Pyrolytic analysis of lignocellulose from agricultural and forestall byproducts

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

Research Centre for Natural Sciences,
Magyar tudósok körútja 2, Budapest H-1117, Hungary

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

Aims

Conversion of renewable raw materials, especially components of lignocellulose found in border region 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.

Agricultural and forestall byproducts

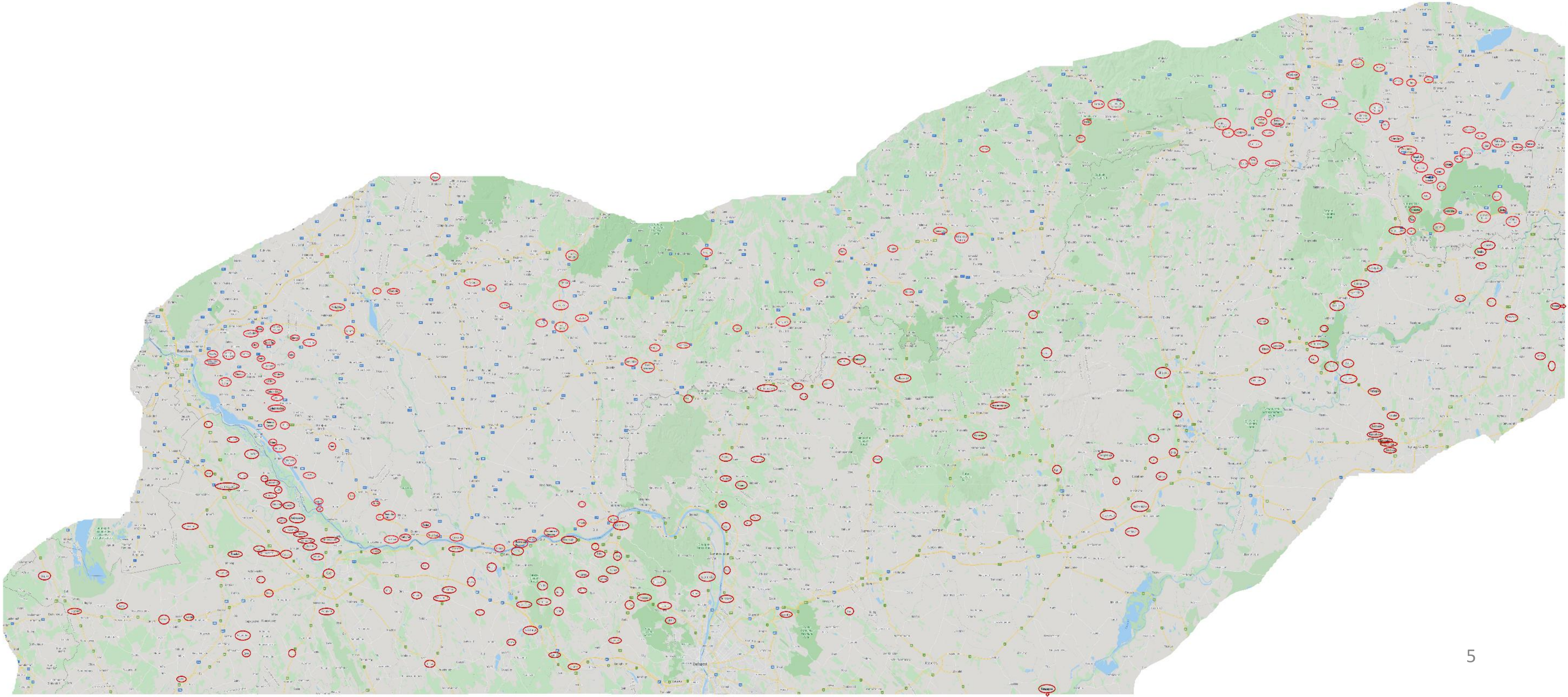
- peas
- grapes
- barley
- invasive plants
- maize
- poppy
- mustard
- oats
- wheat
- rye
- rape
- sunflower
- soya
- reed

