BioBank of lignocellulosic samples of agricultural and forestall by-products and their analysis by Py-GCMS

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Closing meeting
„Joint chemical laboratory for the service of bioeconomy in the Slovak-Hungarian border region"
Interreg, SKHU/1902/4.1/001/Bioeconomy

Faculty of Chemical and Food Technology STU in Bratislava
Radlinského 9, 812 37 Bratislava, Slovak Republic

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ttk
Interreg Slovakia-Hungary
Building Partnership
STU SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

Aims

Collection and conversion of renewable raw materials, especially components of Agricultural lignocellulosic waste, found in the border regions of Slovakia and Hungary, into chemicals and materials with high added value as components of the circular economy.

Fast pyrolysis of lignocellulosic biomass in a microreactor connected with GC-MS systeme.

Collected agricultural and forestall byproducts


pea


soya


rye


barley


cane


mustard


vine


sunflower


oats


invasive plants


wheat

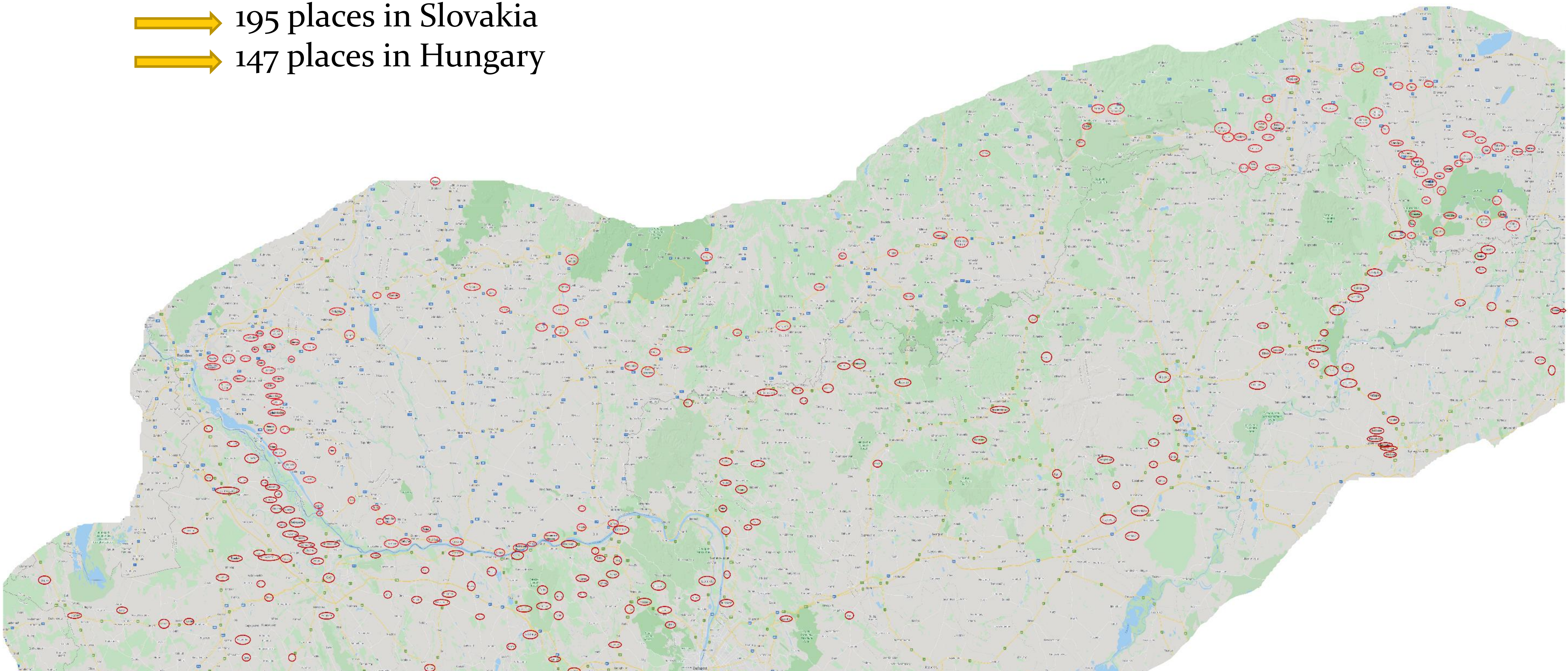

rape


poppy


corn

Map of collection places

- 195 places in Slovakia
- 147 places in Hungary



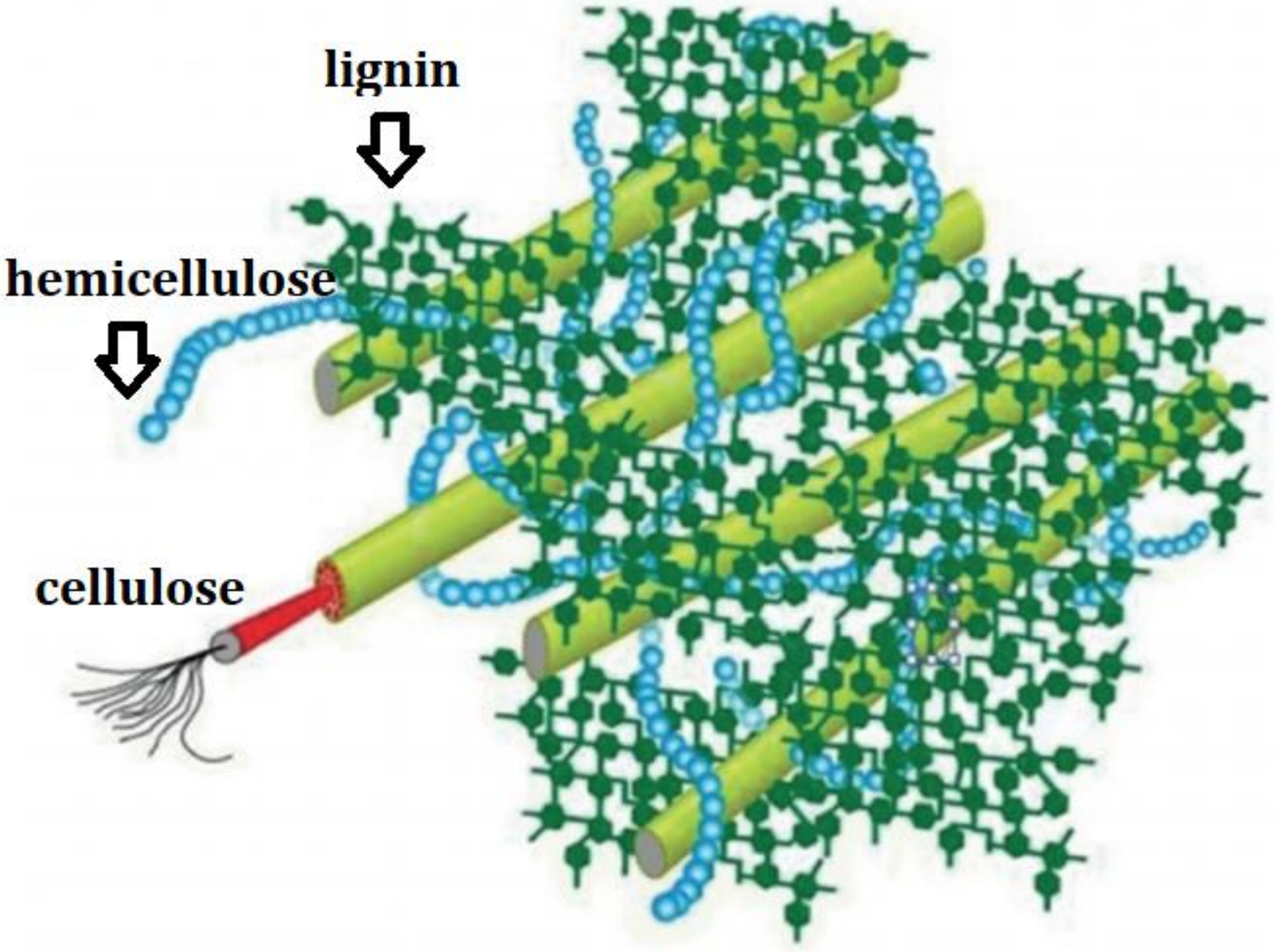
Agricultural and forestall byproducts after collection

850 samples

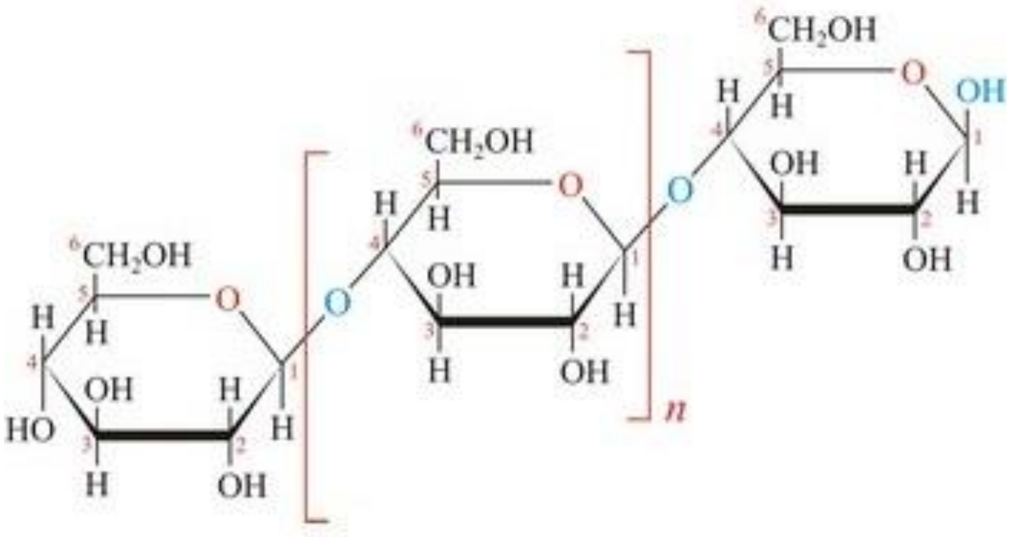
Biobank

850 samples

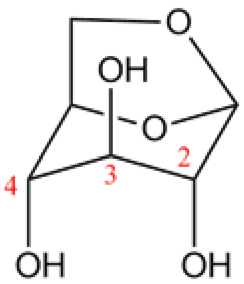
Lignocellulosic biomass



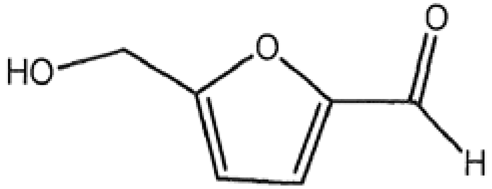
Cellulose



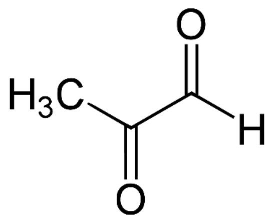
- Linear polysaccharide
- Long β-D-(1,4)-glucopiranose units
- Crystalline and amorphous structure



