VOLATILE COMPOSITION AND THERMAL BEHAVIOR OF HYDROCHARS PRODUCED FROM CARBOHYDRATES AND WOOD BIOMASS

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Introduction

Among the various thermochemical methods for utilizing biomass, hydrothermal carbonization (HTC) is a promising technology. HTC converts renewable carbon sources, such as lignocellulosic biomass, into an energy-dense carbonized solid product known as hydrochar (**HC**). Hydrochars of carbohydrates (i.e., glucose, cellulose, starch) and woody biomass samples (i.e., sawdust of fir and larch) were prepared by HTC at 200 °C for 24 h. The properties of the hydrochars were characterized, and thermal behavior and volatile composition of the solids were also determined.

The findings of this study may enhance the production of hydrochars from different sources, which have the potential to be used as substitute products for coal and other fossil-based energy sources.

Materials

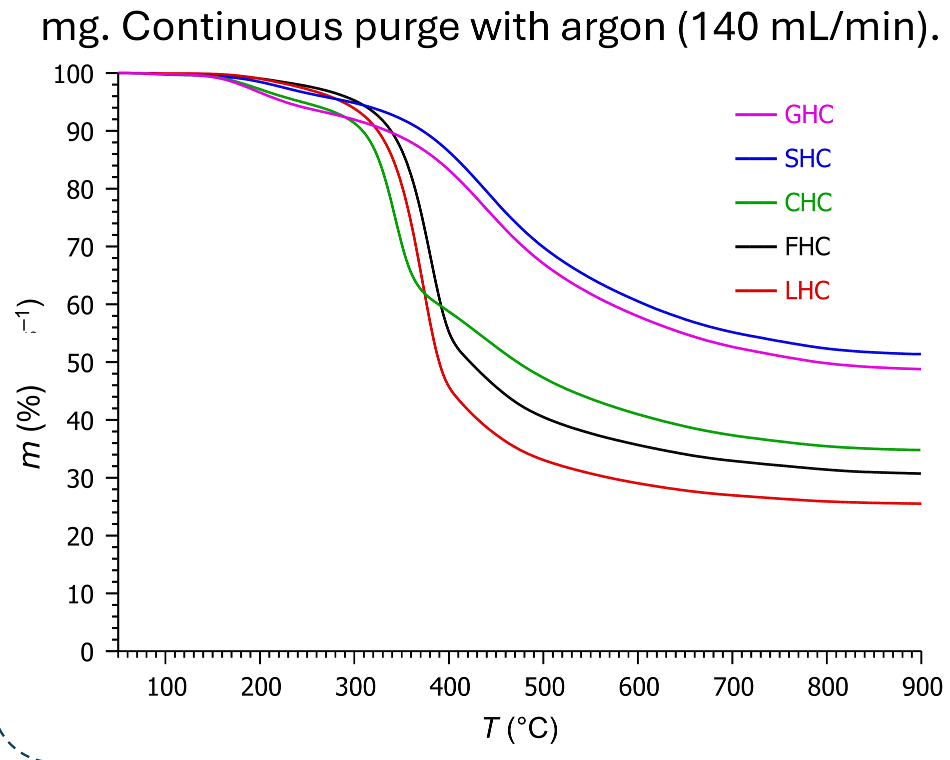
Commercially obtained anhydrous D-(+)-glucose (**G**), starch (**S**) and cellulose (**C**) was used as carbohydrate feedstocks. Fir wood (**F**) and larch wood (**L**) sawdust samples of were obtained from a local wood processing company in Karabük, Turkey.