800 sample s

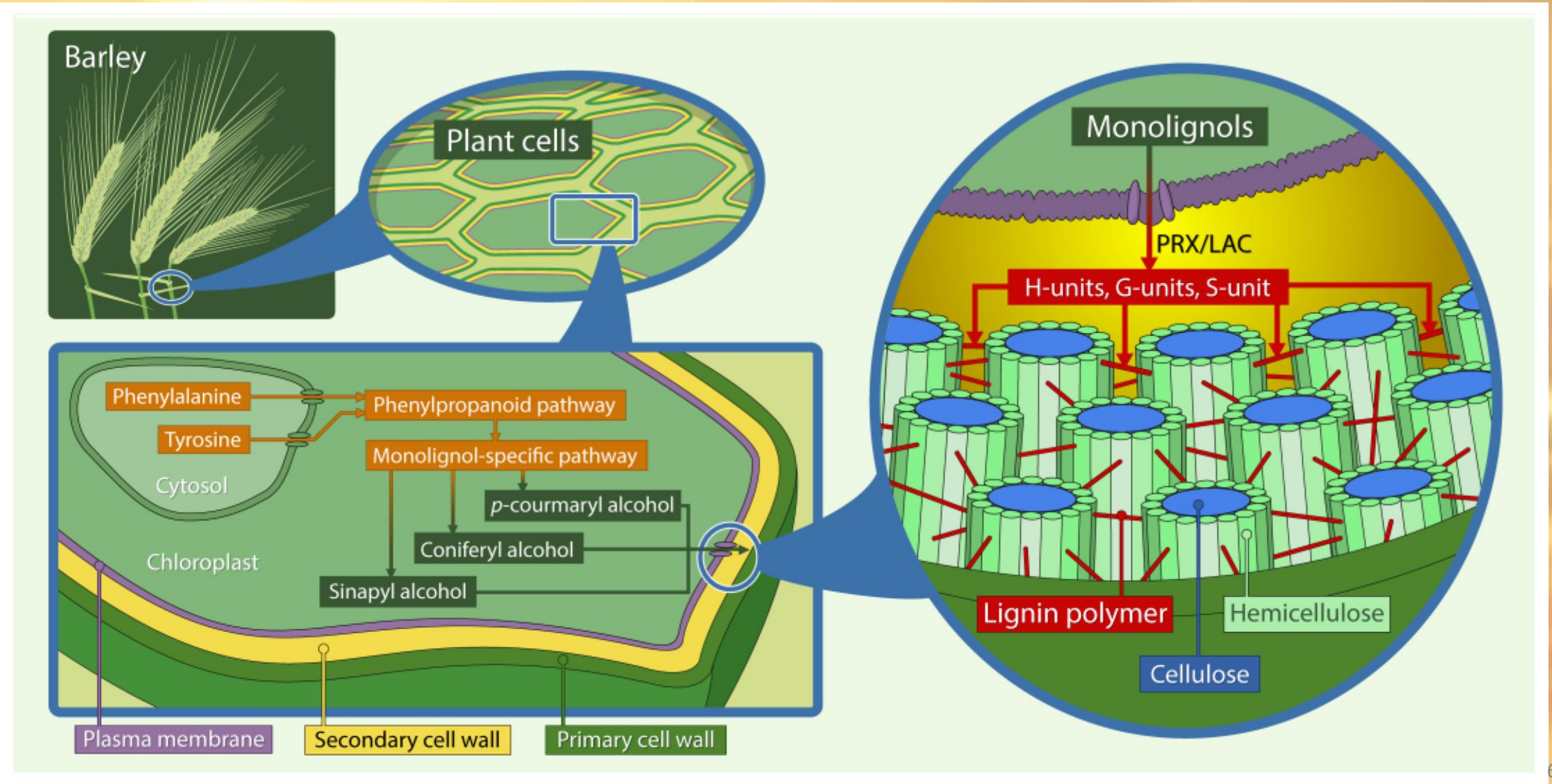
Biobank

800 sample
s

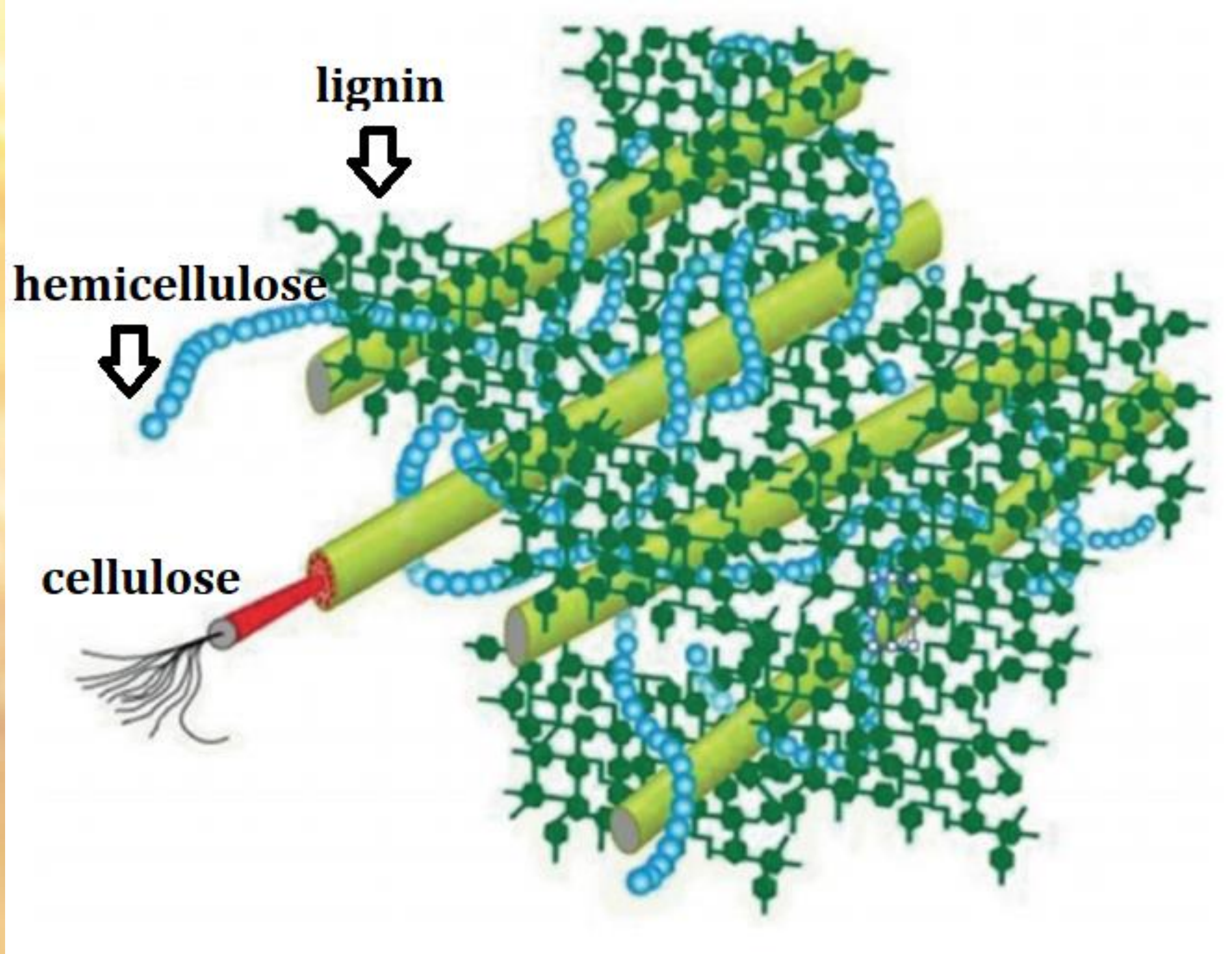
Map of collection places



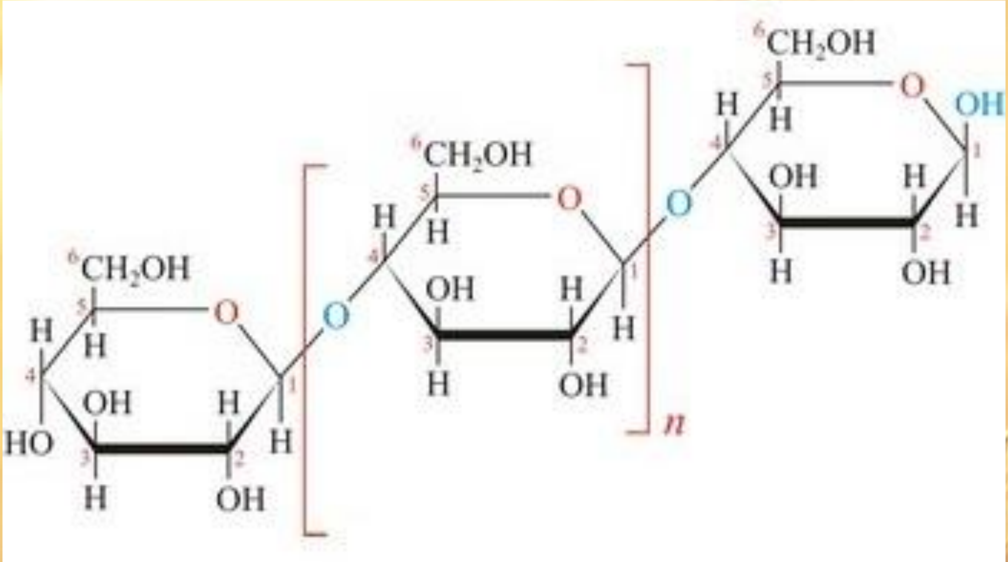
Stem of the plant



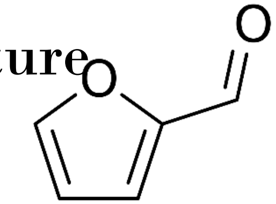
Stem of the plant



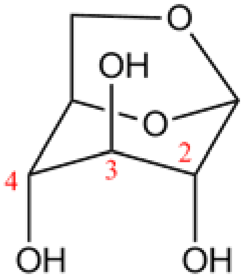
Cellulose



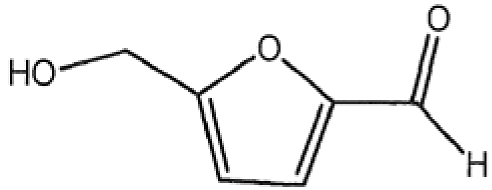
- Linear polysaccharide
- Long β-D-(1,4)-glucopiranose units
- Crystalline and amorphous structure