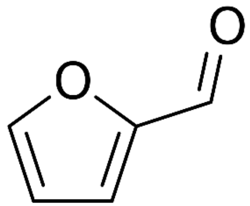
levoglucosan



hydroxymethylfurfural



methylglyoxal



furfural

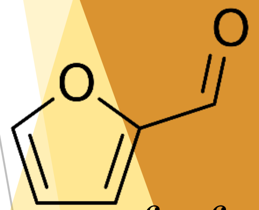
The most characteristic decomposition products

Hemicellulose

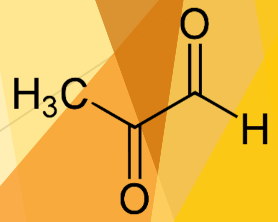
- Short heteropoly-saccharide chains
- Pyrolyses products:

furan derivatives, aldehydes and anhydrosaccharides

- Most abundant compounds:

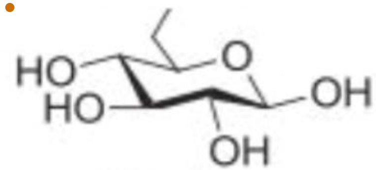


furfural

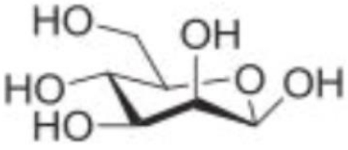


methylglyoxal

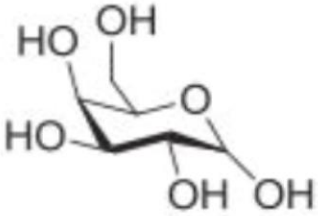
hexoses:



β-D-glucose

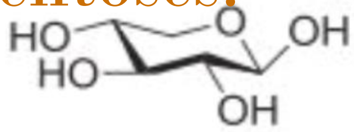


β-D-mannose

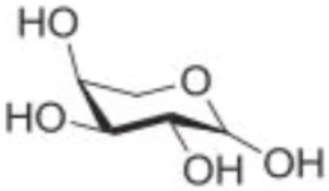


β-D-galactose

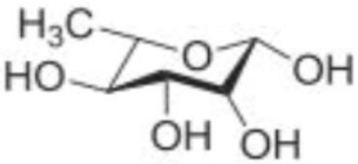
pentoses:



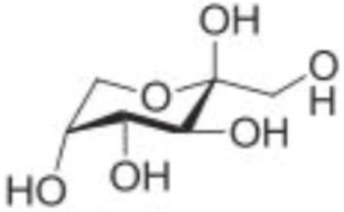
β-D-xylose



α-L-arabinose

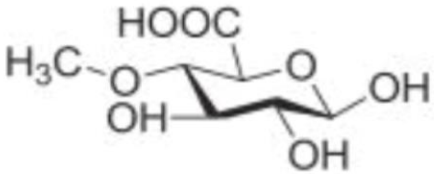


α-L-rhamnose

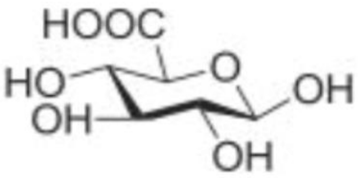


β-D-fructose

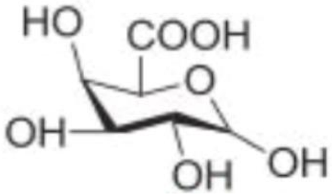
uronic acids:



4-O-methyl-D-glucoronic acid

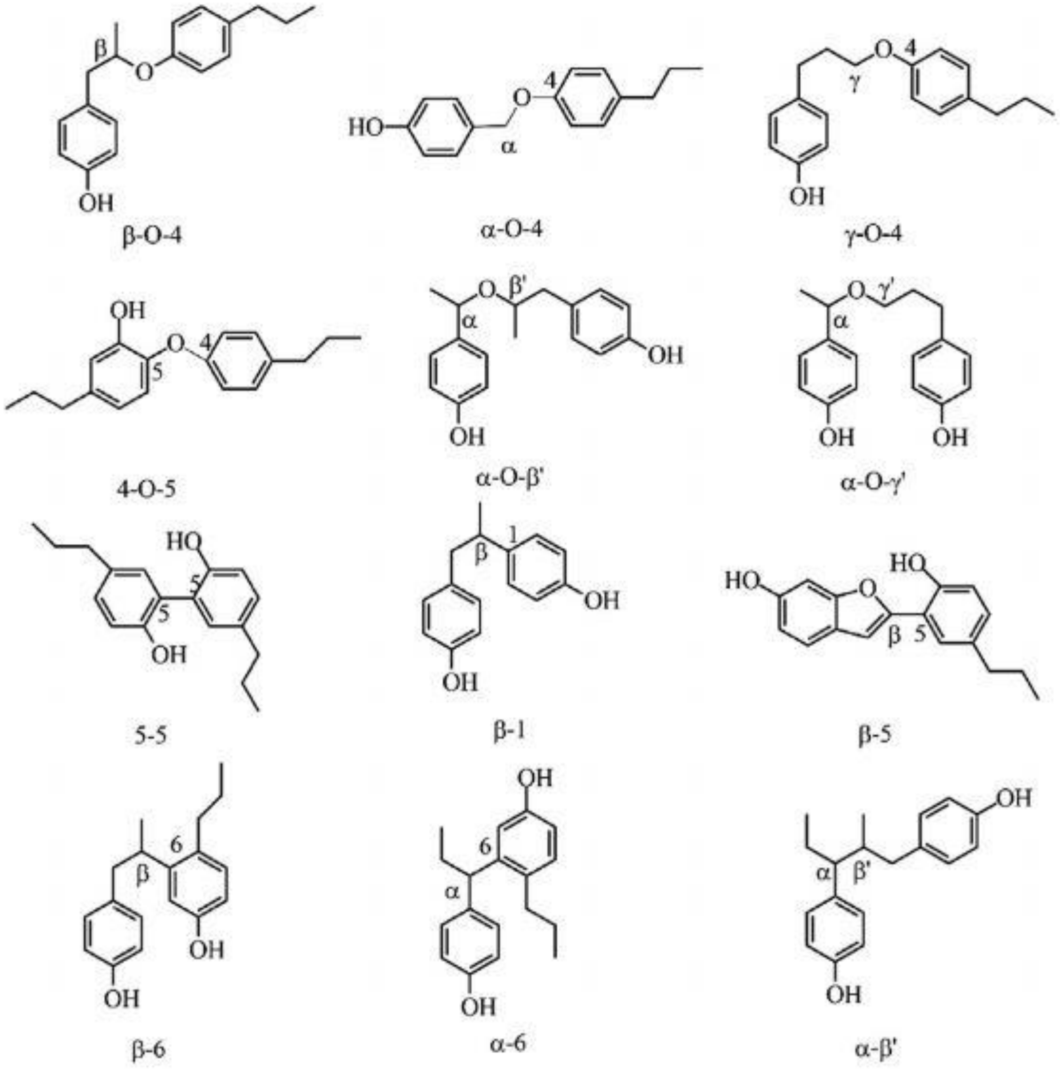


D-glucoronic acid

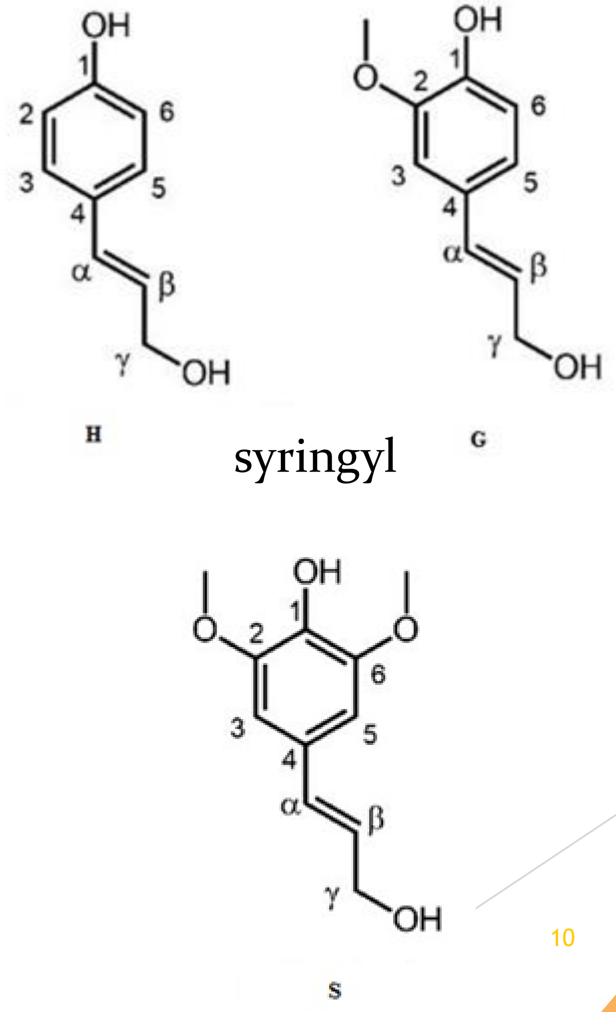


D-galacturonic acid

Lignin



p-hydroxyphenyl guaiacyl

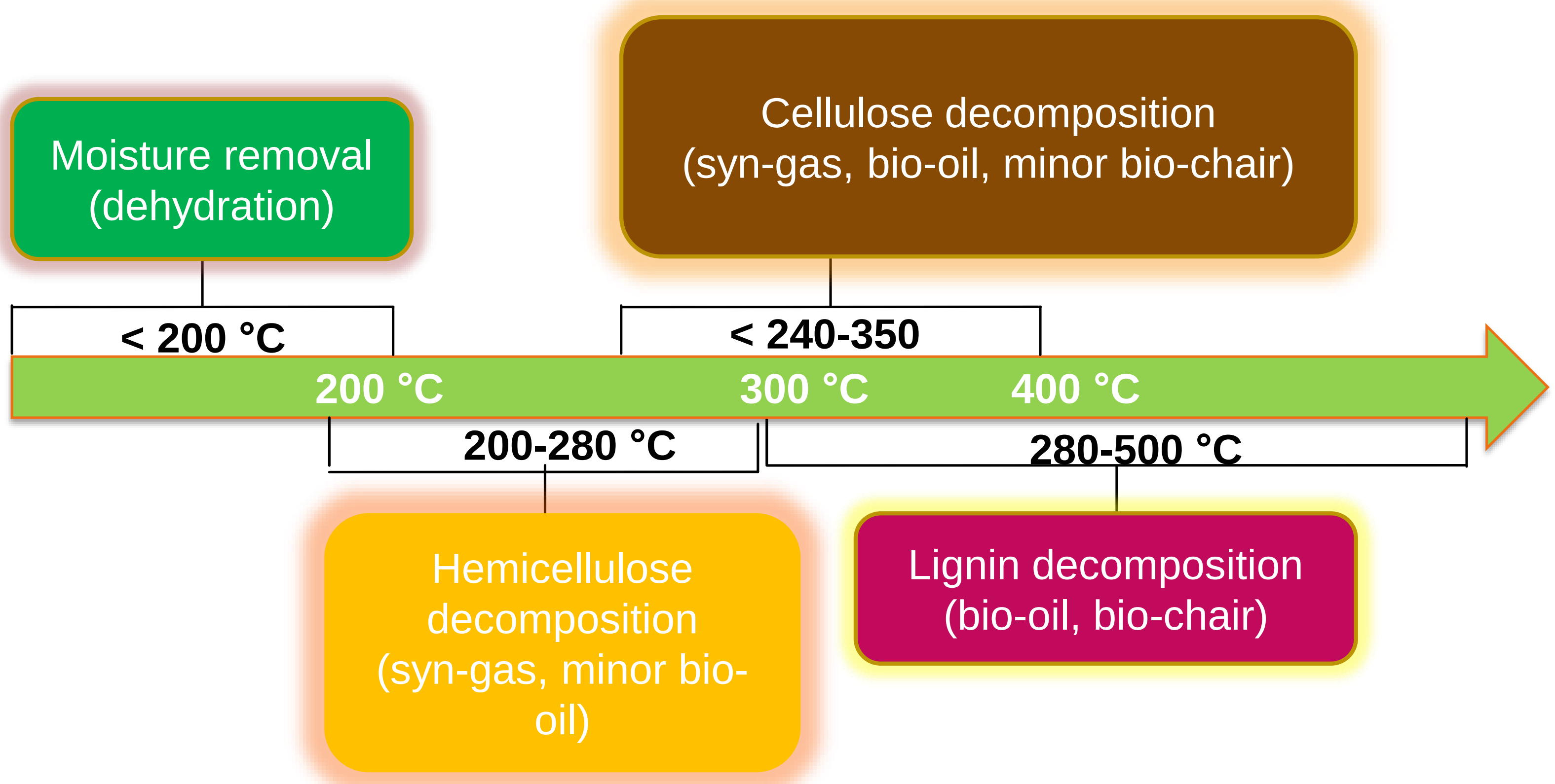


- Aromatic matrix
- Amorphous three-dimensional polymer, consists of three basic units:

1, p-coumaryl (4-hydroxycinnamyl),
2, coniferyl (3-methoxy-4-hydroxycinnamyl)
3, synapil (3,5-dimethoxy-4-hydroxycinn-amyl).

Lignocellulose pyrolysis

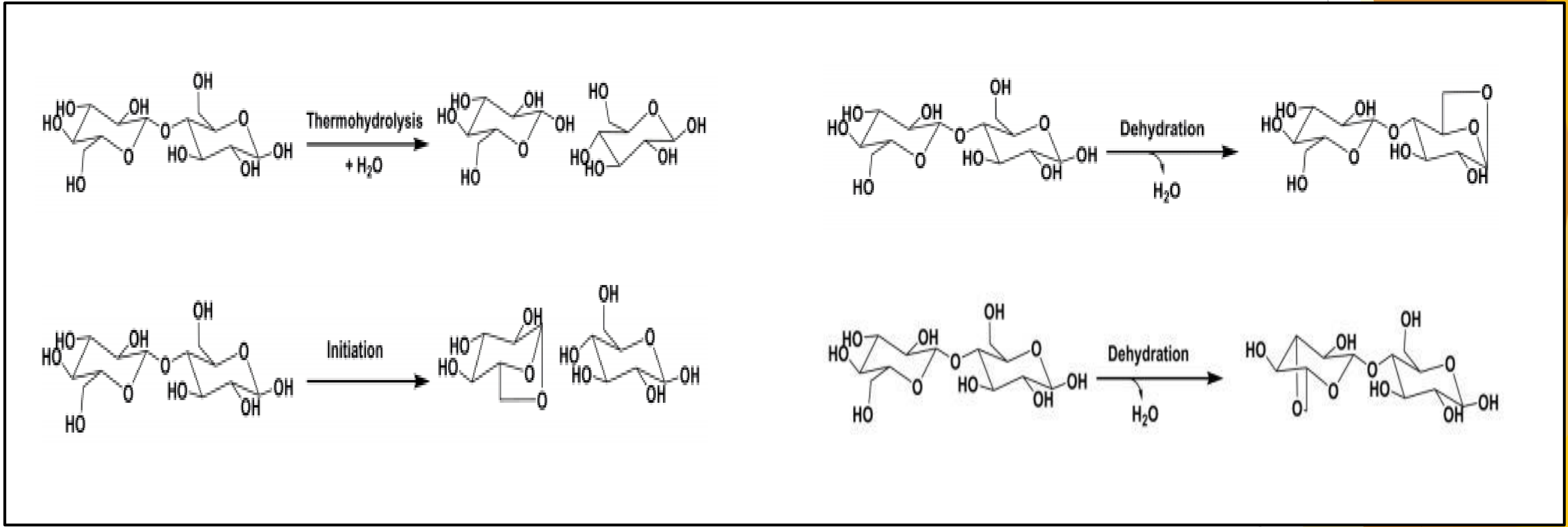
Biomass decomposition at different temperatures



Fast pyrolysis products:

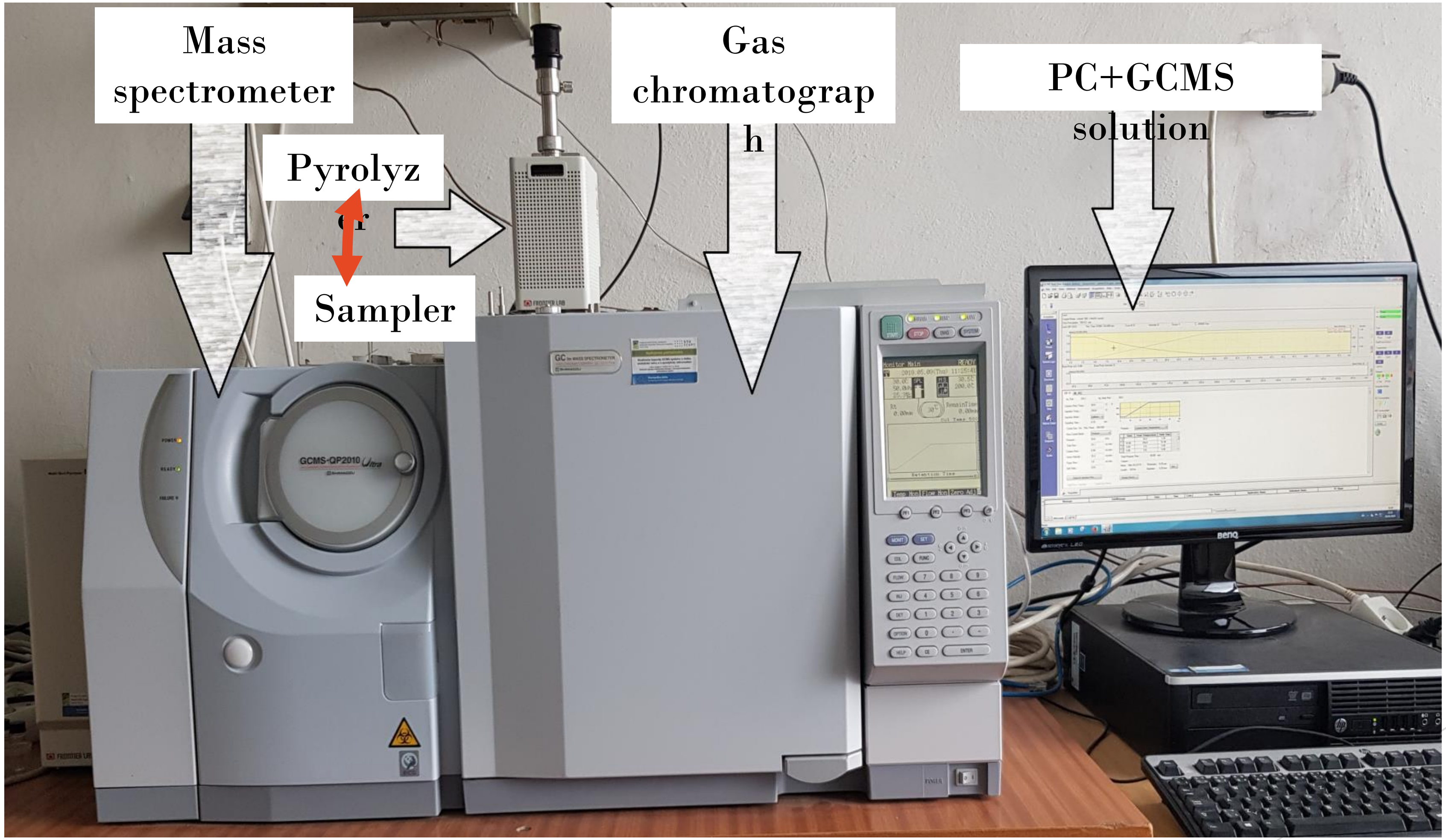
- Phenols
- Anhydrosaccharides
- Furan derivates
- Cyclopentanones
- Linear aldehydes
- Ketones
- Acids

