierced lid at a heating rate of 20 K/min. The gas atmosphere was changed from pure nitrogen to air at 740°C (the gas flow rates were 70 ml/min). Below 740°C, three mass-loss steps of 4.9%, 33.8% and 35.8% occurred which



1 NETZSCH *Perseus* STA 449: The Bruker type "Alpha" FT-IR spectrometer coupled directly to a simultaneous thermal analyzer STA 449 *Jupiter*[®] equipped with an optional automatic sample changer (ASC). The sample space of the furnace, the heated coupling interface as well as the gas cell of the FT-IR spectrometer are shown partially transparent in order to display the path of the evolved gases [1].

were accompanied by one endothermic and two overlapping exothermic effects with enthalpies of 125 J/g

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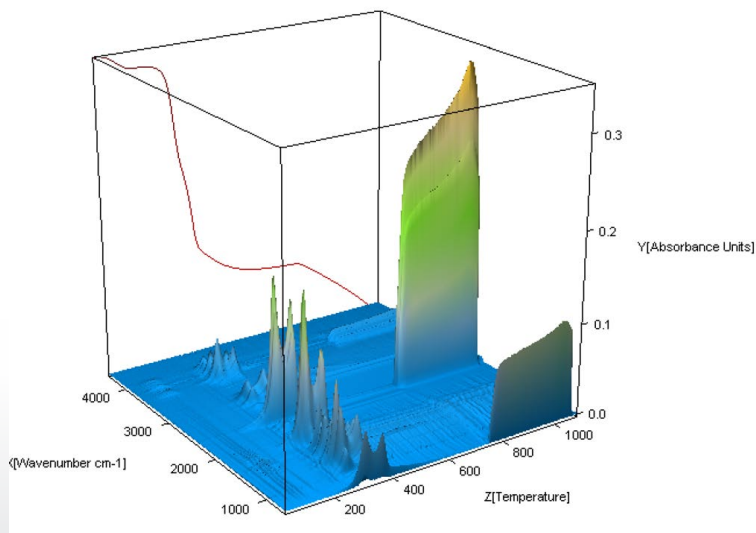


2 Temperature-dependent mass change (TGA) rate of mass change (DTG, dashed), heat flow rate (DSC) and Gram-Schmidt signal (GS) of a straw sample. The gas atmosphere was switched from nitrogen to air at 740°C.

and -115 J/g (see figure 2). During these mass-loss steps, the Gram-Schmidt signal, reflecting the sum of the entire FT-IR absorbances for all wavenumbers, showed maxima at 111°C, 302°C and 360°C which correlate well with the DTG curve. Another mass-loss step of 20.9% as well as an exothermic effect with a total enthalpy of -7.79 kJ/g occurred after switching to air at 740°C. These effects are due to the combustion of the so called pyrolytic soot,

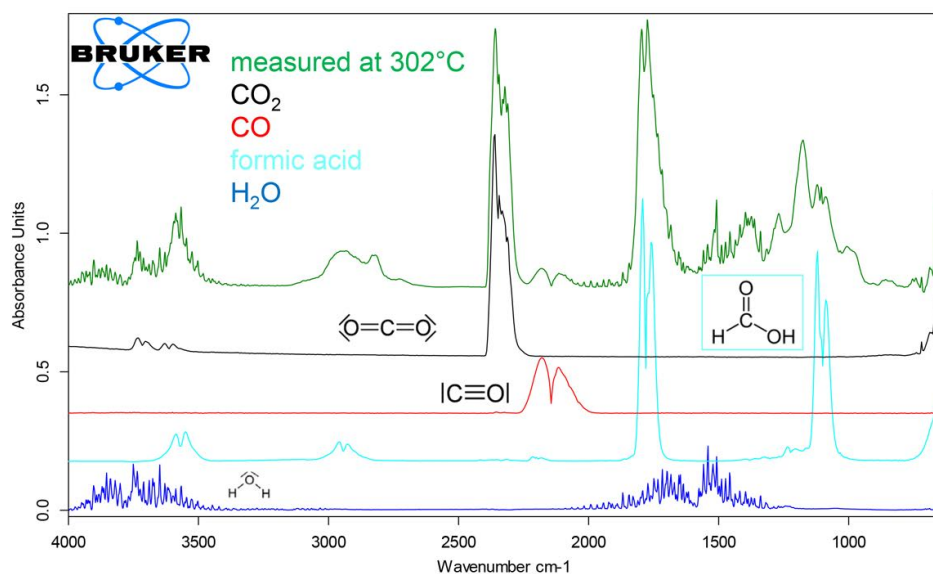
leaving a residual mass of 4.6%, which reflects the ash content.