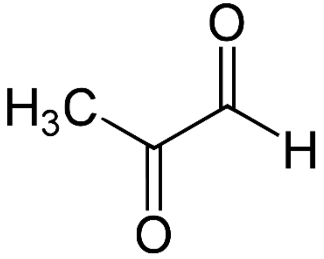
furfural



levoglucosan

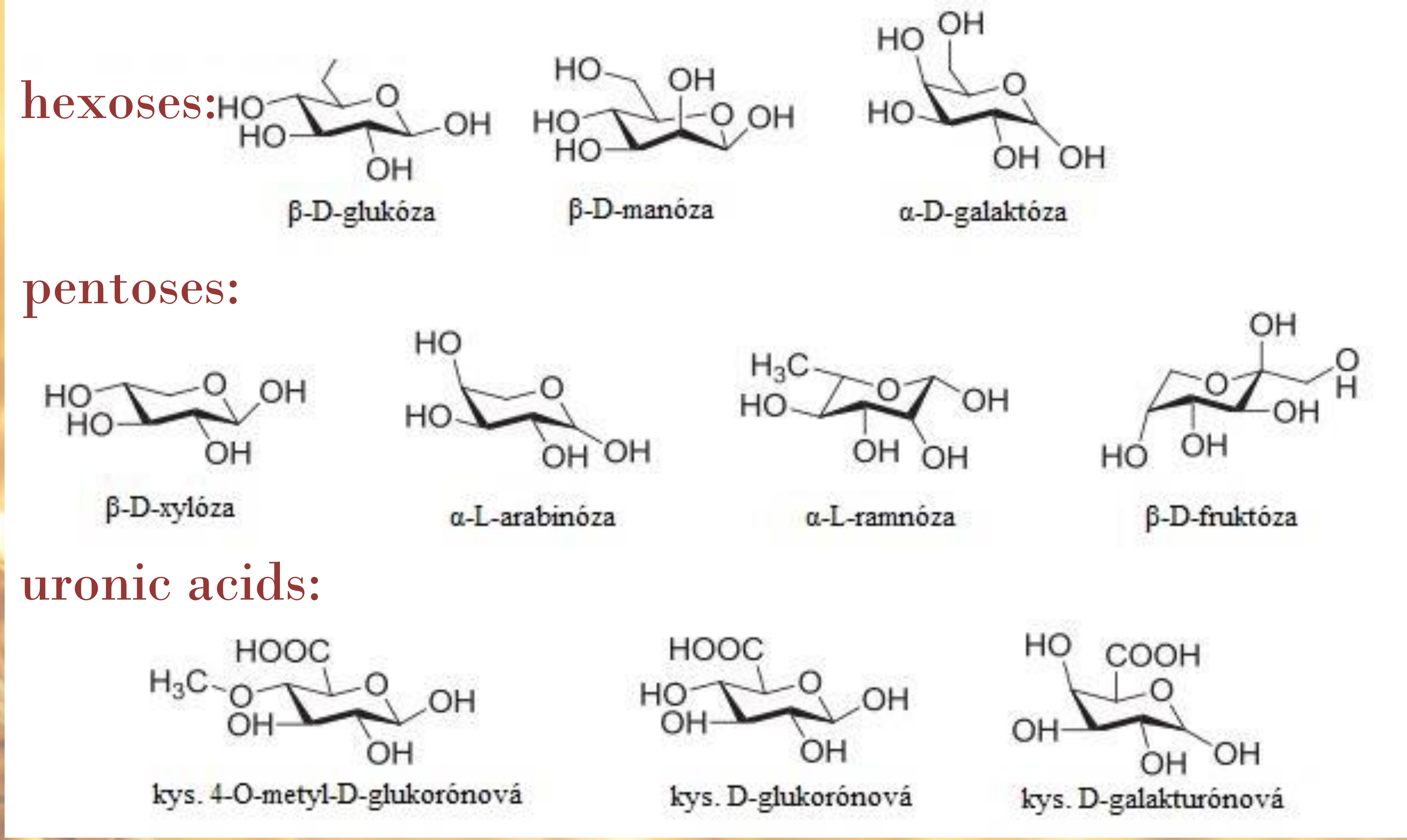


hydroxymethylfurfural



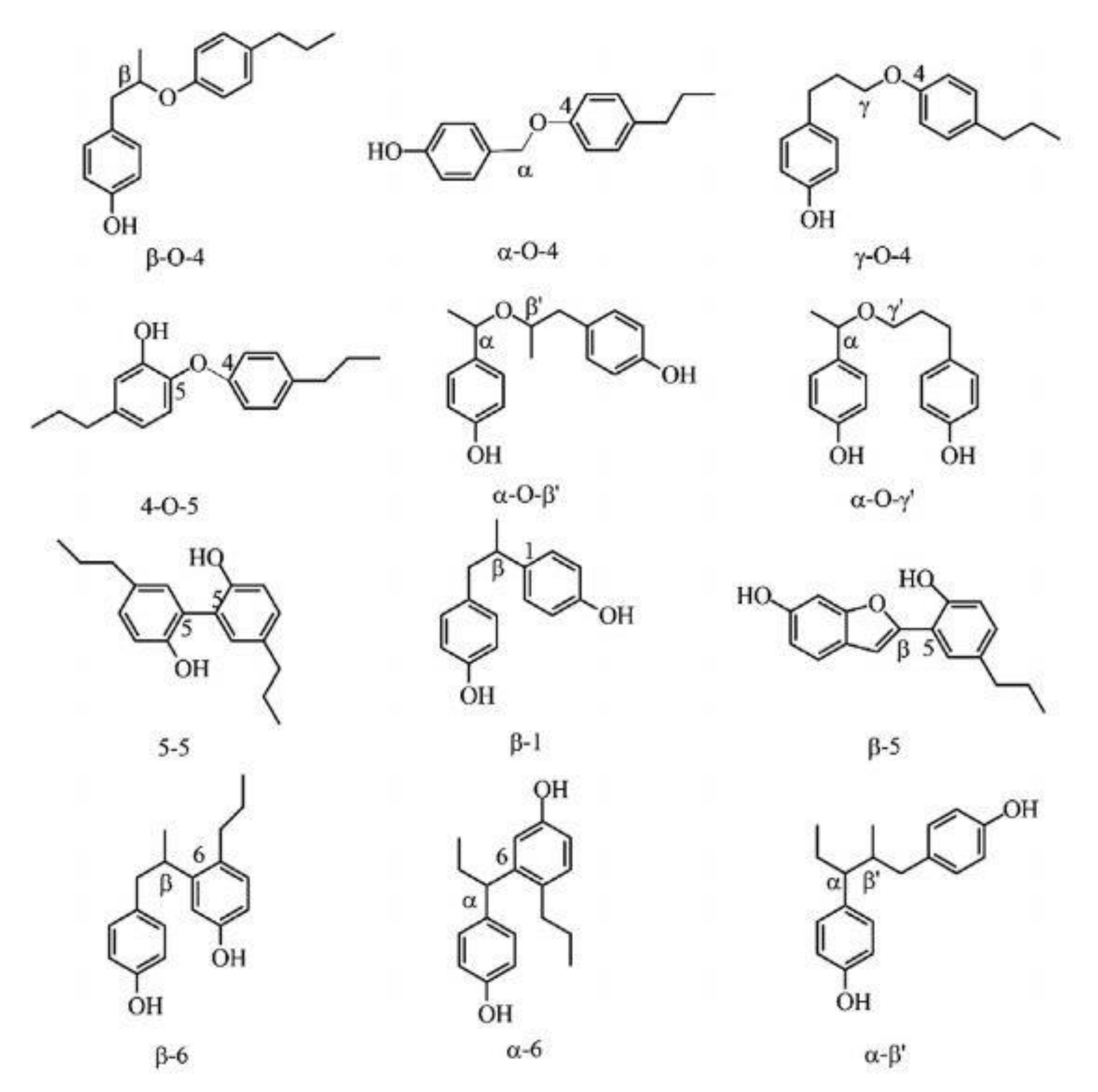
methylglyoxal

Hemicellulose

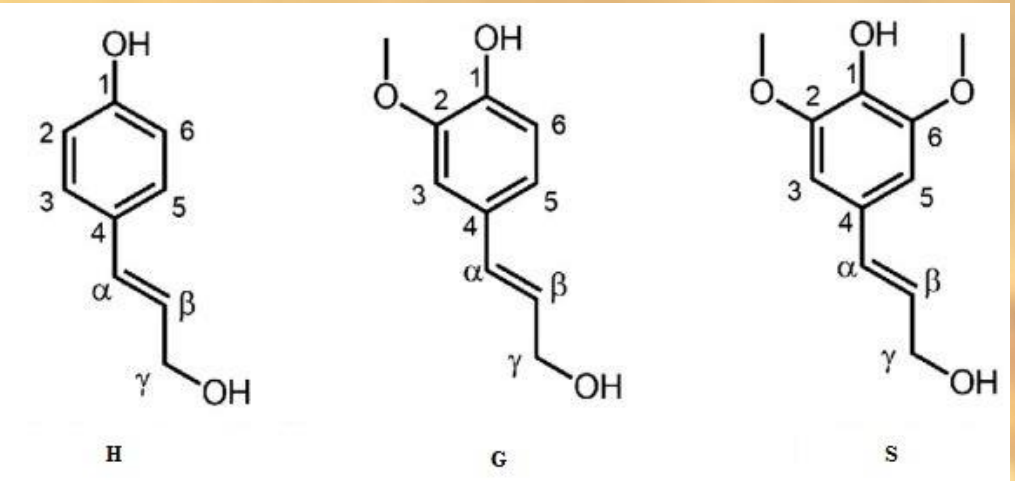


- Short heteropoly-saccharide chains
- 20-25% in plants
- Pyrolyses products: furan derivatives, aldehydes and anhydrosaccharides
- Most abundent compound:

Lignin



p-hydroxyphenyl guaiacyl syringyl



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

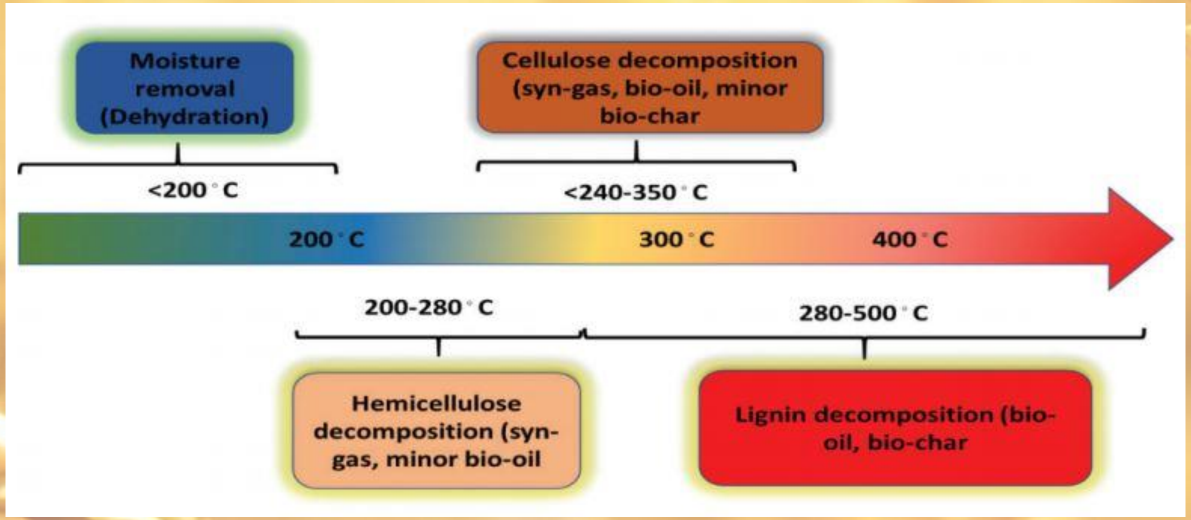
1, p-coumaryl (4-hydroxycinnamyl),

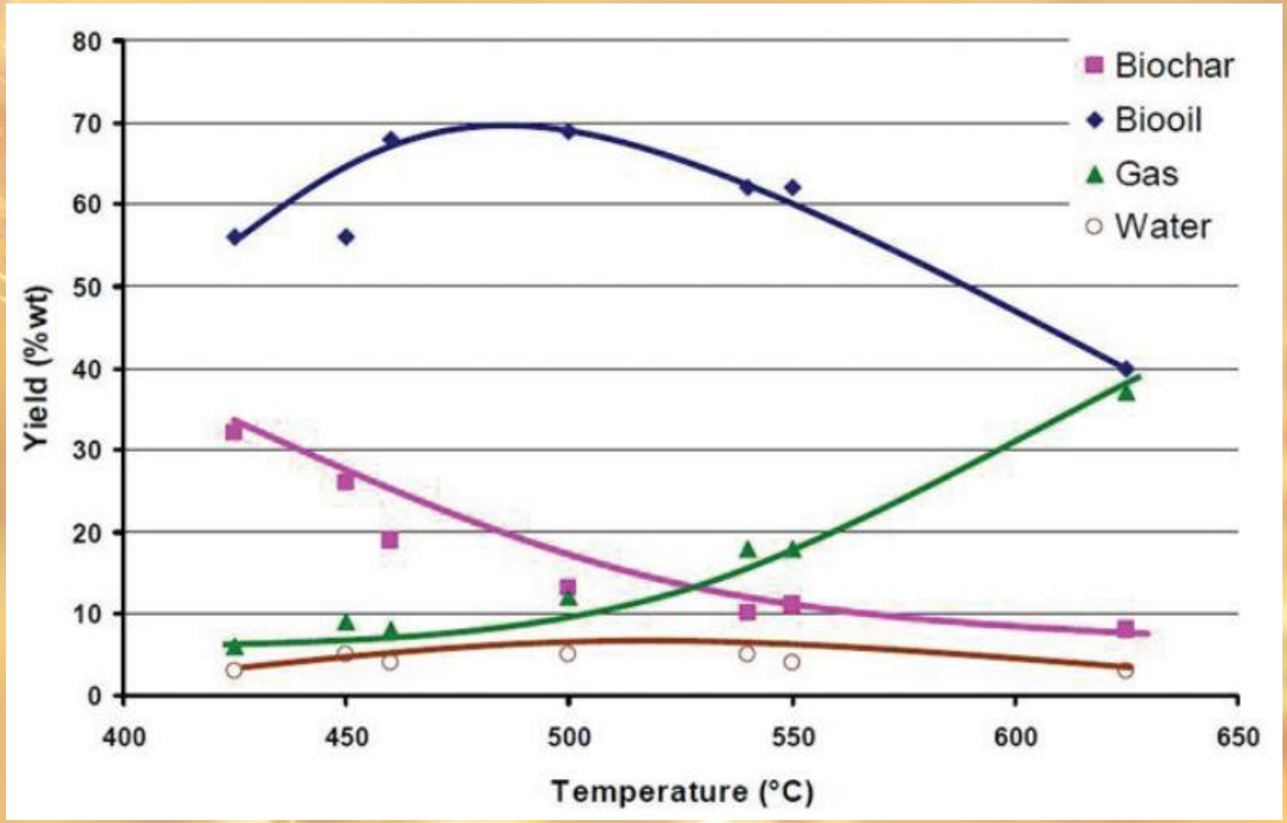
2, coniferyl (3-methoxy-4-hydroxycinnamyl)

3, synapil (3,5-dimethoxy-4-hydroxycinn-amyl)