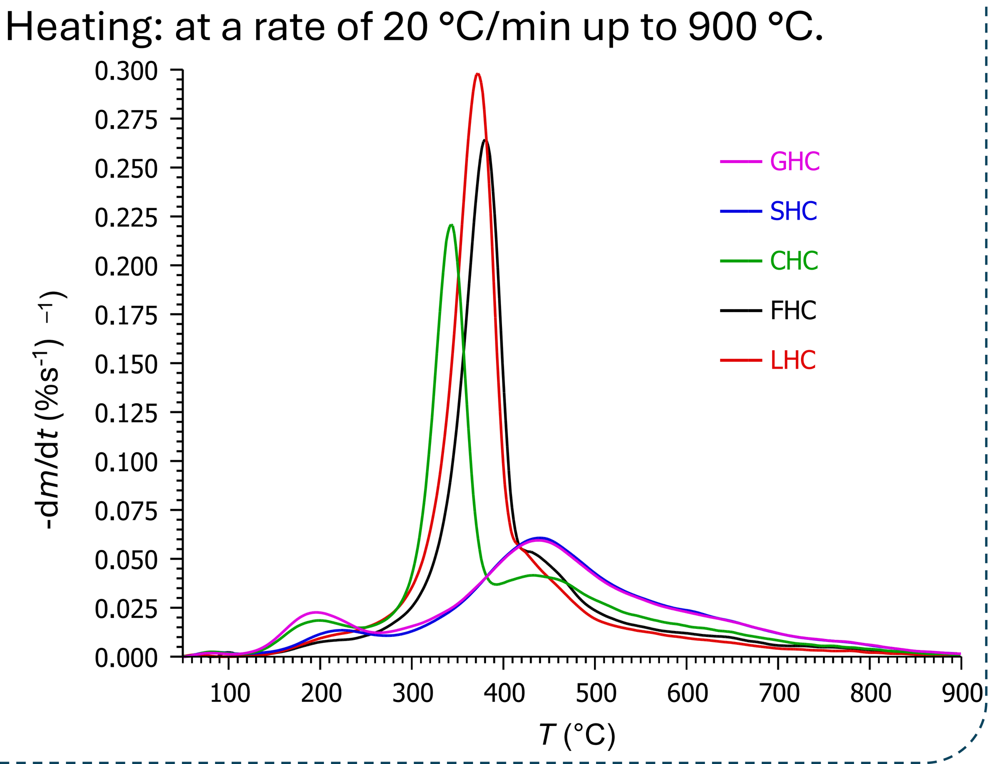
Hydrothermal carbonization

HTC experiments were performed with 2 g sample and 20 mL deionized water in 50 mL PPL-lined stainless-steel autoclaves at 200 °C (24 h). Solid hydrochar was filtered, rinsed with water and dried. Obtained samples: GHC, SHC, CHC, FHC, LHC.

Thermogravimetric analysis (TGA)

Performed using a TGS-2 thermobalance with a modified furnace (Perkin Elmer, USA). Sampling: 4 mg. Continuous purge with argon (140 mL/min). Heating: at a rate of 20 °C/min up to 900 °C.





Sample properties

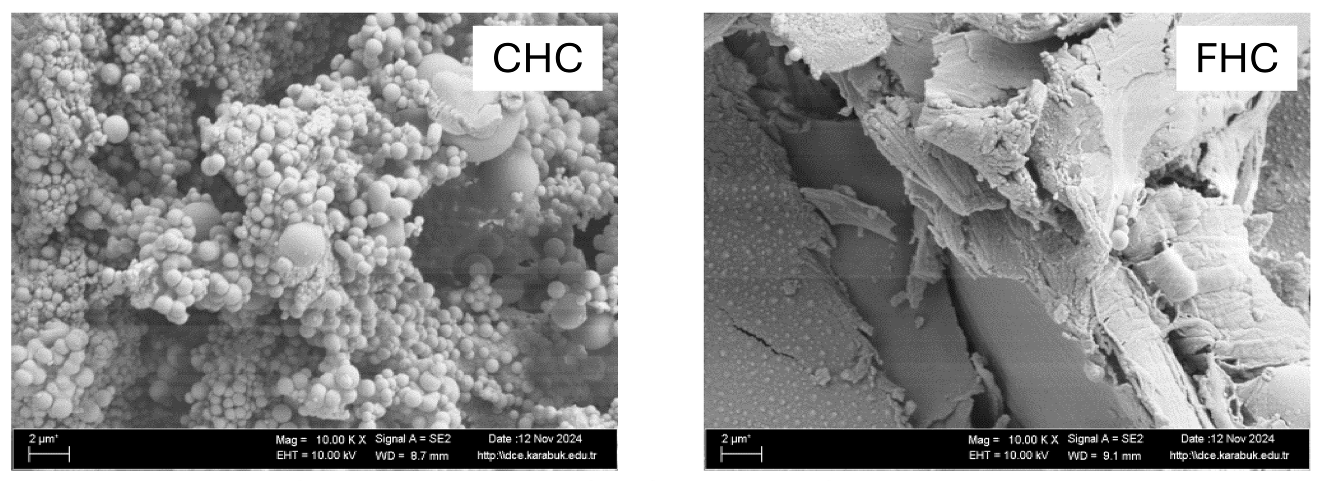
The surface morphologies of the feedstocks and hydrochars were investigated using Carl Zeiss Ultra Plus Gemini FESEM scanning electron microscope (SEM). The Fourier transform infrared (FTIR) spectra were measured with Thermo Scientific Nicolet iS50 FTIR-ATR.