The 3-D view of the FT-IR spectra of the evolved gases collected throughout the decomposition of the straw is shown in figure 3. Of particular interest are the spectra below 740°C where pyrolysis of the sample occurred. The strong FT-IR absorbance at higher temperatures is due to the release of CO₂ as a result of combustion.



3 Wavenumber-dependent FT-IR absorbance of the straw sample as a function of temperature. The corresponding TGA curve is shown in the rear ZY plane.

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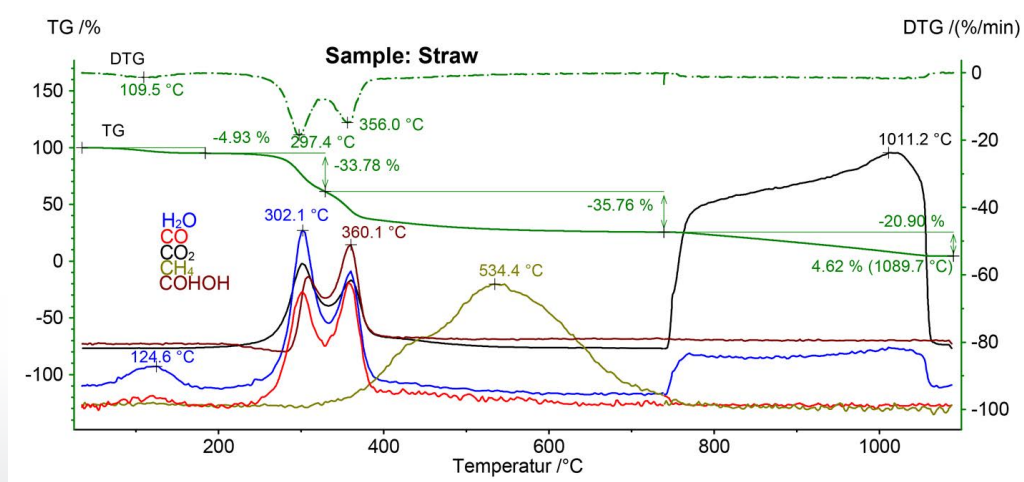


4 FT-IR spectrum of the straw sample measured at 302°C together with the database spectra of CO₂, CO, formic acid HCOOH and H₂O (from top to bottom). The spectra were rescaled and shifted for clarity.

The evolved gas species were identified by comparing individual, extracted 2-D spectra at specific temperatures with library spectra. For example, figure 4 shows that the spectrum of the gases evolved at 302°C is consistent with a mixture containing CO₂, CO, H₂O, and formic acid (HCOOH). The evolution of individual gas species over the course of the sample decomposition can be traced by integrating a characteristic FT-IR absorbance range for the molecules and overlaying the curve of the integration values as a function of temperature with the TGA and DTG curves from the analysis. The range between 2200 and 2450 cm⁻¹

was integrated for CO₂, between 1950 and 2150 cm⁻¹ for CO, between 1300 and 1600 cm⁻¹ for H₂O and between 1000-1150 cm⁻¹ for HCOOH.

As can be seen from figure 5, H₂O was released during the 1st mass-loss step (evaporation of moisture) and during the 2nd and 3rd mass-loss step (pyrolysis), during which CO, CO₂ and HCOOH were also evolved. CH₄ was evolved over a broad temperature range with a maximum at 534°C and CO₂ was detected again above 740°C as a result of the combustion of the sample in air.



5 Temperature-dependent mass change (TGA), rate of mass change (DTG) and FT-IR traces for H₂O, CO, CO₂, formic acid HCOOH and CH₄ (each trace in individual arbitrary units). The gas atmosphere was switched from nitrogen to air at 740°C.

Conclusion

Use of the very compact STA-FT-IR coupling system NETZSCH *Perseus* STA 449 for characterizing the pyrolysis and combustion of straw [1] was demonstrated. Good correlation between the detected mass-loss steps and gas evolution was observed demonstrating the advantage of a direct coupling interface. Identification of the gases evolved by means of a database search allows for detailed interpretation of the chemistry involved in the mass-loss steps associated with pyrolysis, in particular.

Literature

[1] A. Schindler, G. Neumann, A. Rager, E. Füglein, J. Blumm, T. Denner: *J Thermal Anal Calorim*, DOI 10.1007/s10973-013-3072-9 (online and freely available at <http://link.springer.com/article/10.1007%2Fs10973-013-3072-9>)