Thermal Analysis Application

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Study of a Biomass Sample by TGA-GC/MS and TGA-Micro GC/MS

Introduction

Since about the year 2000, there has been a marked change to the use of more renewable and sustainable energies. This change has been catalyzed by the prospect of limited resources of fossil fuels, the greatly increased awareness of environmental and atmospheric problems, and the unsolved problems associated with the operation and decommissioning of nuclear power plants. Renewable energy is energy derived from resources, which are naturally replenished on a short timescale. These include hydro- and wind-power, biomass, solar energy, geothermal power, and biofuels. Related technologies such as fuel cells, batteries or energy storage systems utilize special compounds that can be investigated by thermal analysis.

Biomass refers to renewable, non-fossil, organic substances from which energy can be obtained. Different kinds of biomass such as wood, straw, corn, sugar cane, eucalyptus, and oilseed rape are readily available and fast growing. Before biomass can be used as an energy resource, it has to be suitably treated [1, 2]. For example, liquefied biofuels are used for transport, whereas solid biomass is needed for heat and electricity generation. Several complex processes are available to do this. Thermal analysis was used to characterize empty fruit branches of oil palm – a biomass material commonly used in biofuels; the sample was measured by TGA coupled to GC/MS and Micro GC/MS to determine its moisture content, dry mass, and the gases released during pyrolysis.

Sample

Empty fruit branches of oil palm

Conditions

Measuring cells:	TGA-IST-GC/MS and TGA-Micro GC/MS with Modules A (Molsieve 5 column), Module B (Pora-PLOT U column) and Module C (Sil 5 CB column) connected to MS
Crucible:	Aluminum oxide 150 µL
Sample preparation:	As received, about 20 mg
TGA Measurement:	Heating from 40 to 1100 °C at 5 K/min
Atmosphere:	Nitrogen at 40 mL/min
Micro GC/MS	Run time: 120 s
GC:	Oven: isothermal at 40 °C for 10 min, heating from 40 to 310 °C at 10 K/min, isothermal at 310 °C for 30 min Column flow: 0.8 mL/min, split: 5:1 Injector temperature: 300 °C
MS:	Scan mode: m/z from 5 to 350

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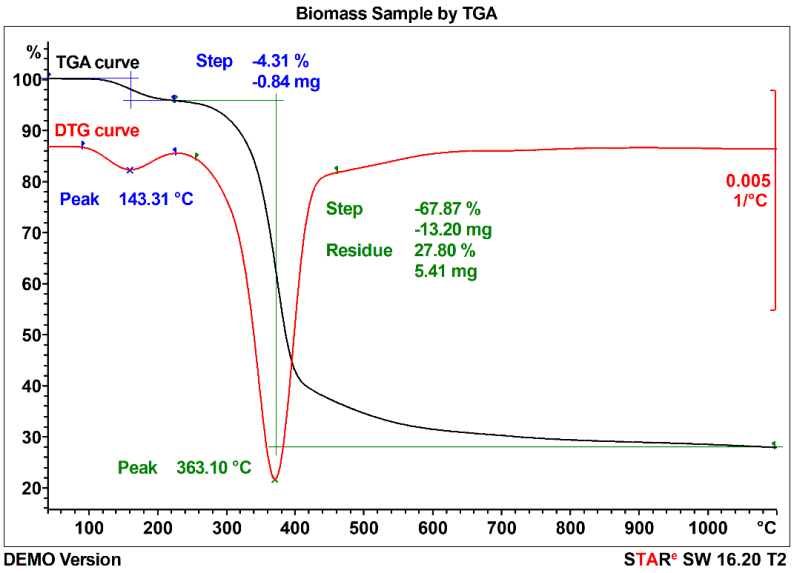

Figure 1. TGA analysis of the biomass sample derived from empty fruit branches of oil palm; the TGA curve is colored black, the DTG curve in red.

Interpretation

Figure 1 shows the TGA mass loss curve in black and the DTG curve in red. The biomass sample exhibits two mass loss steps. In the first step, moisture is released (about 4.3%; Table 1) up to about 200 °C. This is followed by pyrolysis of the organic substances (approximately 67.9%; Table 1).

Evaluation

	TGA step in %	DTG peak temperature in °C
First step (moisture)	4.3	143.3
Second step (organic substances)	67.9	363.1
Residues	27.8	-

Table 1. TGA results

The TGA measurement was used to determine the temperatures at which the decomposition gases were to be analyzed in the TGA-IST-GC/MS experiment. The temperatures are shown in Table 2.