Measure	Glucose	Starch	Cellulose	Fir wood	Larch wood
Hydrochar yield (wt%)	39.8	38.2	41.5	51.4	50.3
$HHV_{feedstock}$[a] (MJ kg^{-1})	12.6	12.1	12.1	16.7	18.7
$HHV_{hydrochar}$[a] (MJ kg^{-1})	22.7	21.0	17.9	21.3	21.4
EDR[b]	1.80	1.74	1.47	1.27	1.14
EY[c] (%)	71.6	66.5	60.9	65.3	57.3

[a]HHV: higher heating value,
[b]EDR: energy densification ratio ($HHV_{hydrochar}$ /$HHV_{feedstock}$),
[c]EY: energy yield (hydrochar yield × EDR).

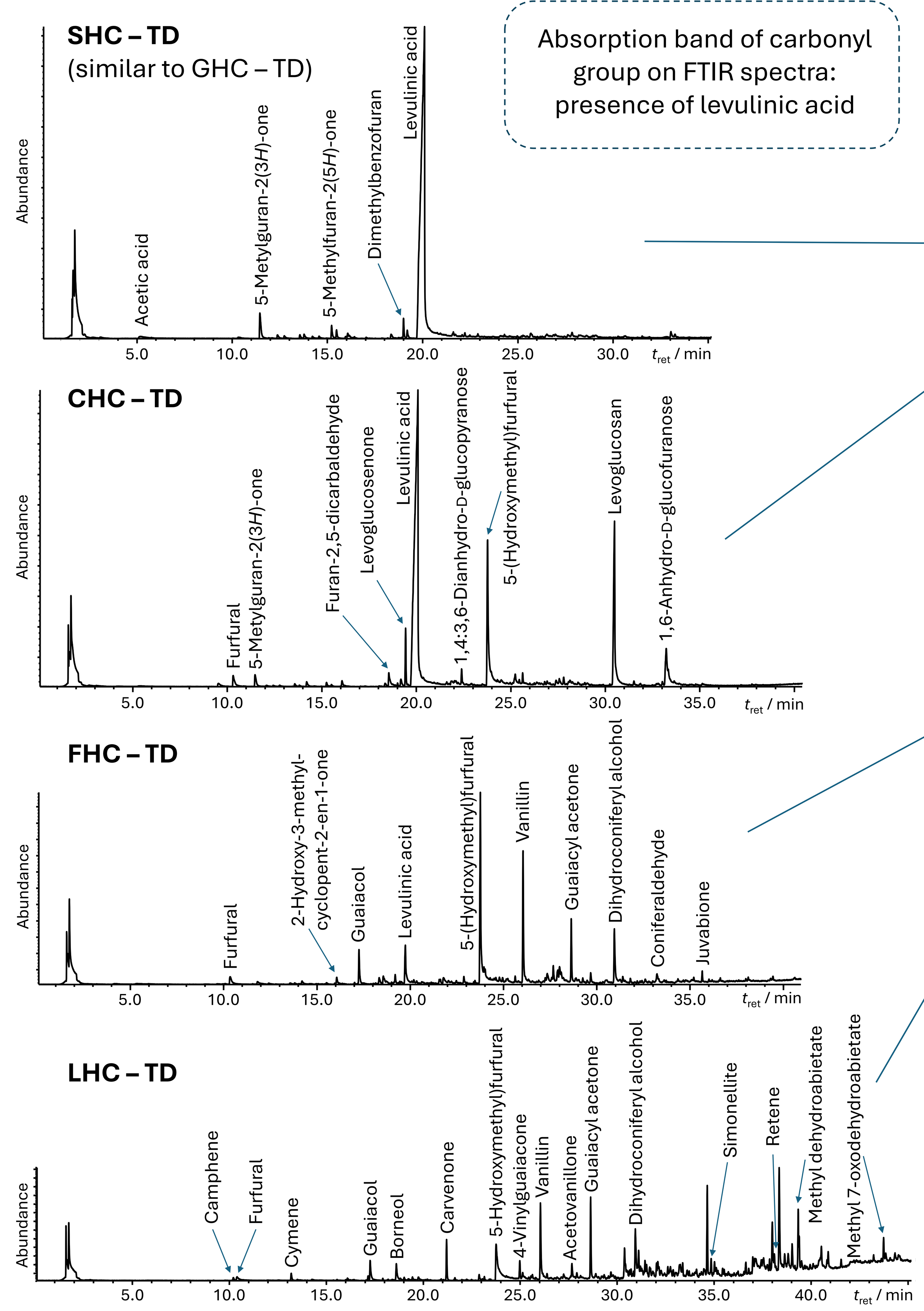
Py-GC/MS analysis

Frontier EGA/Py-3030D multi-shot pyrolyzer mounted on Agilent 7890A/5977B GC/MS instrument. Thermal