Lignocellulose pyrolysis

Biomass decomposition at different temperatures



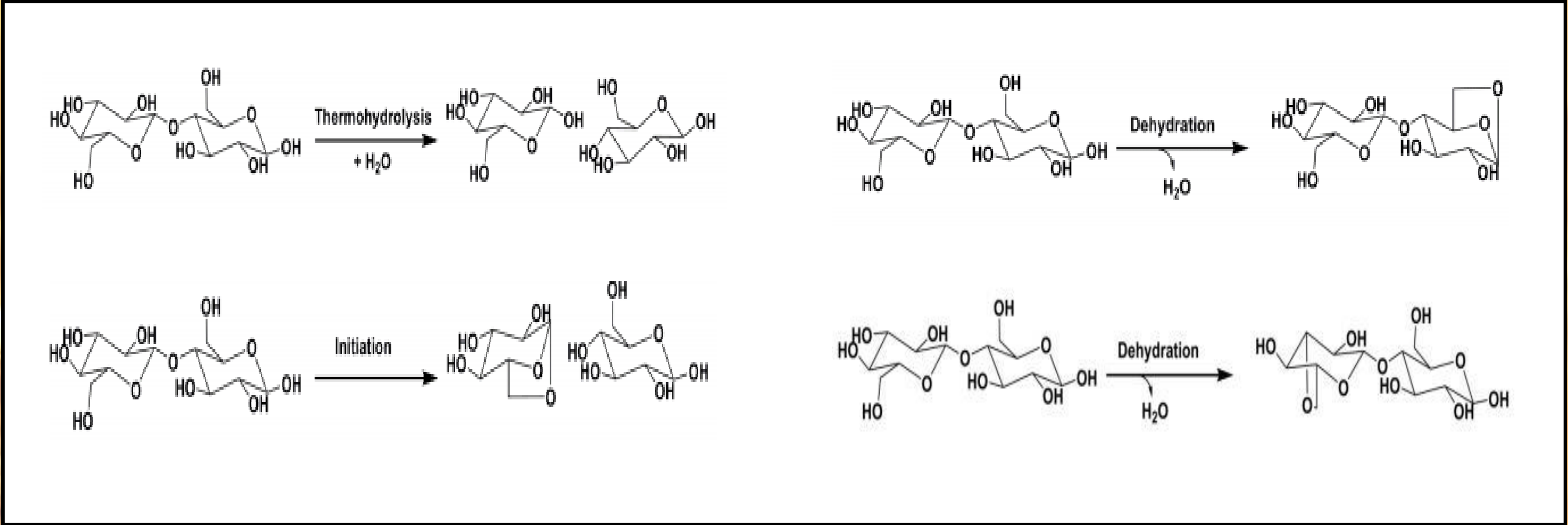


Decomposition of biomass pyrolysis products

Mechanism of fast pyrolysis on cellubiose

Fast pyrolysis products:

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

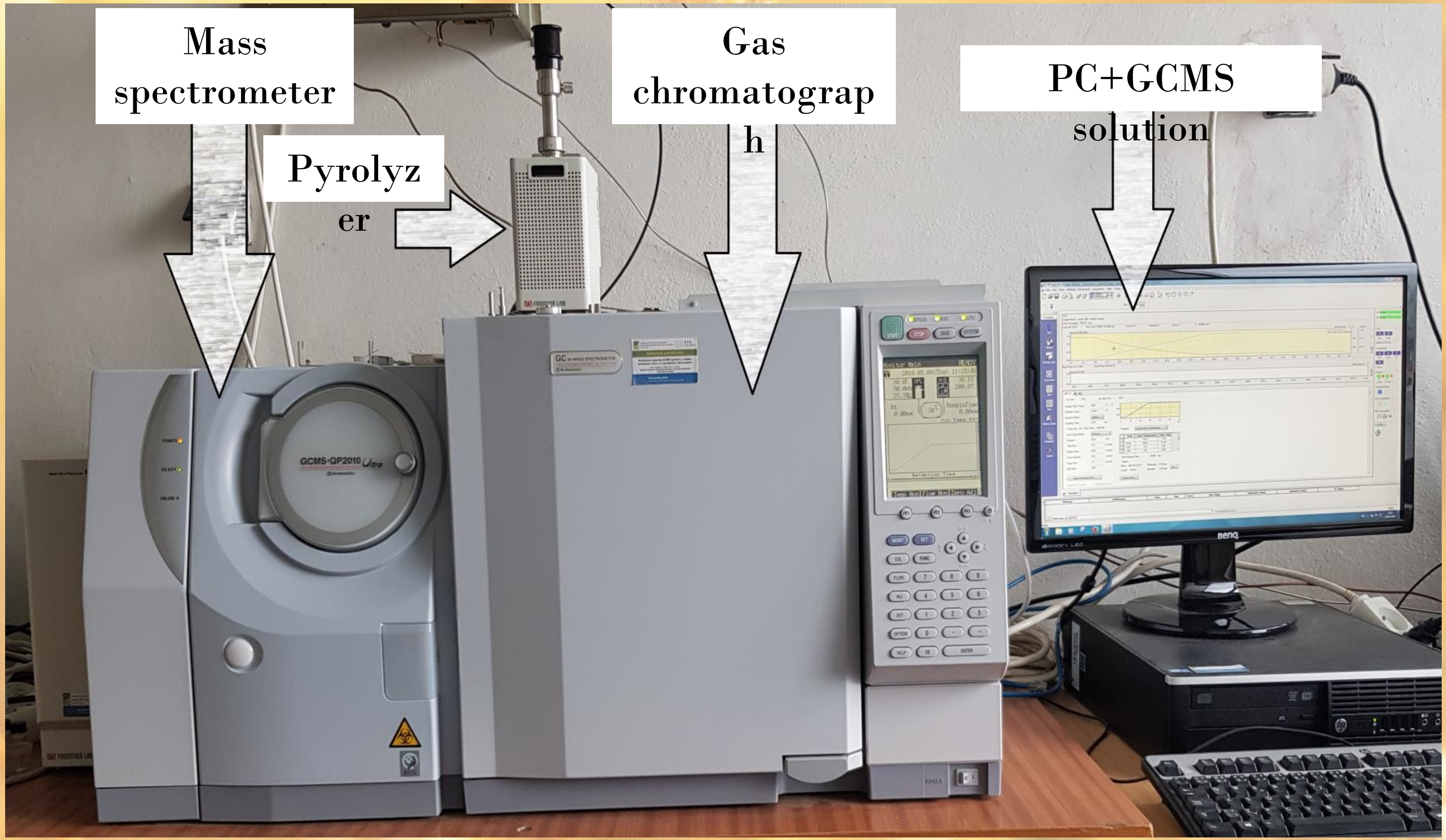


Effect of heating rate and temperature on the fast pyrolysis process

- The fast pyrolysis process requires rapid heating and subsequent cooling of the primary vapours to minimise the extent of secondary reactions.
- Secondary reactions are undesirable and have a negative effect on product quality.
- Slow heating results in higher yields of biochar.
- At lower temperatures, adverse effects such as incomplete decomposition of the biomass can also occur, leading to a higher proportion of solids in biochar.
- Increasing the pyrolysis temperature, typically to 400-550°C, increases the yield of liquid products, while other factors also influence its formation.
- Pyrolysis above 550°C leads to secondary reactions causing vapour decomposition and condensed products (compounds) become more dominant.

Equipment

GC-MS-QP2010 ULTRA



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

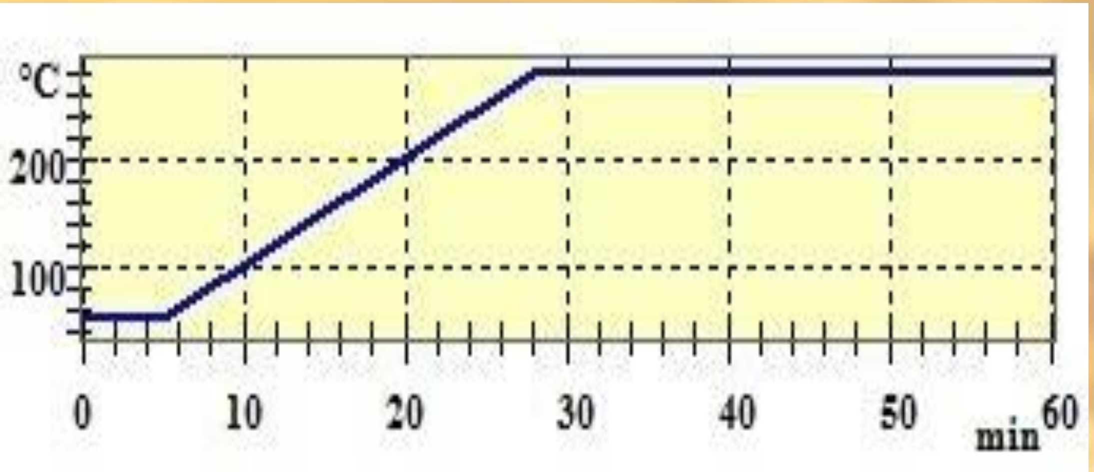
Carrier gas: Helium

- Total flow: 23 ml/ min

Injection mode: Splitless

Analysis time: 60 min

Temperature profile of the column:

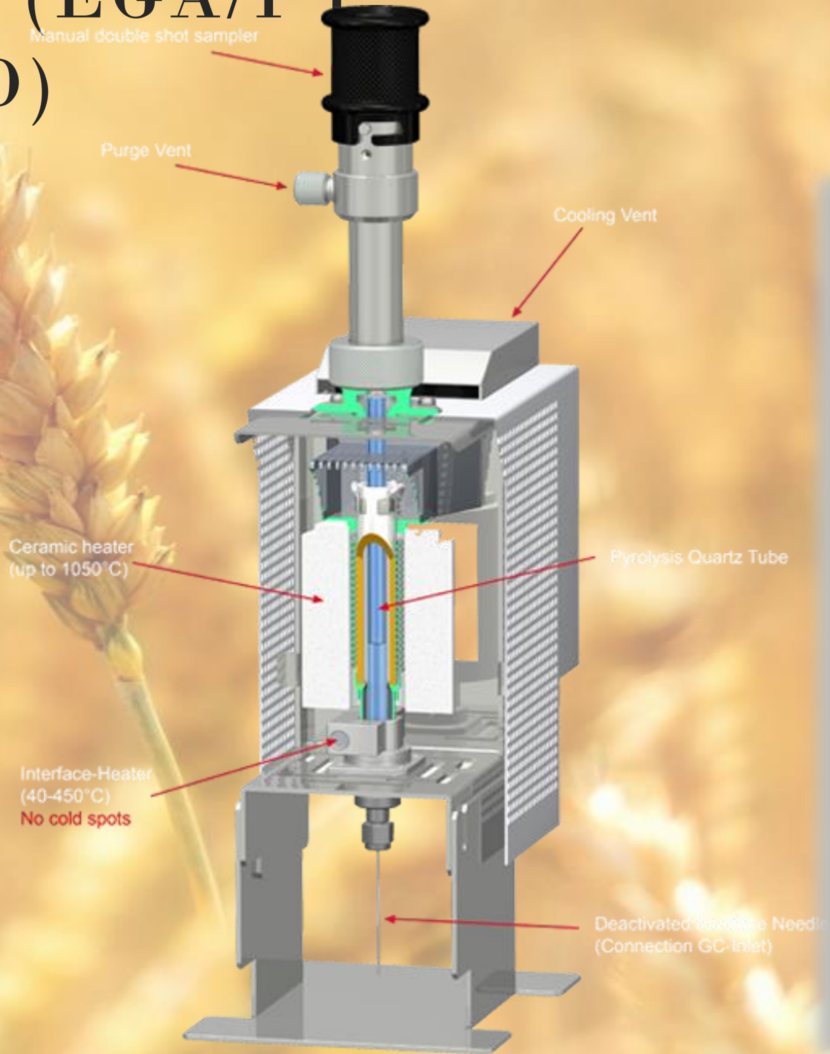


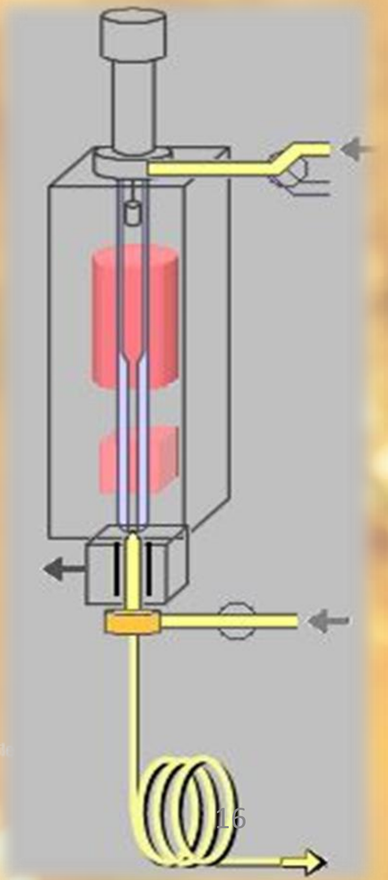
GC injection temperature: 250 °C

Ion source temperature: 200 °C

Equipment

MULTI-SHOT PYROLYZER (EGA/PY 3030D)