TGA Temperature in °C	100	200	250	300	370	420	500	600	700	800	900	1000
IST Loop	1	2	3	4	5	6	7	8	9	10	11	12

Table 2. The TGA temperatures at which gas samples were collected and stored in storage loops of the storage interface.

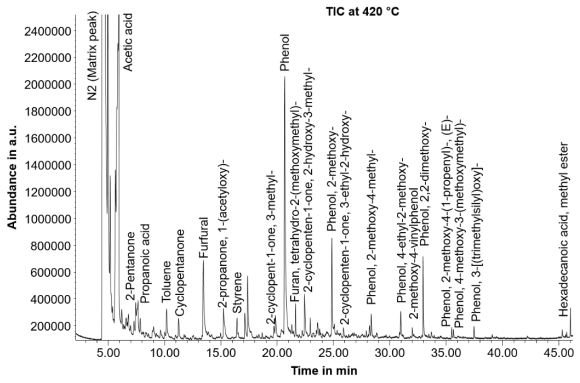

Figure 2. TIC chromatogram corresponding to a TGA temperature of 420 °C; some of the peaks identified are labeled.

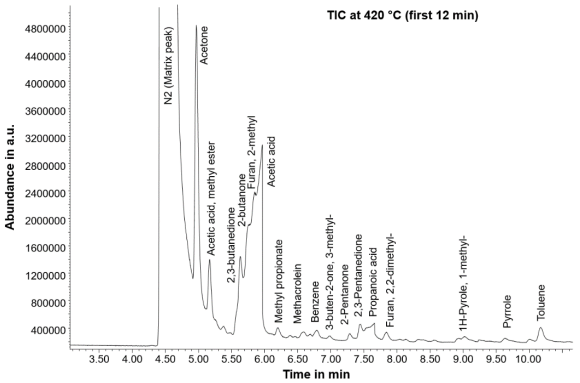

Figure 3. The first 12 minutes of the TIC chromatogram corresponding to a TGA temperature of 420 °C; the main peaks identified peaks are labeled.

Interpretation

Figure 2 shows the TIC chromatogram of the gas sample stored at 420 °C. Each peak in the TIC corresponds to a different compound. For better visualization, the first 12 min of the same TIC are shown on an expanded time scale in Figure 3. Over 50 different compounds were identified (see Table 3), mainly ketones, aldehydes, heterocyclic organic compounds, carboxylic acids, phenol, esters and furan. The most important detected compounds for biofuel production include acetic acid, phenol, acetone, BTEX, and furfural.

Evaluation

Main compounds evolved and detected by TGA-GC/MS	
Ketones and aldehydes	
acetone	cyclopentanone, 2-methyl-
2,3-butanedione	cyclopentanone, 3-methyl-
methacrolein	2-propanone, 1-(acetyloxy)-
2-butanone	2-cyclopenten-1-one, 2-methyl
3-buten-2-one, 3-methyl	butyrolactone
2-pentanone	2-cyclopent-1-one, 3-methyl-
2,3-pentanedione	2-cyclopenten-1-one, 2-hydroxy-3-methyl-
3-heptanone	2-cyclopenten-1-one, 2,3-dimethyl-
cyclopentanone	2-cyclopenten-1-one, 3-ethyl-2-hydroxy-
Cyclic organic compounds	
benzene	ethylbenzene
pyridine	m+p-xylenes
toluene	styrene
Carboxylic acids	
acetic acid	propanoic acid
Phenols	
phenol	phenol, 2-methoxy-
phenol, 2-methyl-	
Esters	
acetic acid, methyl ester	acetic acid, phenyl ester
methyl propionate	benzoic acid, methyl ester
Furans	
furan, 2,2-dimethyl-	benzofuran
1H-pyrole, 1-methyl-	pyrrole
2-methyl-furan	furan, tetrahydro-2-(methoxymethyl)-
furfural	

Table 3. Main evolved compounds detected by GC/MS in a TGA-GC/MS experiment.