Mechanism of fast pyrolysis on cellubiose



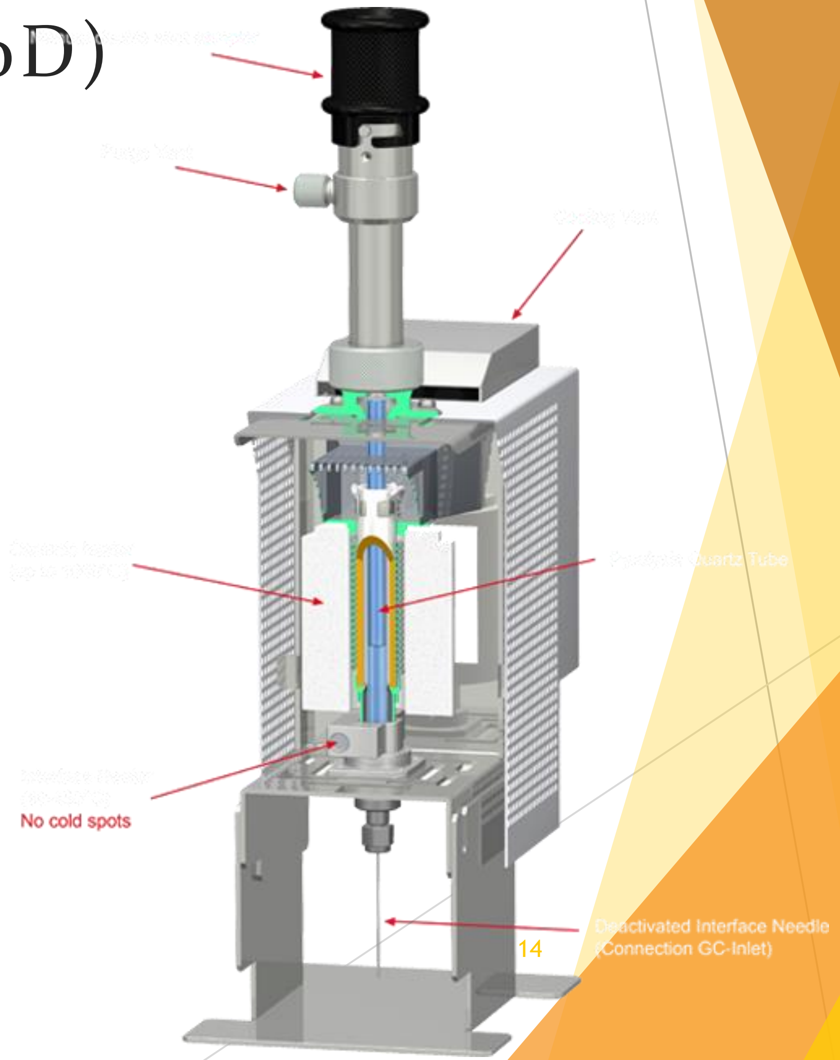
Equipment

GC-MS-QP2010 ULTRA



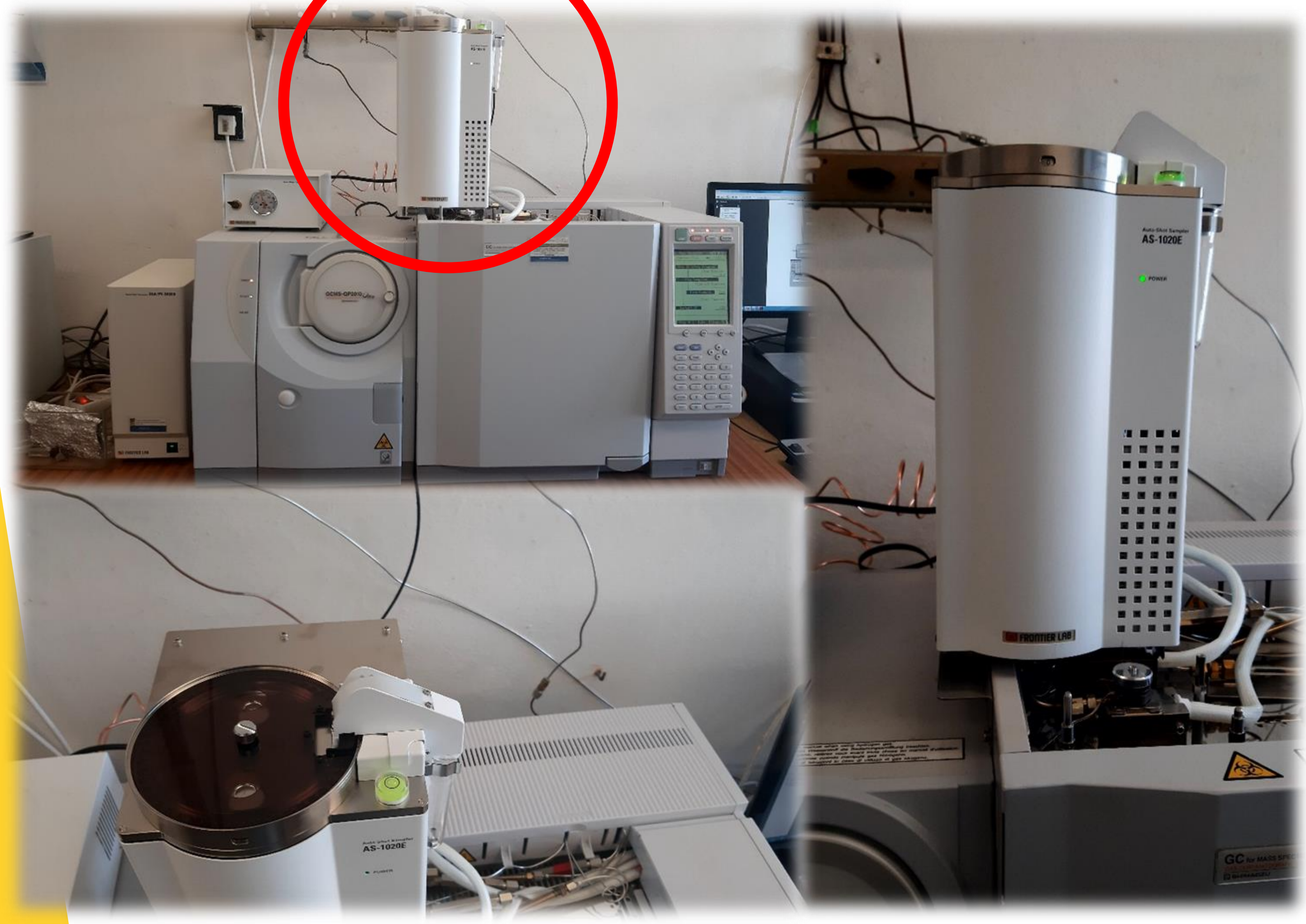
Equipment

MULTI-SHOT PYROLYZER (EGA/PY 3030D)



Equipment

AUTO-SHOT SAMPLER (AS-1020E)



- Continuous analysis of up to 48 samples.
- Continuously or randomly using various analysis modes: Single-shot analysis, Double-shot analysis, Evolved gas analysis, Heart-cut EGA analysis
- The system operation combined with optional accessories can be automated, further saving of labor and improved reliability.

Conditions

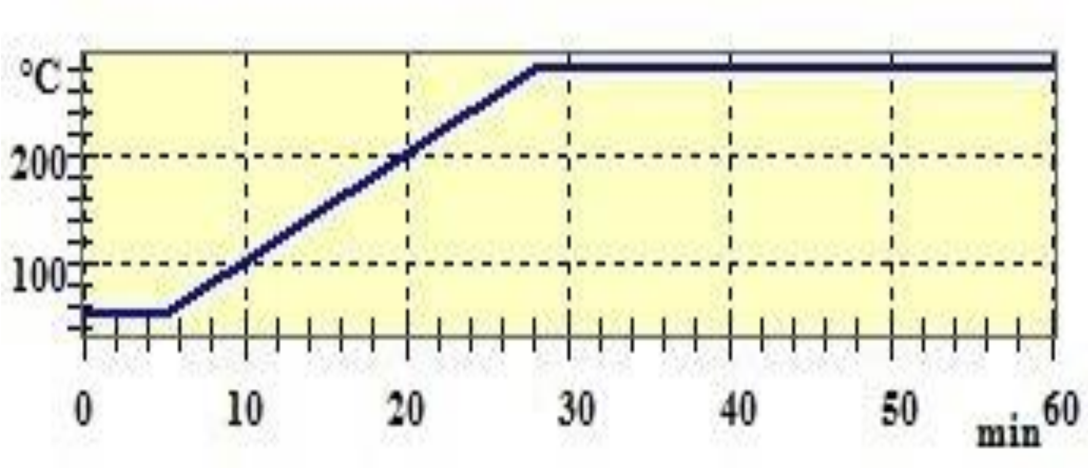
Column
- Type: Ultra ALLOY-5
- Length: 30 m
- Diameter: 0,25 mm
- Thickness of the anchored phase: 0,25 µm
- Carrier gas flow: 0,96 ml/ min
- Pressure: 50 kPa
- Split ratio: 20,0

Carrier gas: Helium
- Total flow: 23 ml/ min

Injection mode: Splitless

Analysis time: 60 min

Temperature profile of the column:

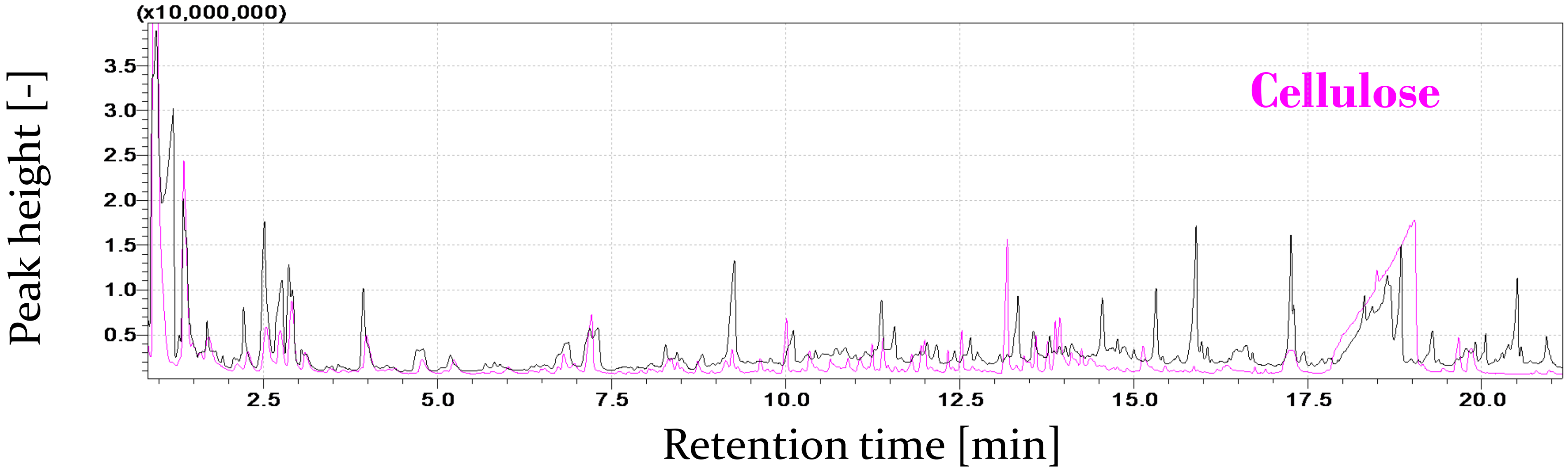


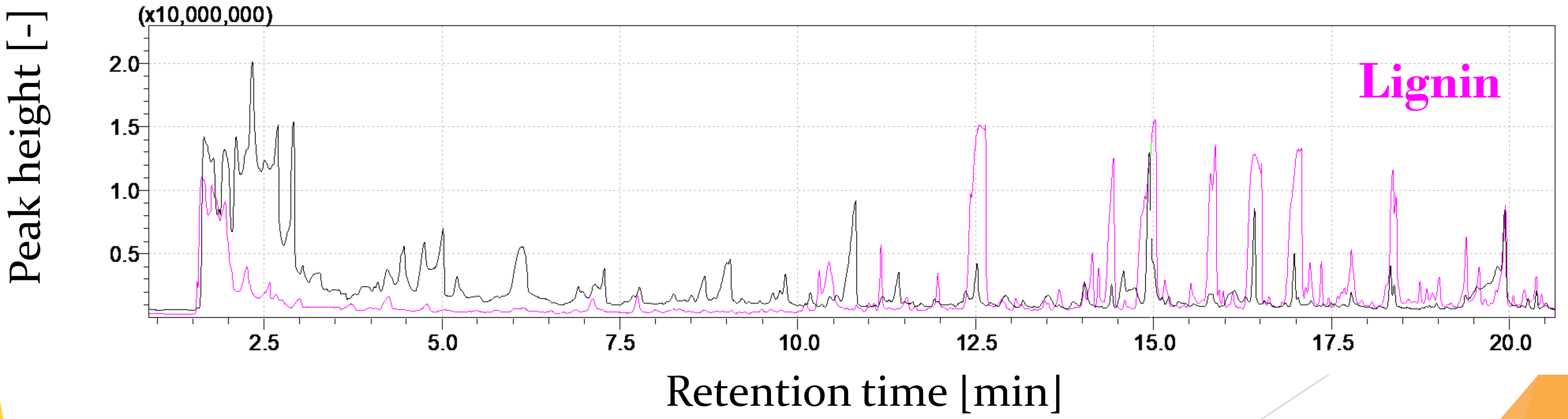
GC injection temperature: 250 °C

Ion source temperature: 200 °C

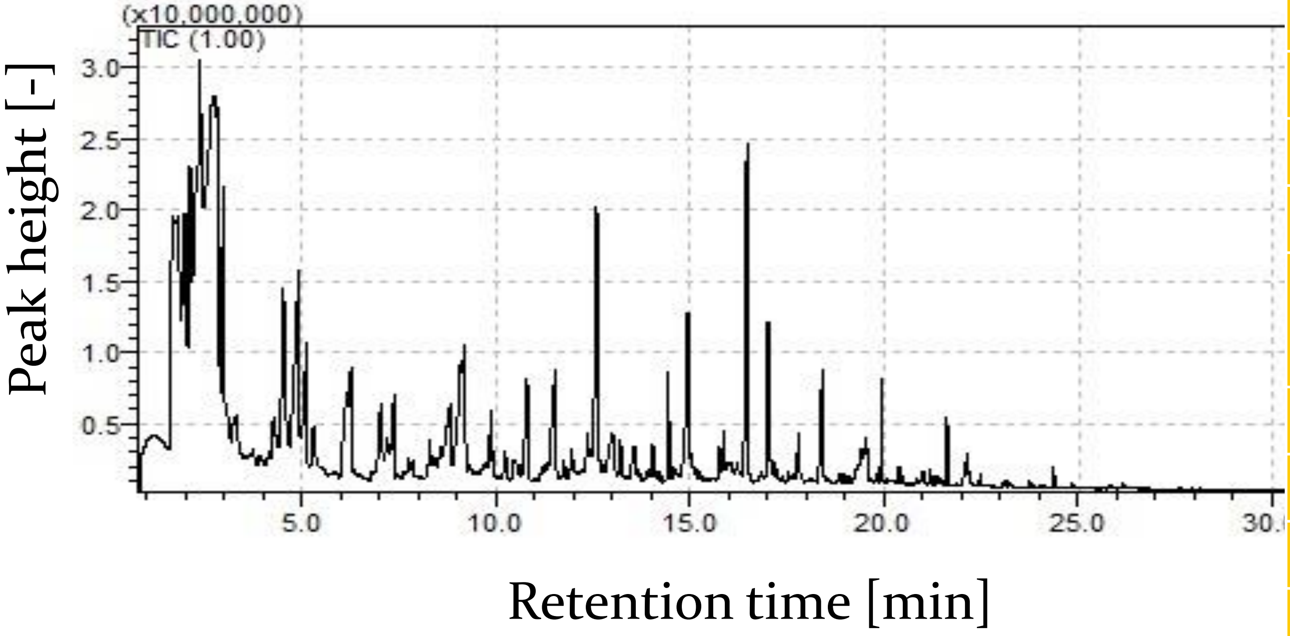
Pyrolysis products

Sample of straw





Pyrolysis products of **straw**

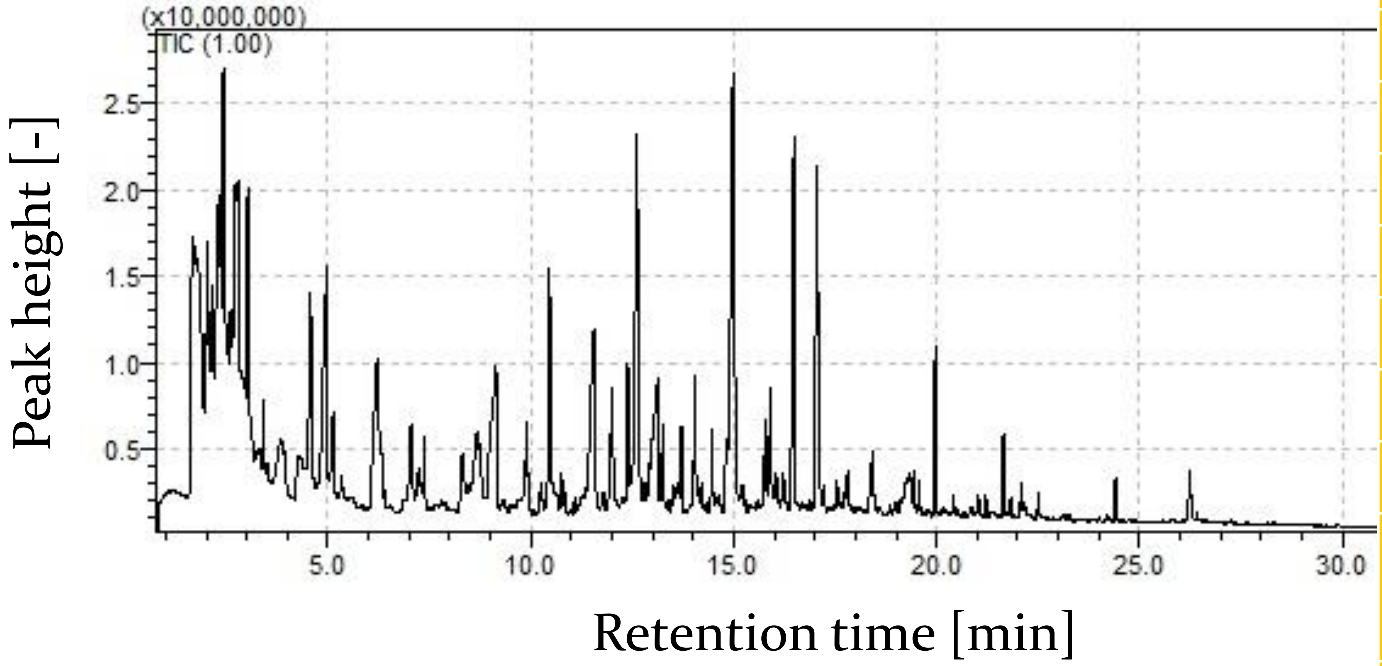


Gas chromatograph record (pyrogram) of pyrolysis products of the glossy surface of untreated straw pyrolysed at 500°C.