desorption (**TD**): 2 mg HC heated at 280 °C (30 s). Pre-heated pyrolysis (**pPy**): 2 mg GHC or SHC pre-heated at 300 °C (1 min), then flash pyrolysis at 550 °C (30 s); 3 mg CHC, FHC or LHC pre-heated at 400 °C (1 min), then flash pyrolysis at 550 °C (30 s). Chamber helium flow: 100 mL/min. Inlet temperature: 280 °C. Column type: DB-1701. Column flow: 1 mL/min. Oven temperature program: 40 °C (4 min) – 6 °C/min – 280 °C (11 min). Electron ionization at 70 eV. Scan mode: *m/z* 14–500.



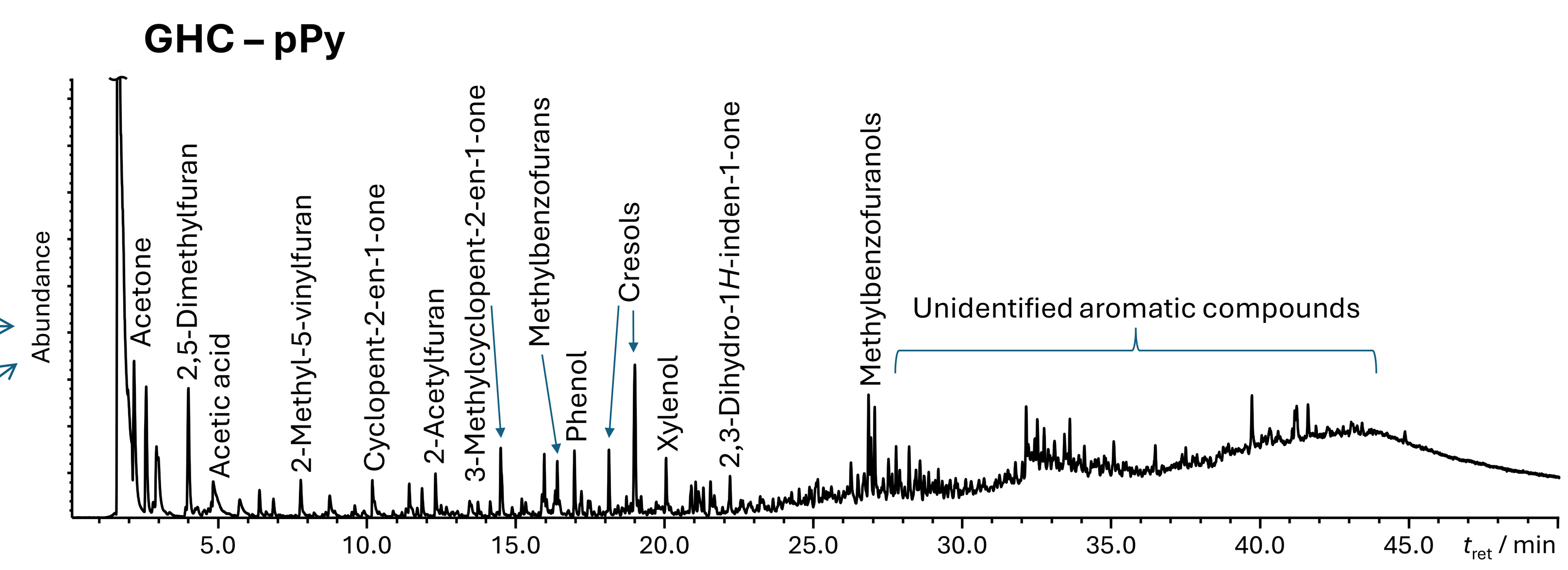
SEM images of CHC and FHC samples

TD chromatogram of the hydrochars:

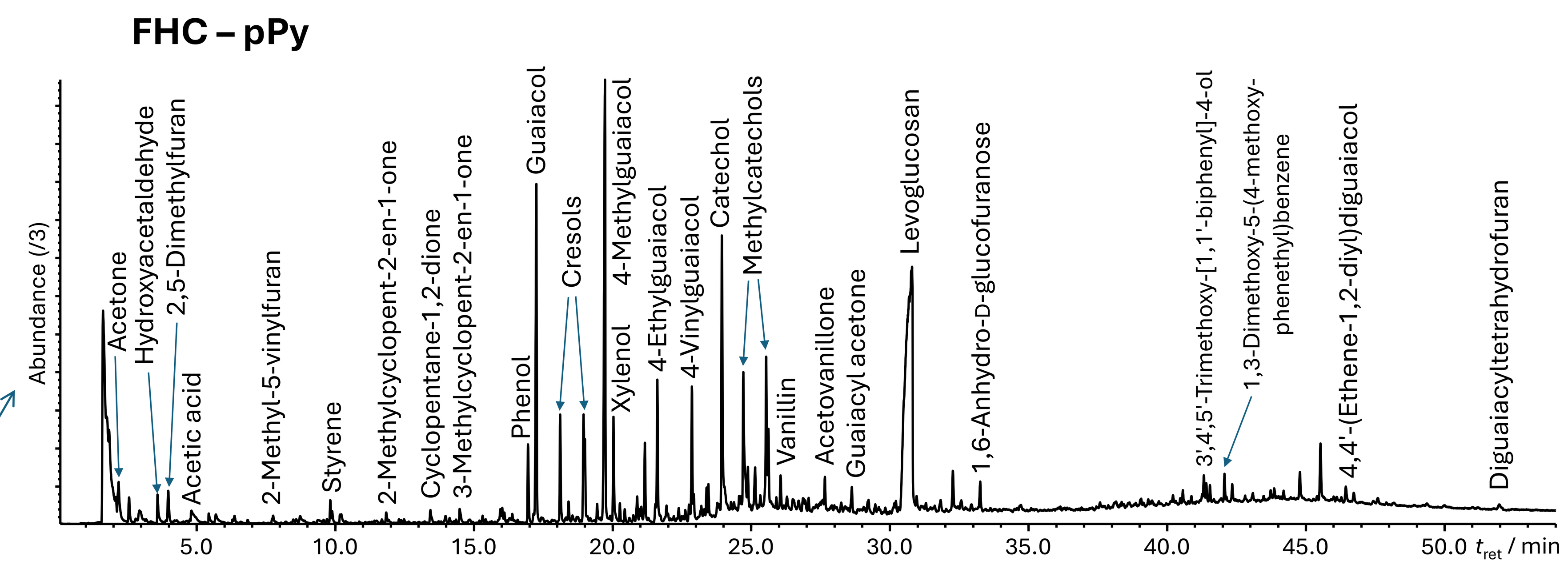


Flash pyrolysis chromatogram of preheated hydrochars:

– of carbohydrate hydrochars:



– of wood hydrochars:



Conclusion

The comparison of the thermogravimetric curves showed that the carbohydrate contents significantly degraded during HTC, but a smaller volatile fraction remained in each hydrochar. Based on this observation, two-staged Py-GC/MS measurements of the hydrochars were performed for the detailed analysis of the volatile contents of the hydrochars of carbohydrates and woody biomass samples. TD of the carbohydrate hydrochars (GHC, SHC and CHC) showed that their volatile contents has significant amounts of levulinic acid. While the thermally more stable part of these samples (pearl-shaped structures on SEM images) showed also similar composition of mainly versatile aromatic compounds. The cellulose content of wood samples (FHC and LHC) produced more 5-(hydroxymethyl)furfural than levulinic acid. The volatile fraction of LHC had significant amount of terpenoids and resin components. The thermally more stable fraction of wood hydrochars were almost identical, dominated by monomeric and dimeric lignin decomposition products.

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