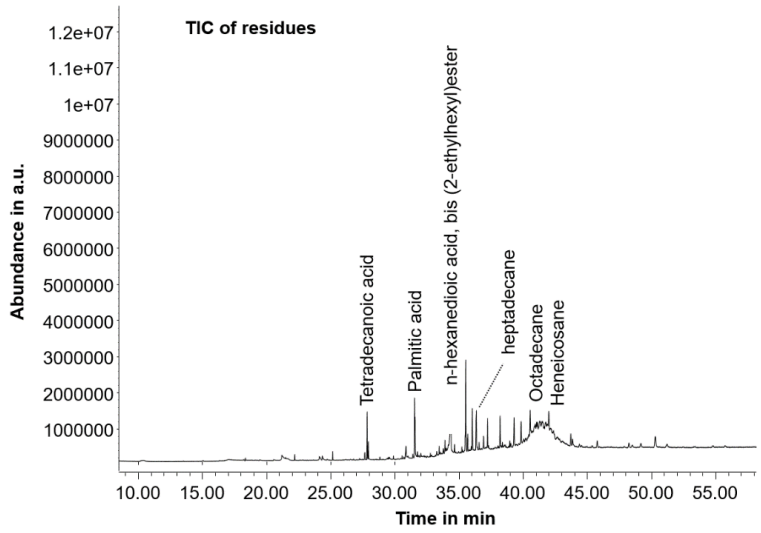

Figure 4. GC/MS analysis of residue (evolved products that condensed in the protective tube).

Interpretation

After the TGA-IST-GC/MS experiment, the condensed products remaining in the protective tube between the TGA and IST were collected (see Section 4.3) and dissolved in isopropanol. A small volume of this solution (1 µL) was then injected manually into the GC using the same method as for the storage loops but with a 50:1 split ratio. Figure 4 shows the evolved compounds detected by GC/MS; these are mainly fatty acids and alkanes with high boiling points.

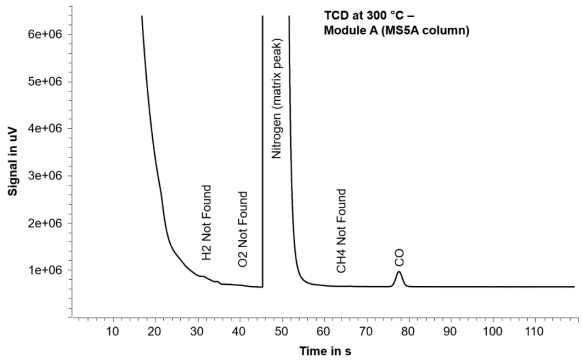

Figure 5. TCD chromatogram of Module A at about 300 °C.

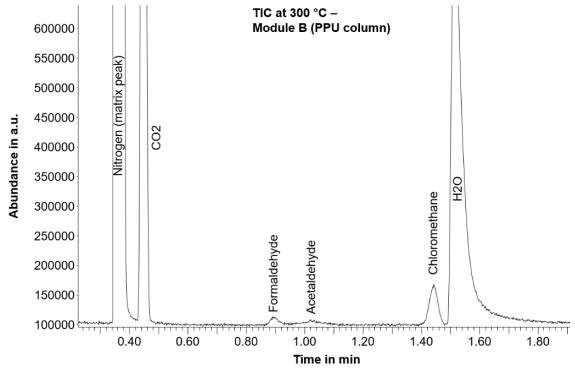

Figure 6. TIC chromatogram of Module B at about 300 °C.

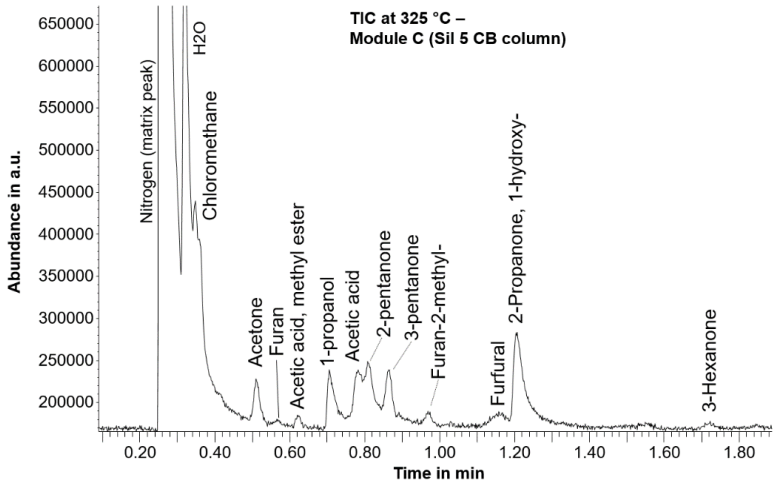

Figure 7. TIC chromatogram of Module C at about 325 °C.