Characteristic products of pyrolysis of untreated straw:

	Retention time [min]	Compliance [%]	Substance
CELLULOSE	2,81	94	acetic acid
	2,95	86	methyl acetate
	2,97	86	1-hydroxy-2-propanone
	4,49	90	1-hydroxy-2-butanone acetate
	4,88	87	methylpentanal
	5,09	91	2-oxo-propanoic acid methyl ester
	6,14	85	furfural
	6,25	89	cyclopenten-3-one
	8,81	89	2(5H)-furanone
	9,08	91	3-methylcyclopentanone
LIGNIN	11,49	94	3-methyl-1,2-cyclopentadienone
	12,56	94	methoxy-phenol (guaiacol)
	14,44	94	2-methoxy-p-cresol
	14,93	91	benzofuran
	16,45	90	2-methoxy-4-vinylphenol
	17,00	88	2,6-dimethoxy-phenol syringol

Pyrolysis products of corn

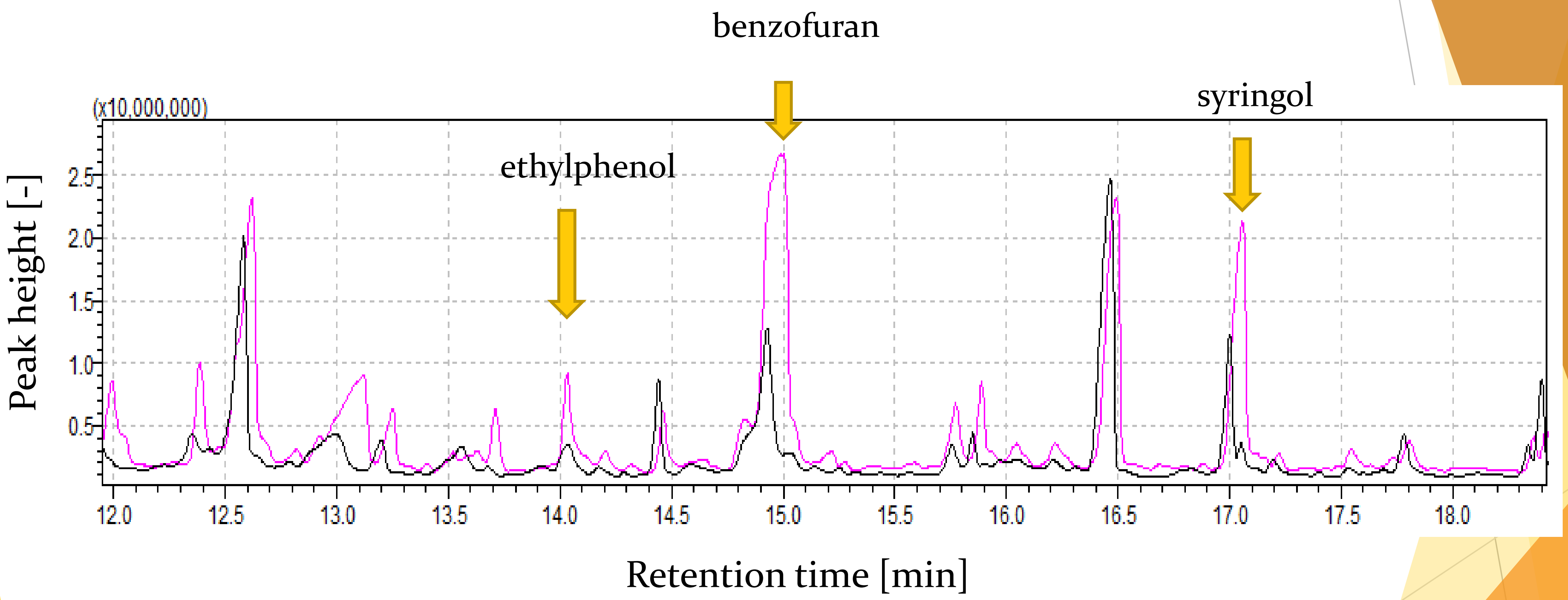


Gas chromatograph record of pyrolysis products of the glossy surface of untreated corn pyrolysed at 500 °C

Characteristic products of pyrolysis of untreated corn:

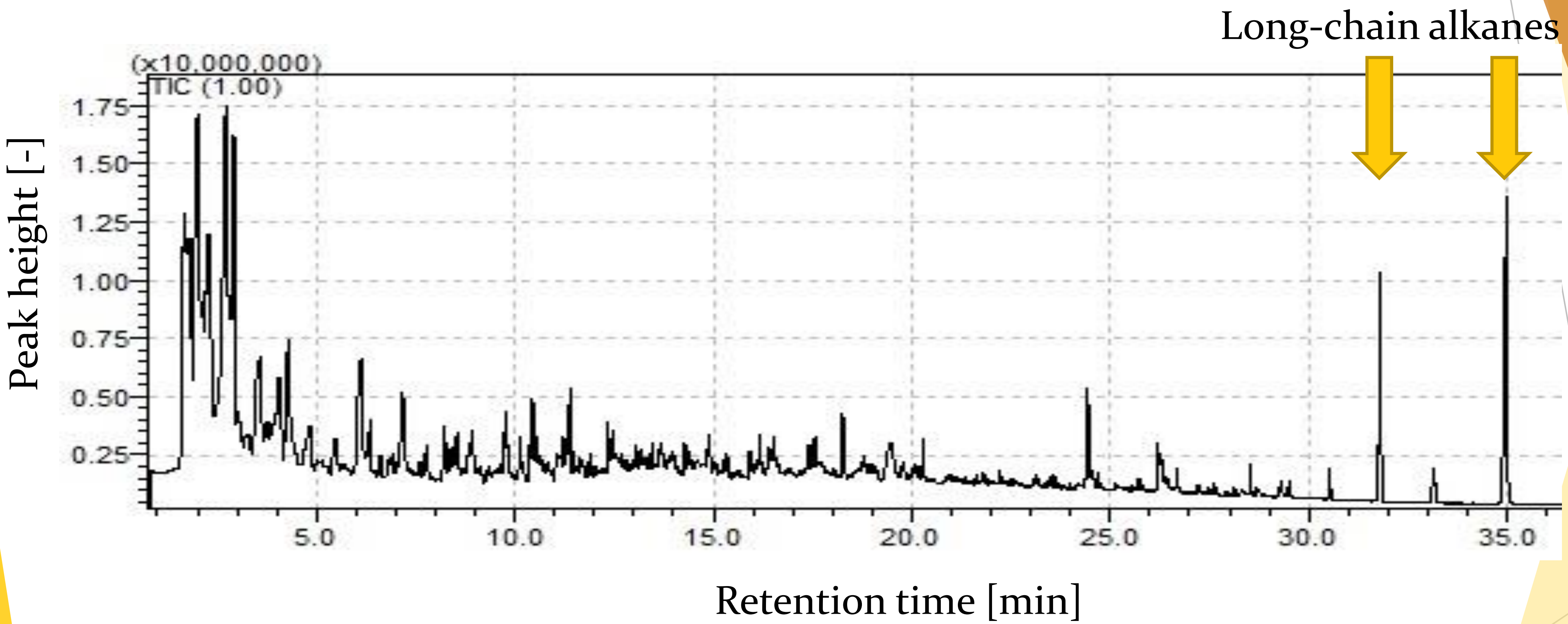
Retention time [min]	Compliance [%]	Substance
2,81	80	acetic acid
3,05	8	1-hydroxy-2-propanone
4,57	91	1-hydroxy-2-butanone
4,93	87	methylpentanal
6,21	80	furfural
6,30	80	cyclopenten-3-one
9,13	87	1,2-cyclopentadienone
10,47	96	phenol
11,52	91	3-methyl-1,2-cyclopentadienone
12,62	95	methoxy-phenol (guaiacol)
13,11	85	derivative of pentanal
14,98	91	benzofuran
16,47	91	2-methoxy-4-vinylphenol
17,05	88	syringol

Pyrolysis products of corn and straw



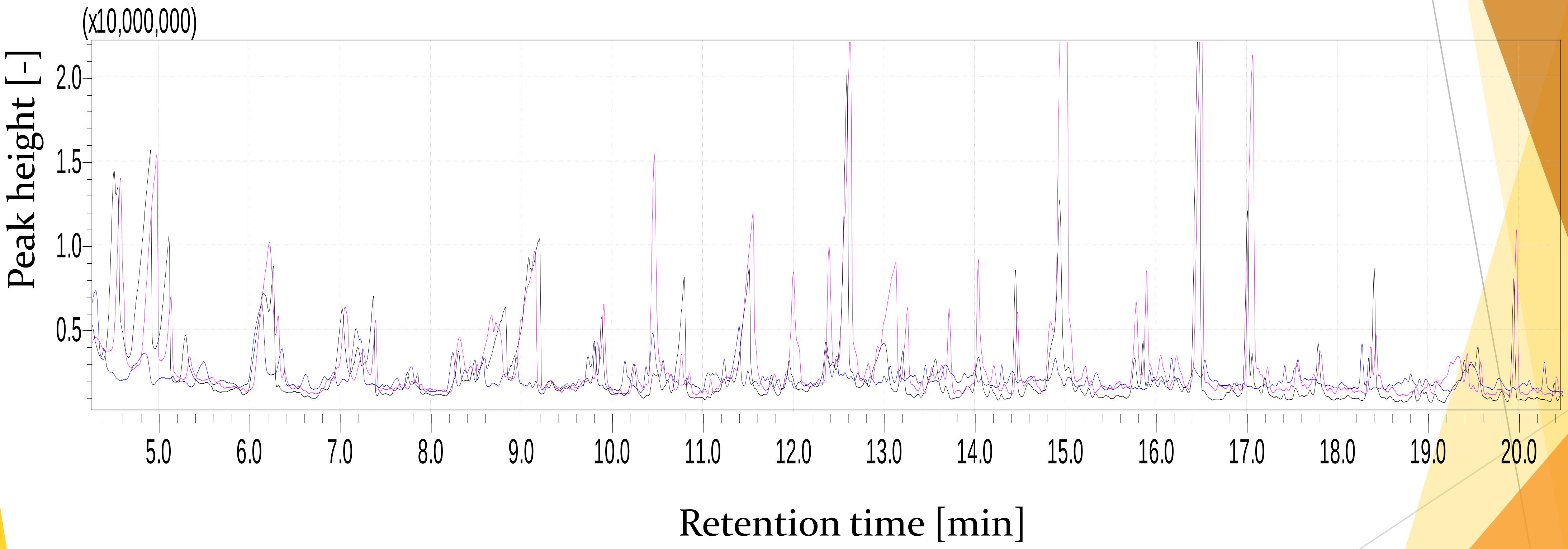
Comparison of pyrogram of straw and corn obtained at 500°C.