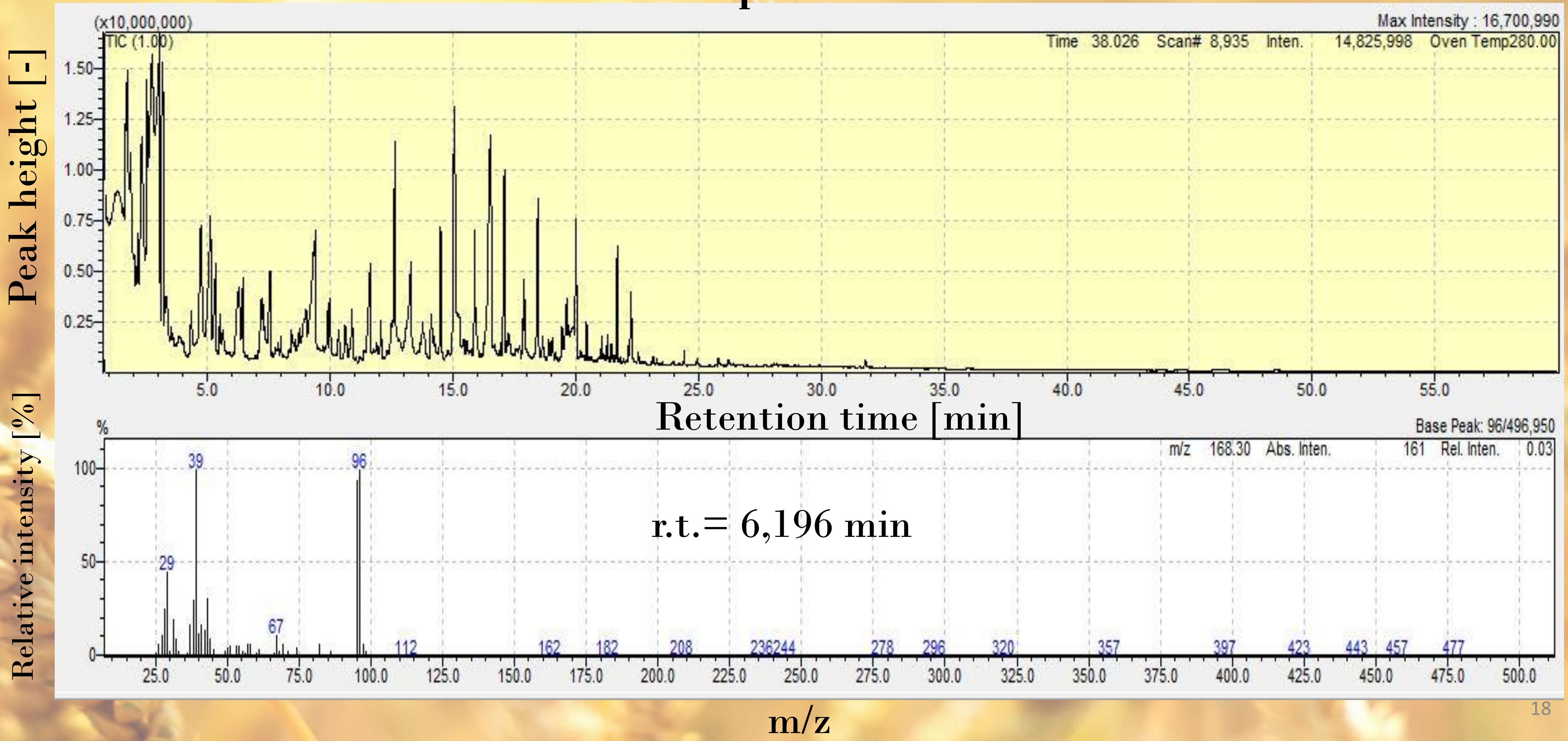
Equipment

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

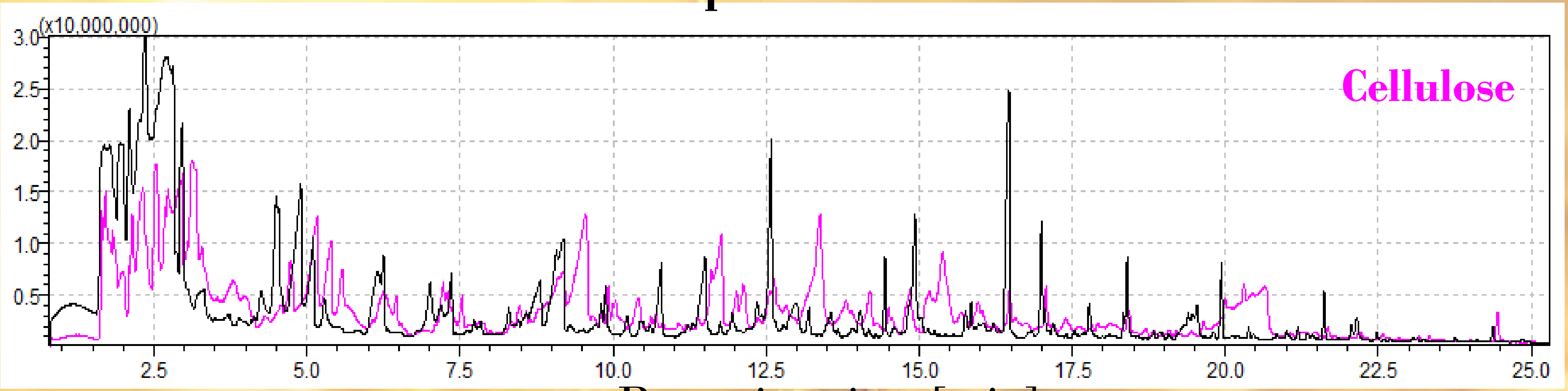
Procedure for evaluating measured data

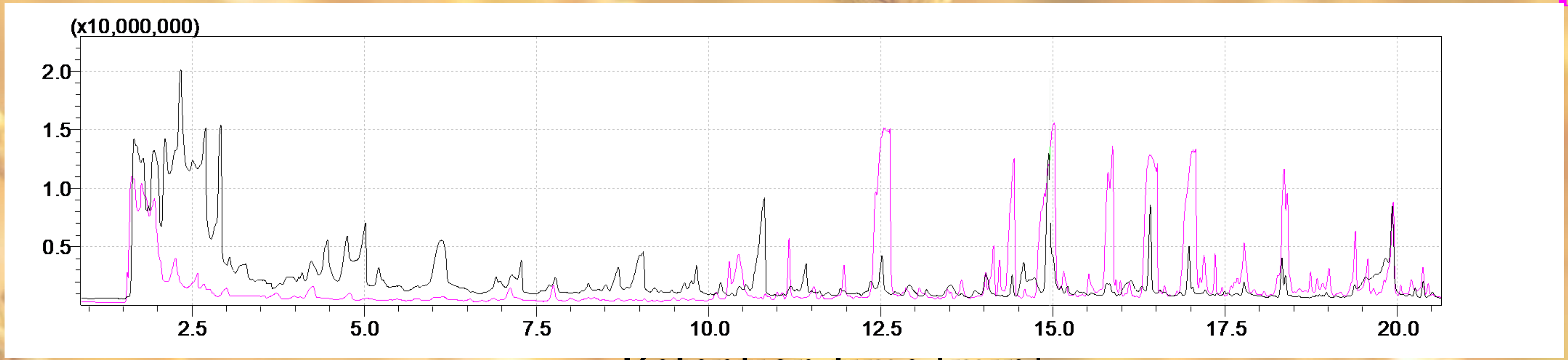
Sample of reed



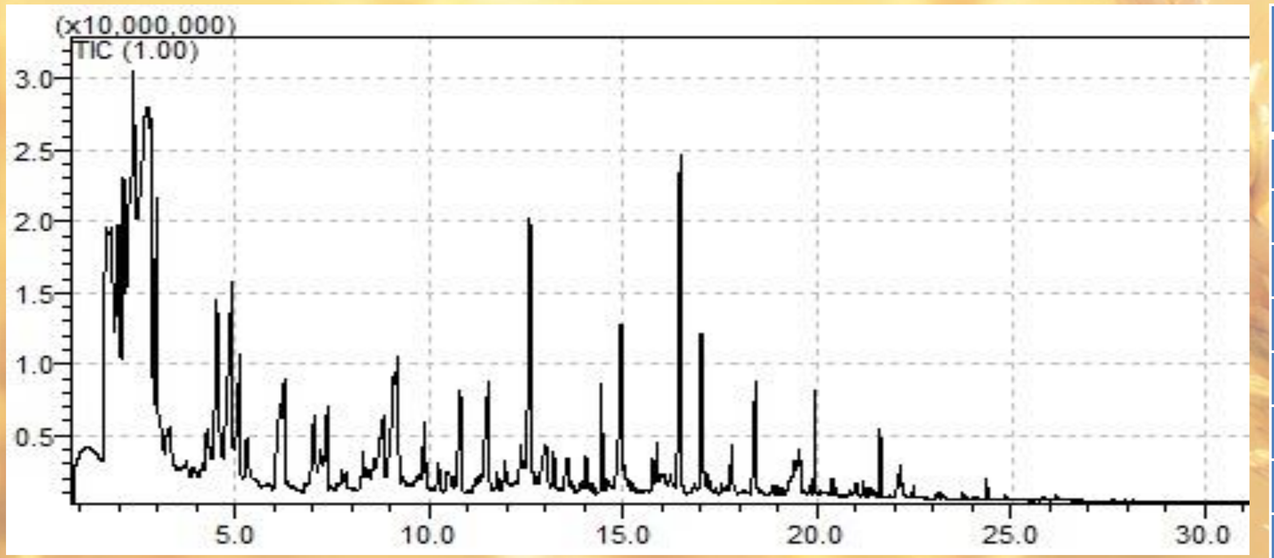
Pyrolysis products

Sample of straw





Pyrolysis products of straw

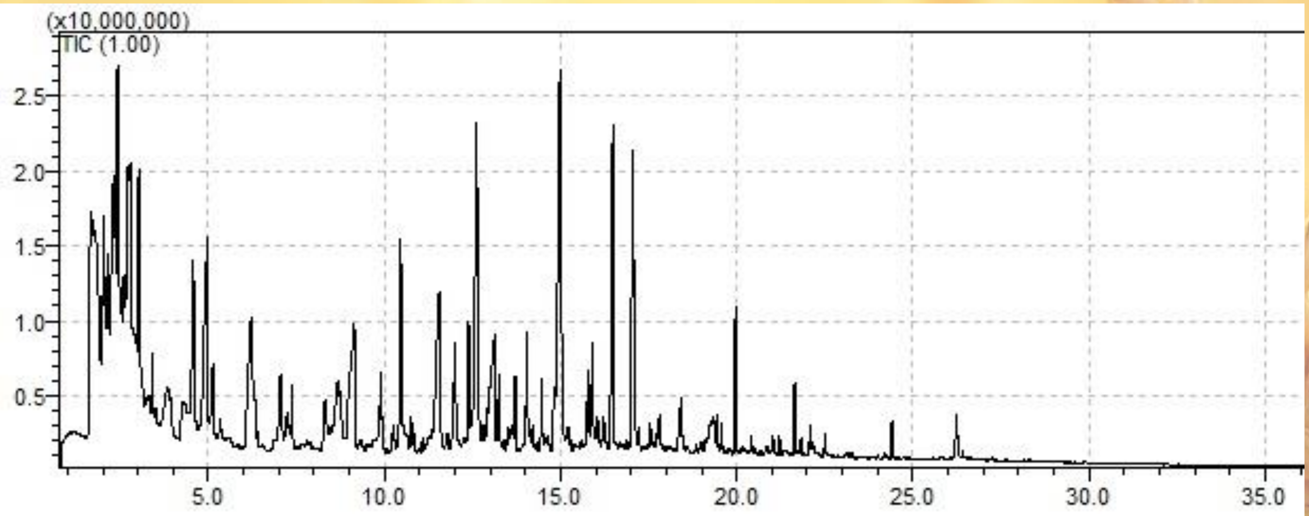


Gas chromatograph record of pyrolysis products of the glossy surface of untreated straw pyrolysed at 500°C.

Characteristic products of pyrolysis of untreated straw:

Retention time [min]	Compliance [%]	Substance
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
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
19,55	82	Levoglucosan

Pyrolysis products of corn

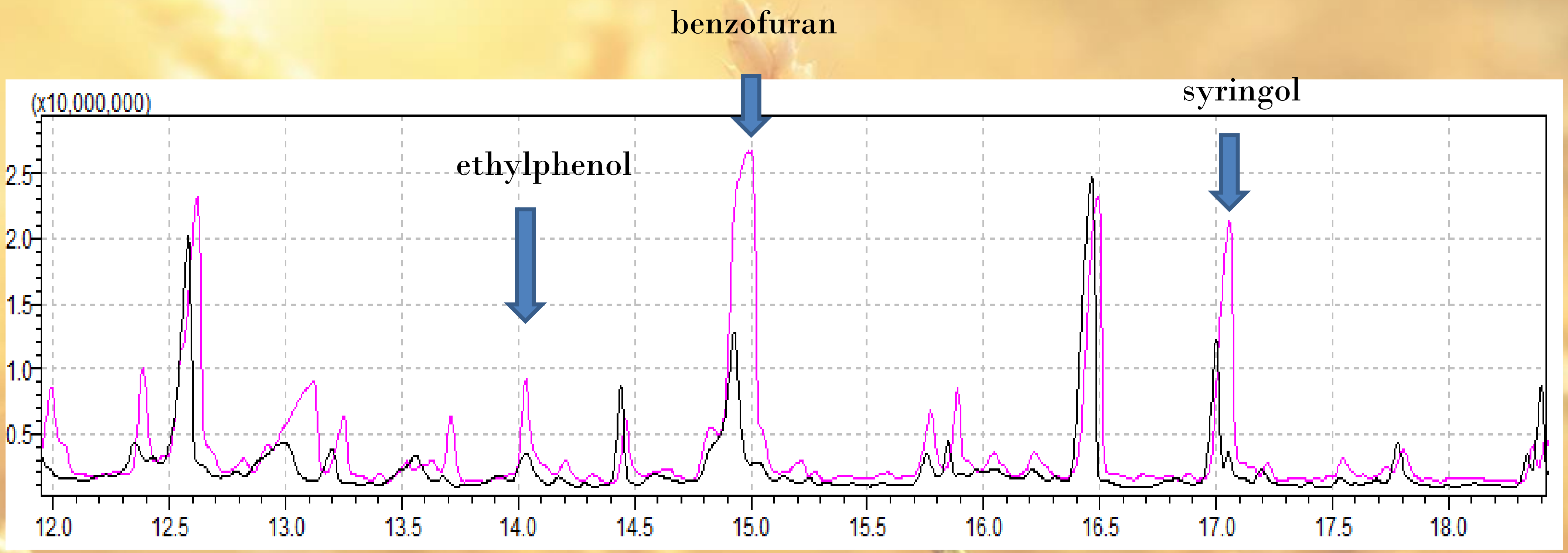


Gas chromatograph record of pyrolysis products of the glossy surface of untreated corn pyrolysed at 500 °C

Characteristic products of pyrolysis of untreated corn:

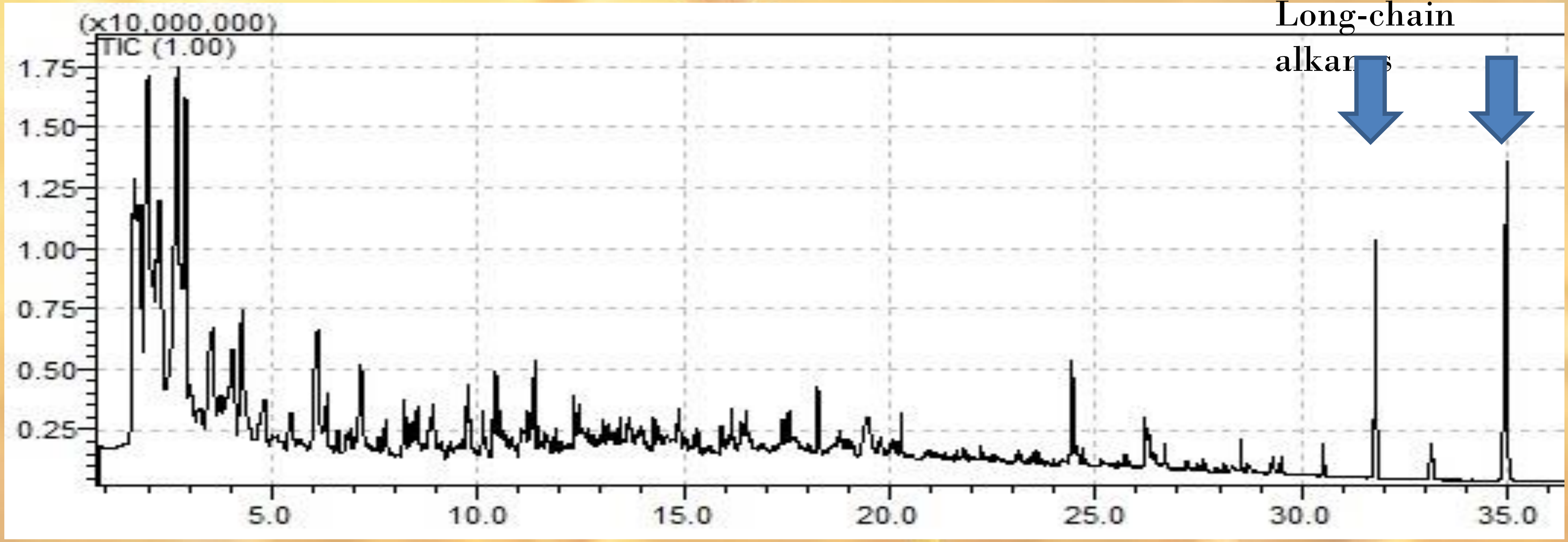
Retention time [min]	Compliance [%]	Substance
2,81	80	Acetic acid
3,05	8	1-hydroxy-2-propanone
4,57	91	1-hydroxy-2-butanone
4,93	87	Methylpentanal
6,21	80	Furfural
6,30	80	Cyclopenten-3-one
9,13	87	1,2-cyclopentadienone
10,47	96	Phenol
11,52	91	3-methyl-1,2-cyclopentadienone
12,62	95	Methoxy-phenol (guaiacol)
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