Interpretation

Two additional TGA-Micro GC/MS experiments were performed. In the first experiment, the MS was connected to Module B and in the second to Module C. Figure 5 displays the chromatogram obtained at about 300 °C using Module A, Figure 6, at 300 °C using Module B, and Figure 7 at 325 °C with Module C. The results confirm that the first decomposition step between 100 and 200 °C corresponds only to the loss of moisture. During the second step, H_20, CO, CO_2, formaldehyde, acetaldehyde, and chloromethane are detected with Modules A and B. Compounds detected with Module C consisted mainly of light ketones such as acetone, light furans, acetic acid and methyl acetate (Table 4).

Evaluation

Main compounds evolved and detected by TGA-Micro GC/MS	
Module A	
carbon monoxide	
Module B	
carbon dioxide	formaldehyde
water	acetaldehyde
chloromethane	
Module C	
acetone	furan
acetic acid, methyl ester	1-propanol
acetic acid	2-pentanone
3-pentanone	furan-2-methyl-
furfural	2-propanone,1-hydroxy-
3-hexanone	

Table 4. Main compounds detected during a TGA-Micro GC/MS experiment.

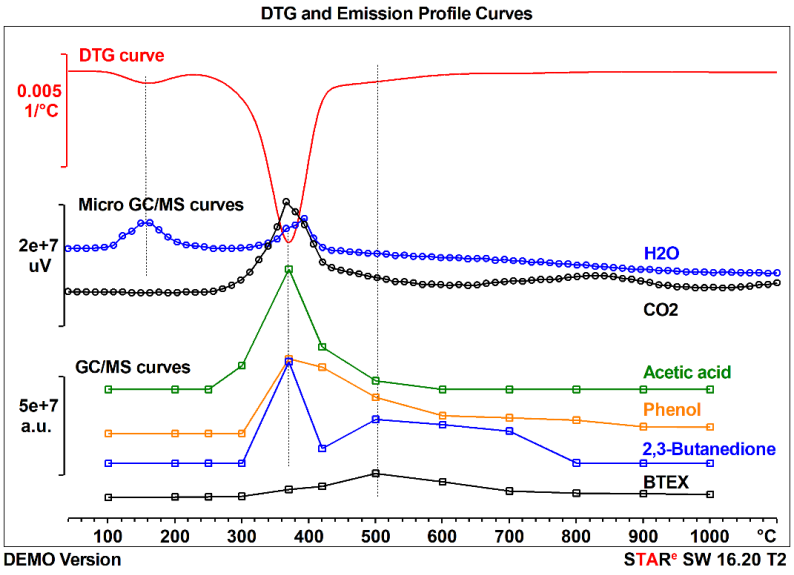

Figure 8. TGA curve and emission profiles of selected evolved compounds.

Interpretation

The Micro GC/MS emission profiles in Figure 8 indicate the release of water during the first and second decomposition steps; most other compounds, excluding BTEX, are evolved in the second step (main peak on the DTG curve). BTEX compounds (benzene, toluene, ethylbenzene and xylenes) show a maximum emission peak at about 500 °C, corresponding to the shoulder in the DTG curve. Here it can also be seen that 2,3-butanedione is released in two stages: first in the second decomposition step (larger peak) and again at 500 °C (smaller peak).

Conclusion

Evolved compounds of biomass can be easily characterized by TGA coupled to a GC/MS (heavy and medium compounds) and Micro GC/MS (permanent and light compounds). The results yielded information about the composition (moisture, ash, carbon) of the biomass material as well as the type of gases that are produced during pyrolysis. These techniques can be used to characterize the structure and composition of the various gases evolved from the thermal decomposition of biomass feedstocks, and hence help assess their potential as a source of energy.

References

[1] Thomas Bührke, Roland Wengenmayr: Erneuerbare Energie Konzepte für die Energiewende, Wiley-VCH, 3. Auflage 2011.

[2] Wiebren de Jong, J. Ruud van Ommen, Biomass as a Sustainable Energy Source for the Future: Fundamentals of Conversion Processes, Wiley, ISBN: 978-1-118-30491-4, Nov 2014.

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