Pyrolysis products of sunflower



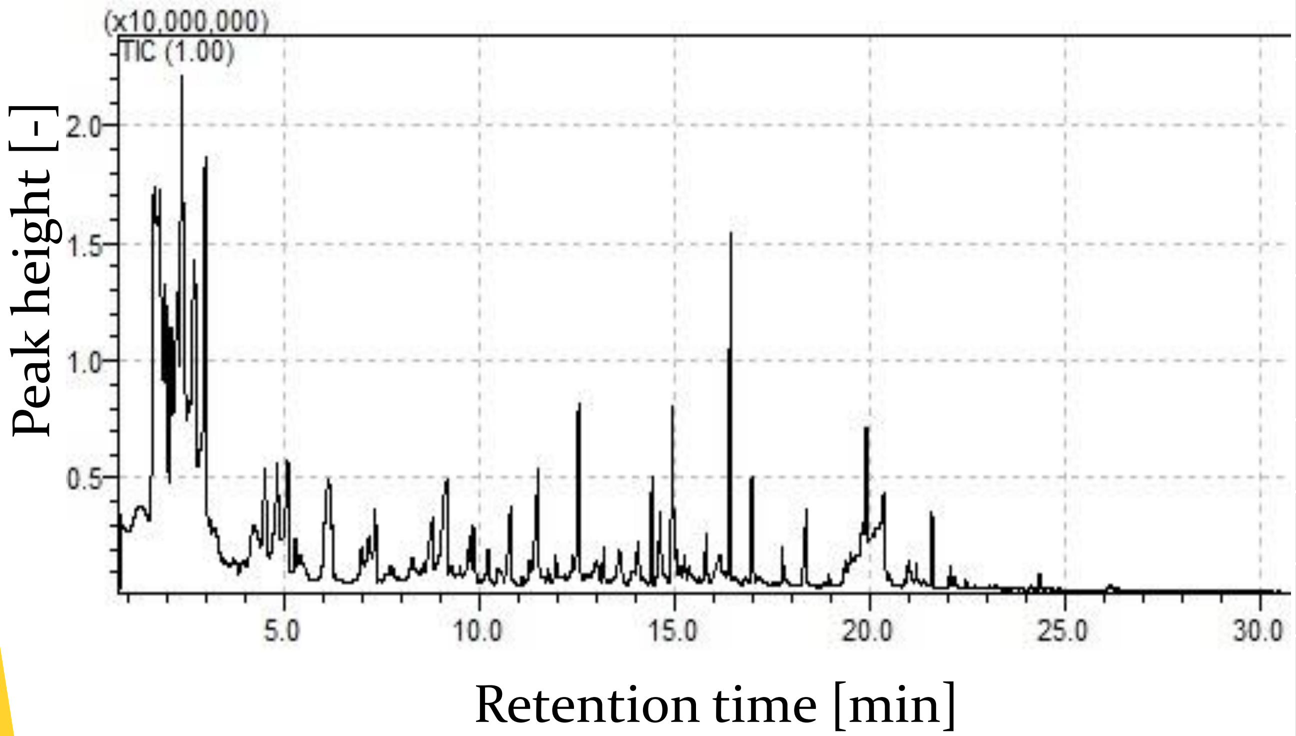
Gas chromatograph record of pyrolysis products of the glossy surface of untreated sunflower pyrolysed at 500°C.

Pyrolysis products of straw, corn and sunflower



Comparison of pyrogram of straw, corn and sunflower obtained at 500°C.

Pyrolysis products of **barley**

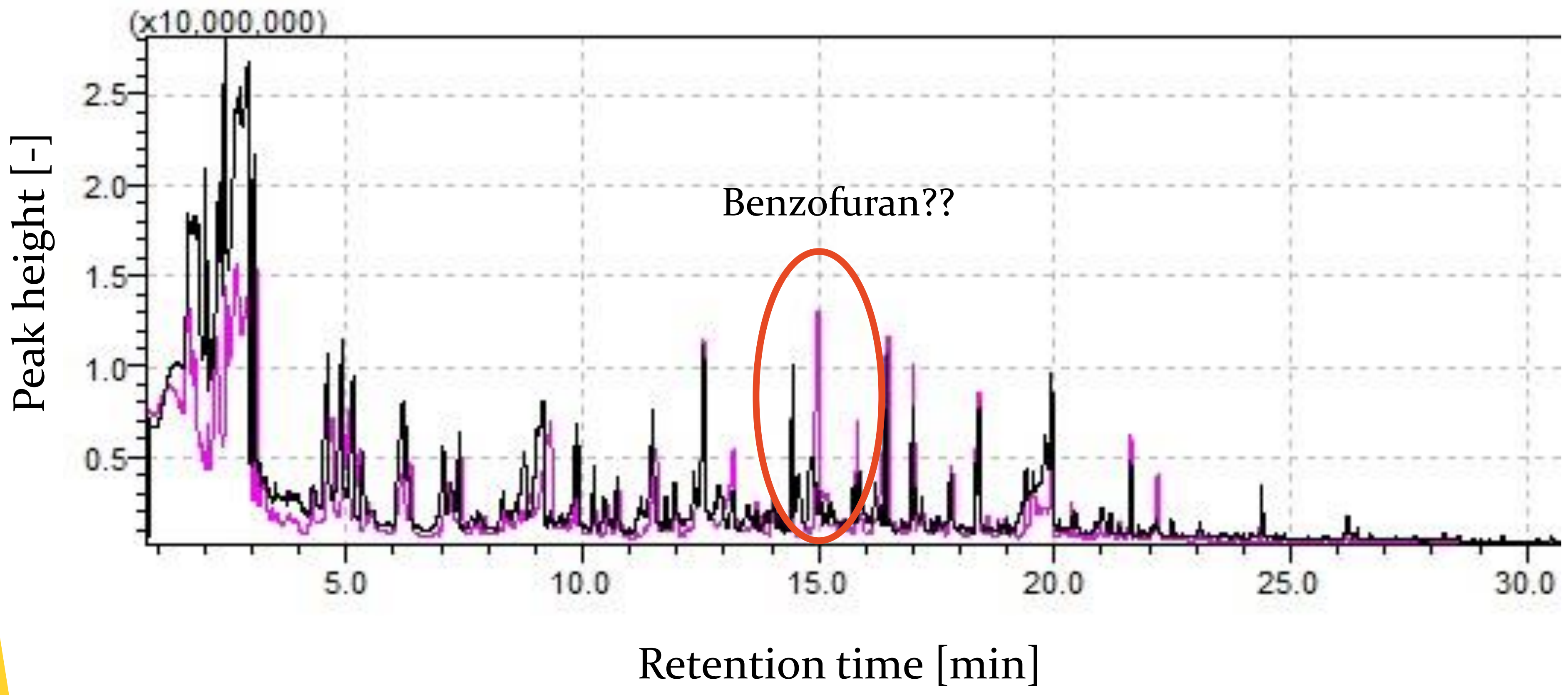


Gas chromatograph record of pyrolysis products of the glossy surface of untreated barley pyrolysed at 500 °C

Characteristic products of pyrolysis of untreated barley:

Retention time [min]	Compliance [%]	Substance
2,68	86	2-oxo-propanoic acid
2,98	92	1-hydroxy-2-propanone
4,50	88	1-hydroxy-2-butanone
4,82	83	methylpentanal
5,09	89	2-oxo-propanoic acid methyl ester
6,13	89	furfural
8,77	93	2(5H)-furanone
9,13	87	cyklohexanone
11,49	94	3-methyl-1,2-cyclopentadienone
12,53	92	methoxy-phenol (guaiacol)
14,40	89	2-methoxy-p-cresol
14,97	84	benzofuran
16,43	91	2-methoxy-4-vinylphenol

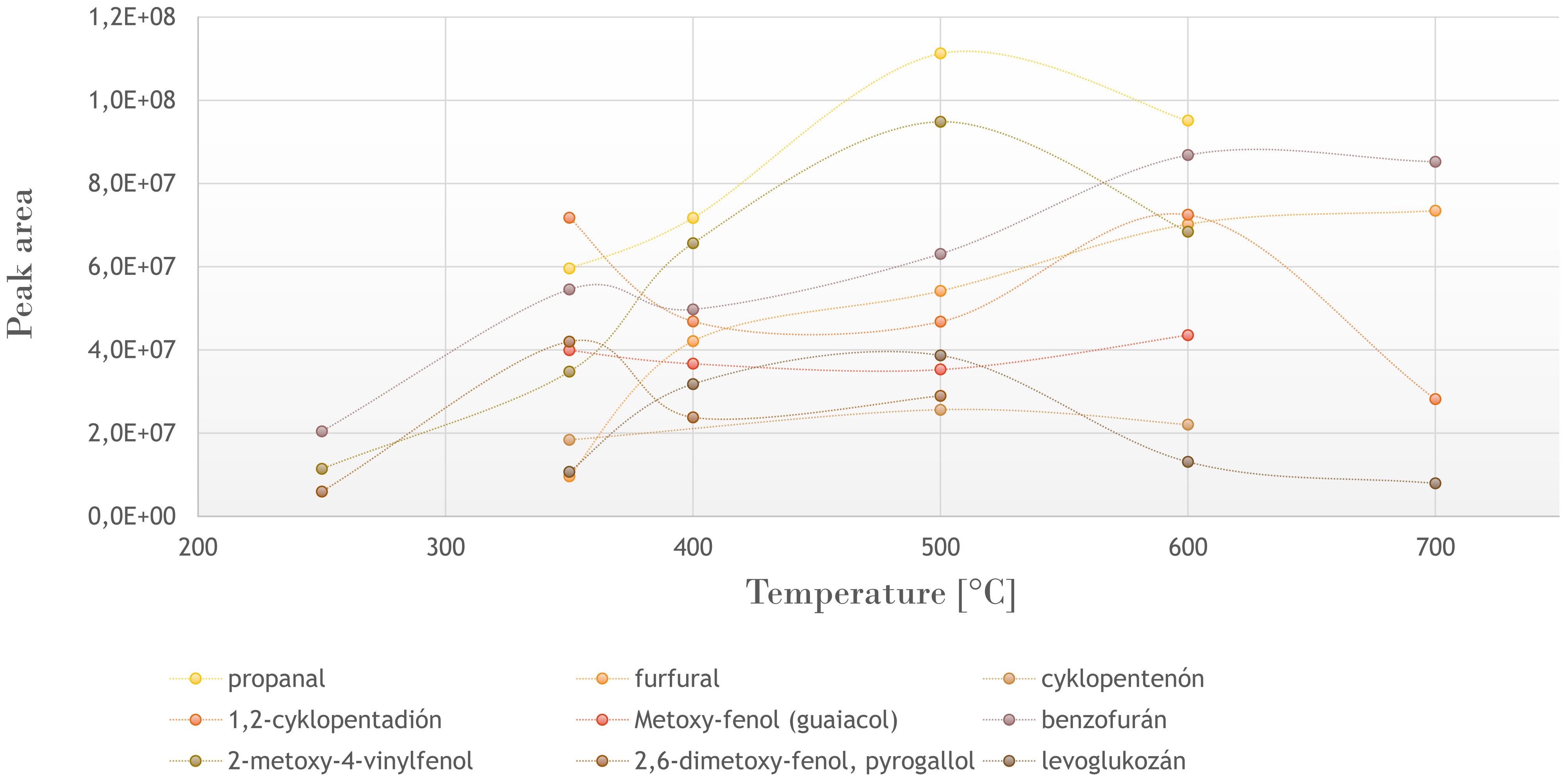
Pyrolysis products of reed and grape stalk



Comparison of gas chromatograph recordings of pyrolysis products of the glossy surface of reed (pink colour) and vine (black colour) pyrolysed at 500°C

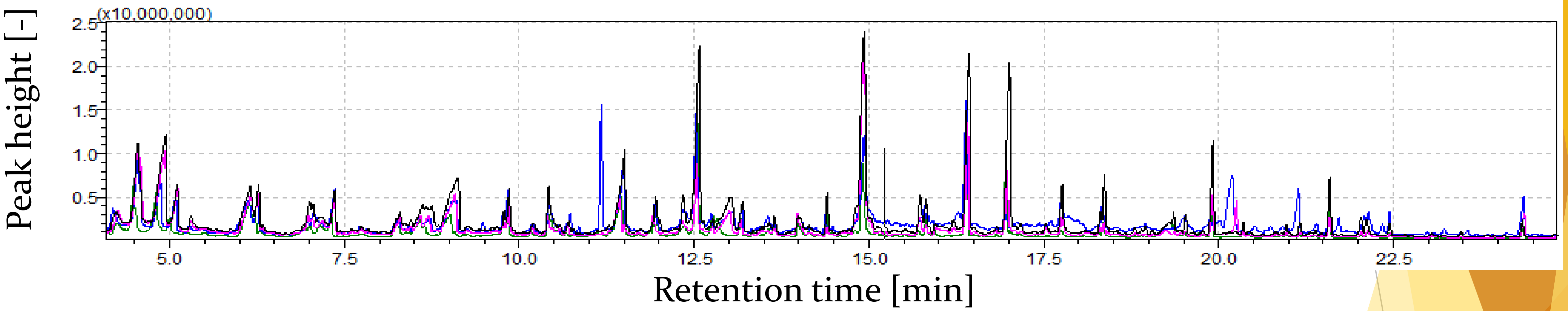
Effect of temperature on the composition of pyrolysis products

Dependence of the formation of straw pyrolysis products on the pyrolysis temperature

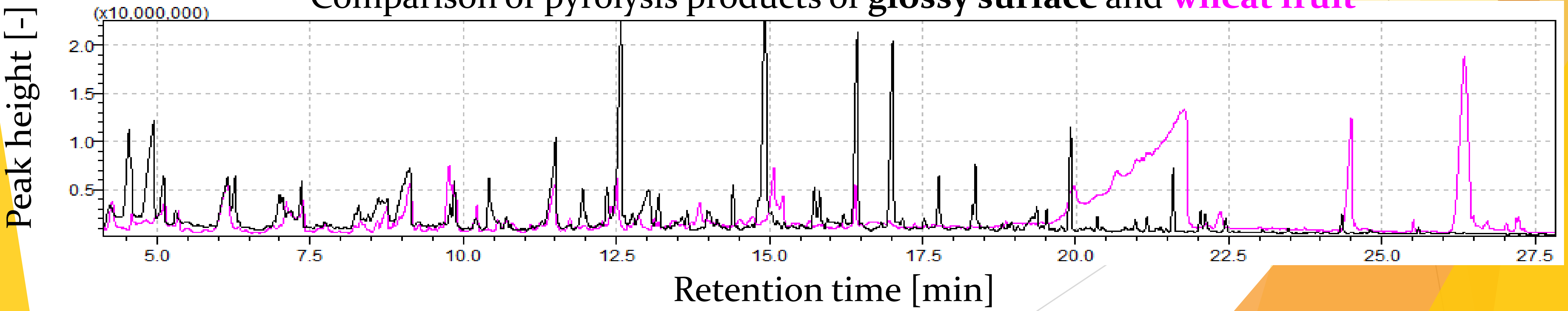


Influence of plant morphology on the composition of pyrolysis products (wheat)

Glossy surface of stem, interior, outer part of stem and leaf



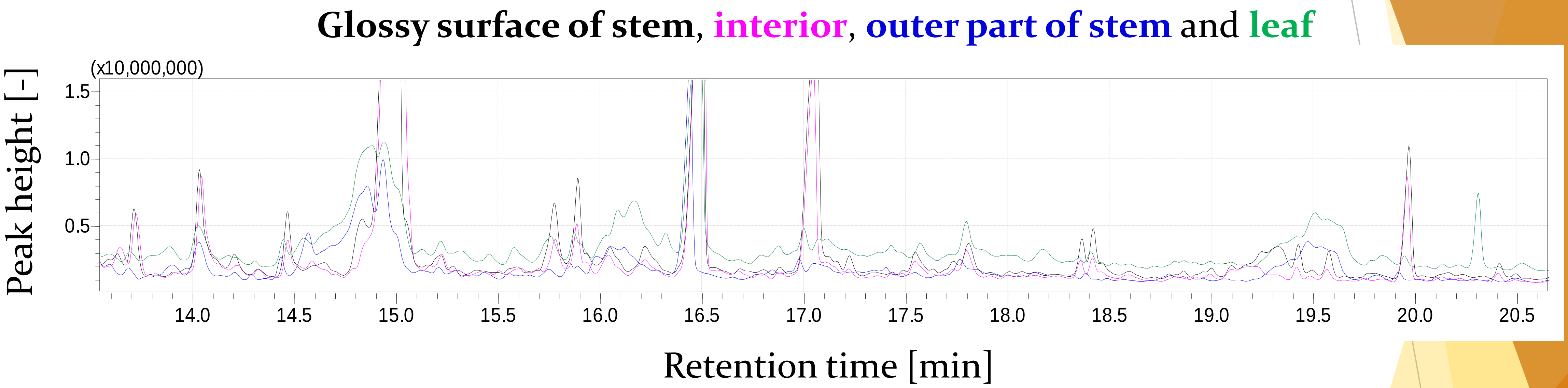
Comparison of pyrolysis products of **glossy surface** and **wheat fruit**



Influence of plant morphology on the composition of pyrolysis products (corn)

Retention time [min]	Part of the plant	Substance
2,6	leaf	Acetic acid
7,33	leaf, outer part of stem	Acetol acetate
10,44	leaf, outer part of stem	Phenol
11,45	leaf, outer part of steem	3-methyl-1,2-cyclopentadienone
13,16	glossy surface of stem, interior	Dialkylpentanal

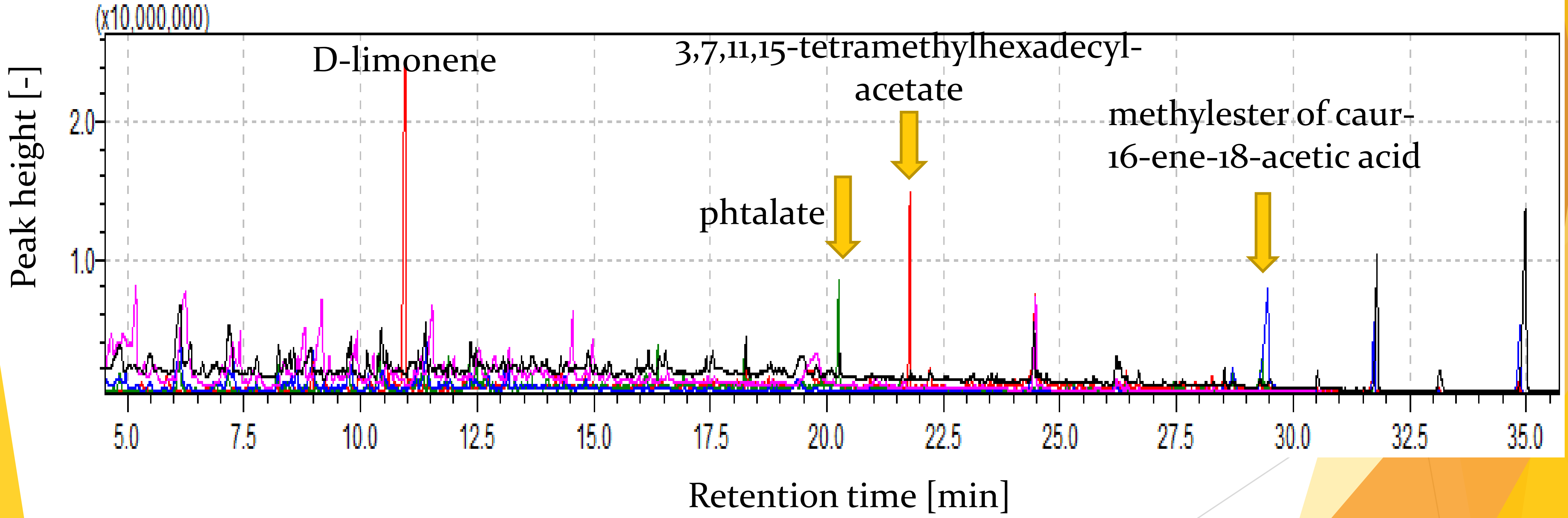
Influence of plant morphology on the composition of pyrolysis products (corn)



Retention time [min]	Part of the plant	Substance
13,73	glossy surface of stem, interior	2,6-dimethylphenol
14,9	glossy surface of stem, interior	benzofuran
16,16	leaf	2-deoxy-D-galactose
17,1	glossy surface of stem, interior	syringol
19,5	leaf, outer part of stem	levoglucosane

Influence of plant morphology on the composition of pyrolysis products (sunflower)

Glossy surface of stem, interior, outer part of stem and leaf



Conclusion

- Decomposition pyrolysis products of straw are formed by:
  - hydrolysis or decomposition of etheric bonds
  - retrocondensation reactions
  - dehydration of –OH groups
- Comparison of the pyrolytic products composition of agricultural residues: practically identical products in different amount and presence of some compounds characteristic of the plant.
- Different morphological parts of the plants supported the formation of different amounts of pyrolytic products, specific also for the cover and the grains themselves.
- We also examined:
  - Decomposition of lignocellulosic samples to humus in the soil
  - Thermal decomposition of tobacco

Thank you for your attention!

Acknowledgement

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy)
www.skhu.eu

Interreg Slovakia-Hungary European Union Building Partnership