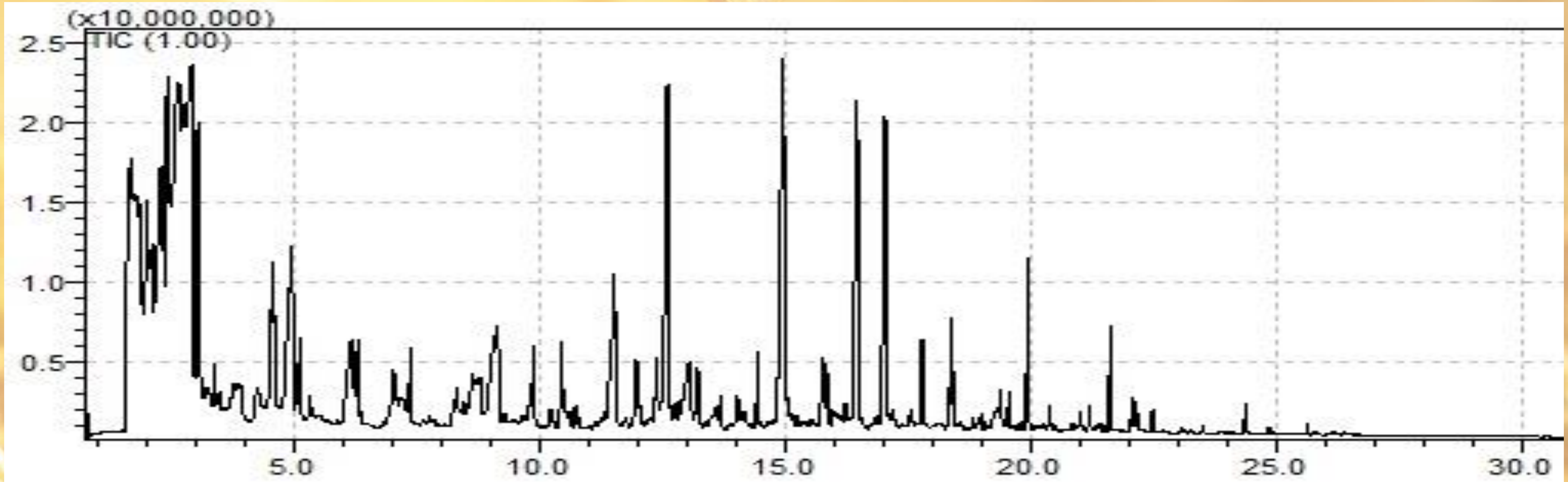
Comparison of pyrolysis products of straw and maize obtained at 500°C

Pyrolysis products of sunflower



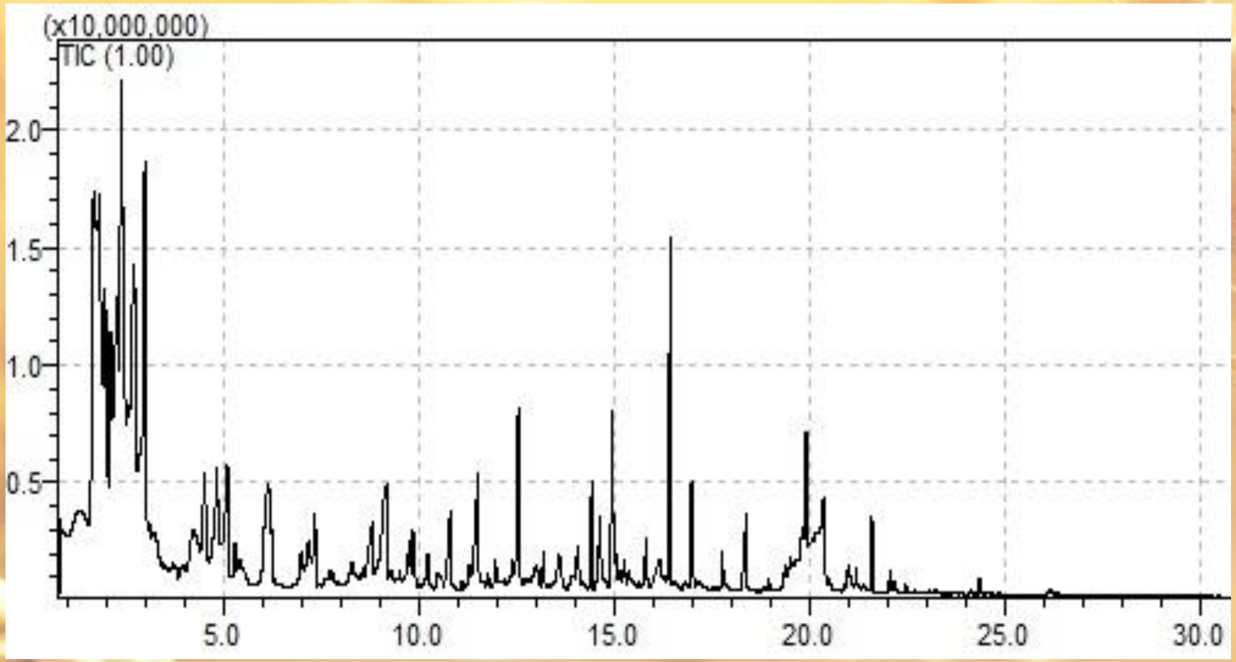
Gas chromatograph record of pyrolysis products of the glossy surface of untreated sunflower pyrolysed at 500°C.

Pyrolysis products of wheat



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

Pyrolysis products of barley

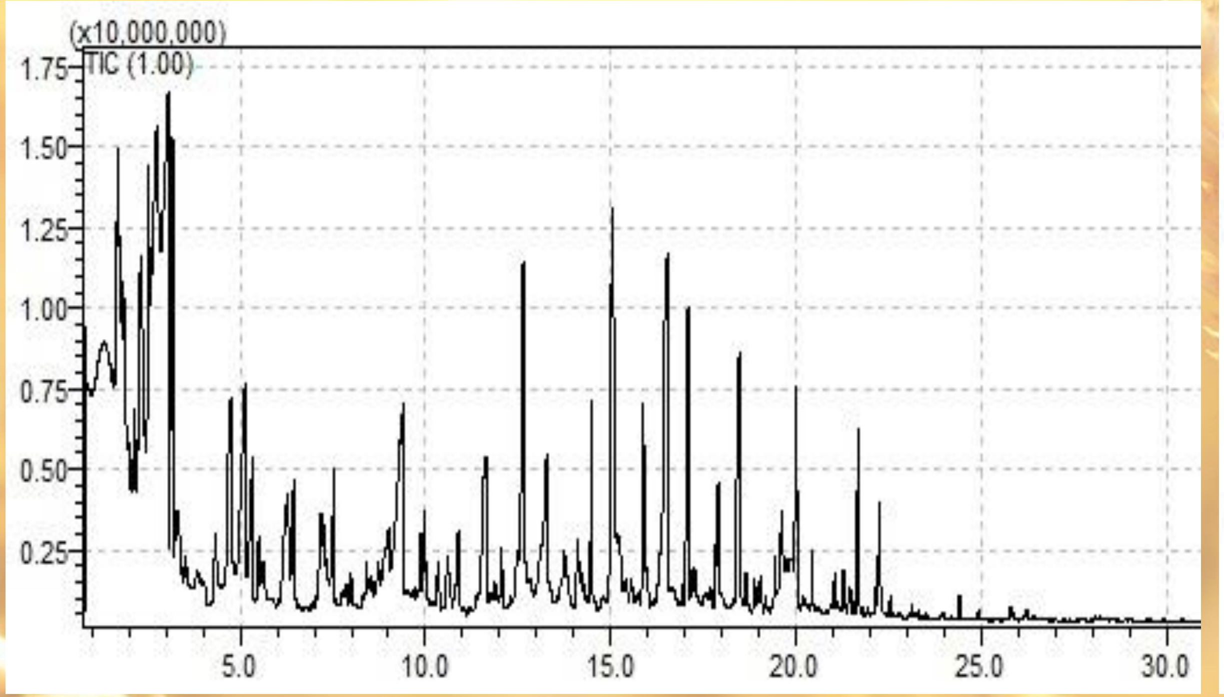


Gas chromatograph record of pyrolysis products of the glossy surface of untreated barley pyrolysed at 500 °C

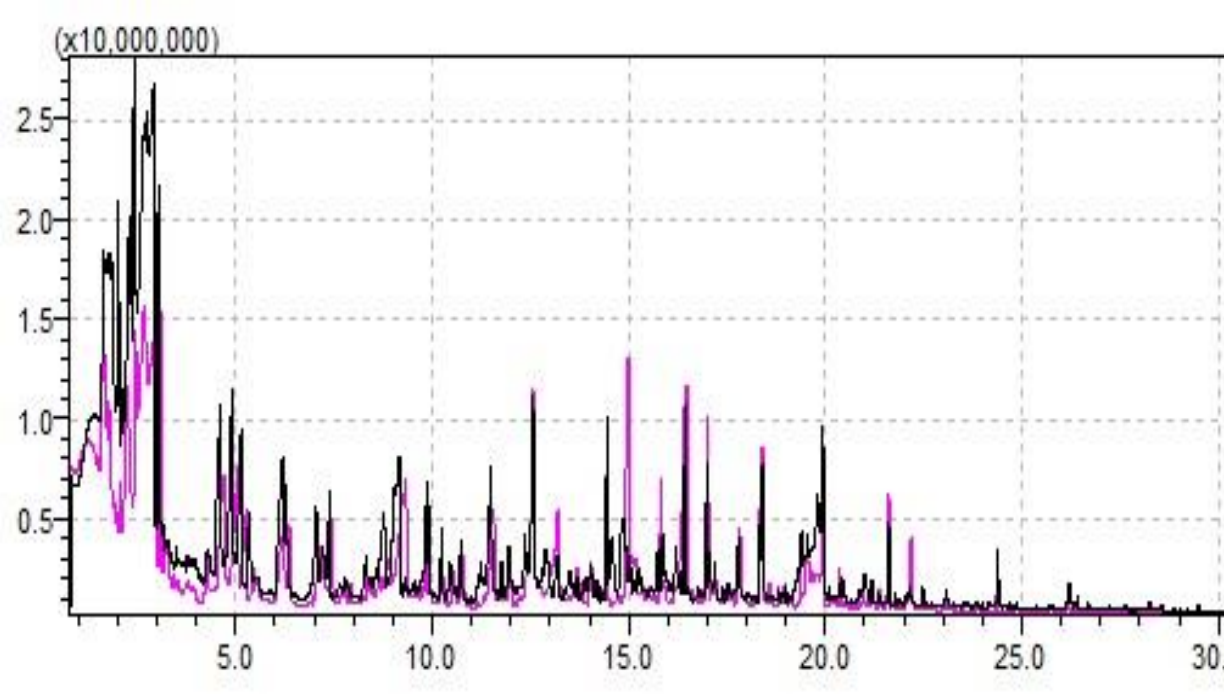
Characteristic products of pyrolysis of untreated barley:

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
19,2 - 20,13	90	levoglucosan

Pyrolysis products of reed and vine

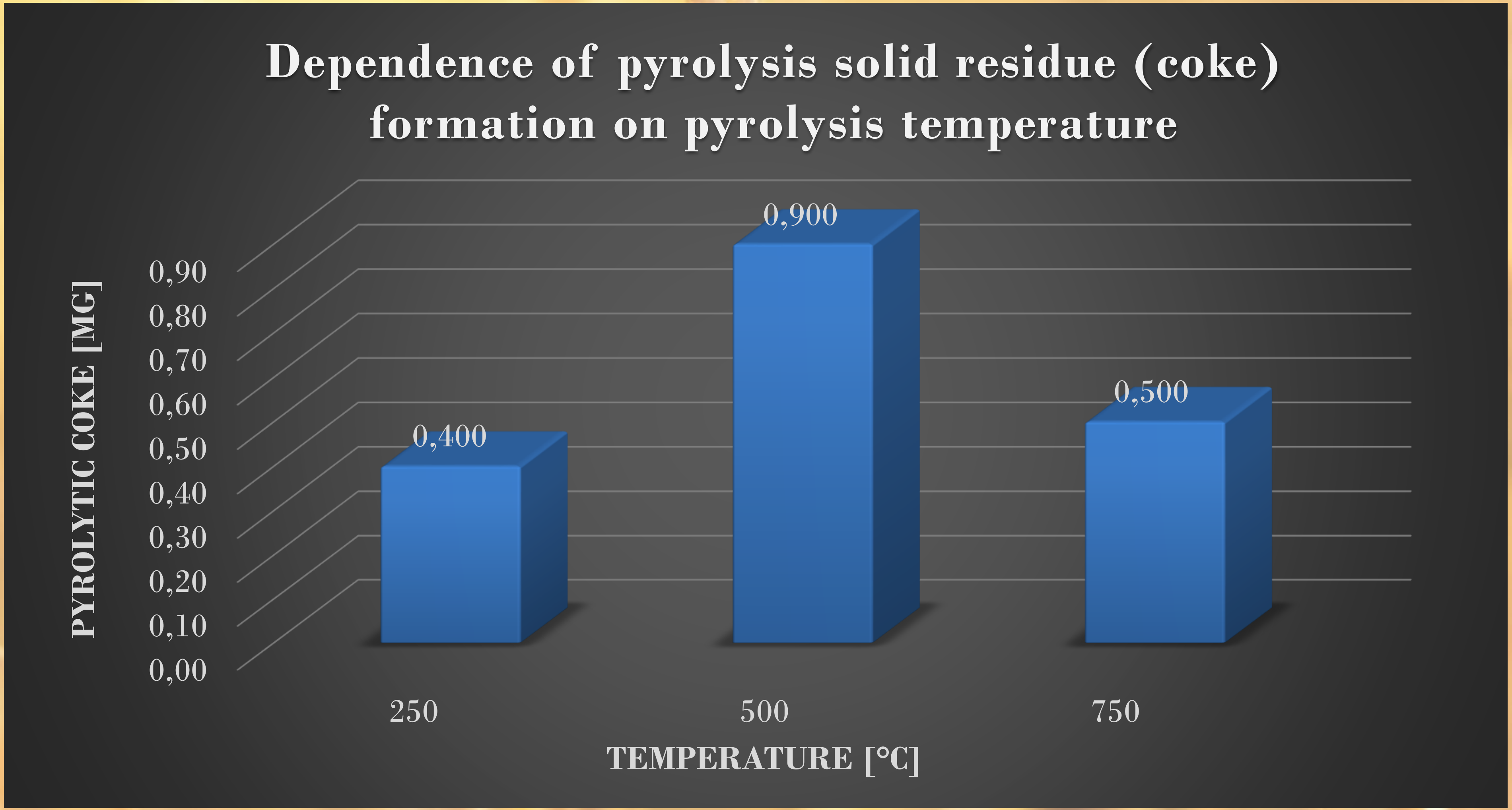


Gas chromatograph record of pyrolysis products of the glossy surface of untreated reed pyrolysed at 500 °C

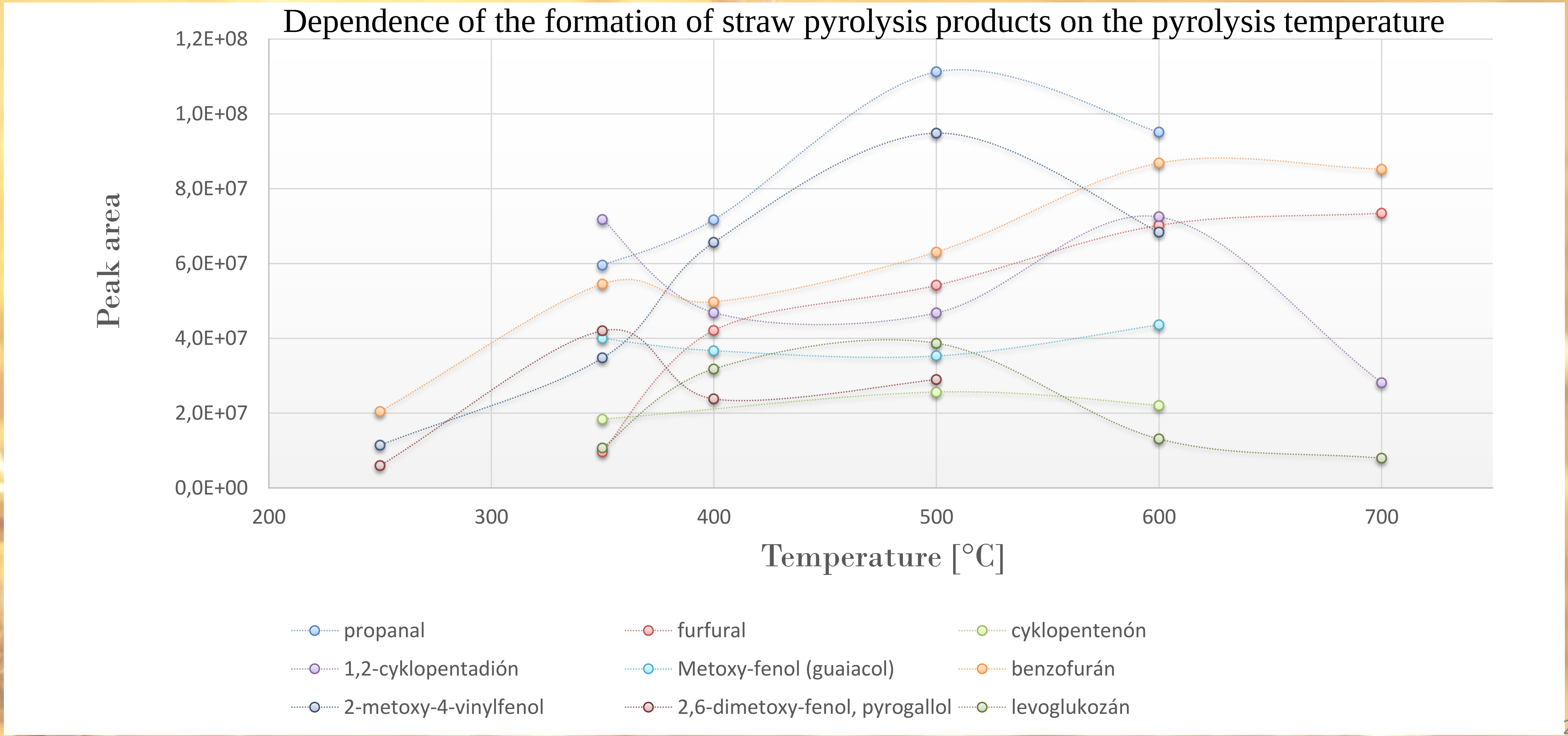


Comparison of gas chromatograph recordings of pyrolysis products of the glossy surface of reed (pink colour) and vine (black colour) pyrolysed at 500°C

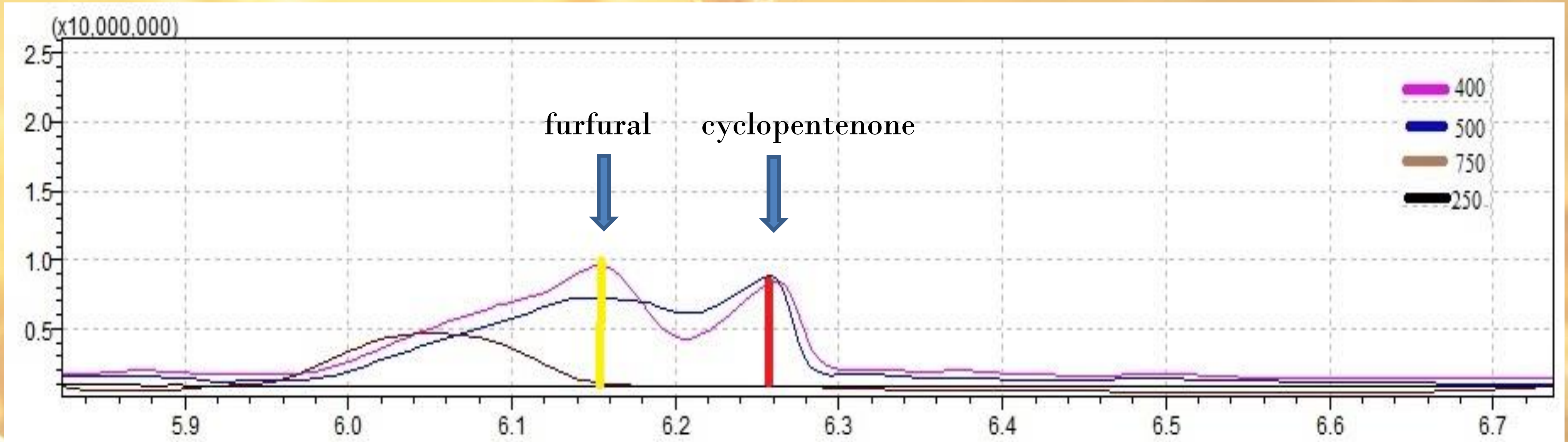
Effect of temperature on the composition of pyrolysis products



Effect of temperature on the composition of pyrolysis products



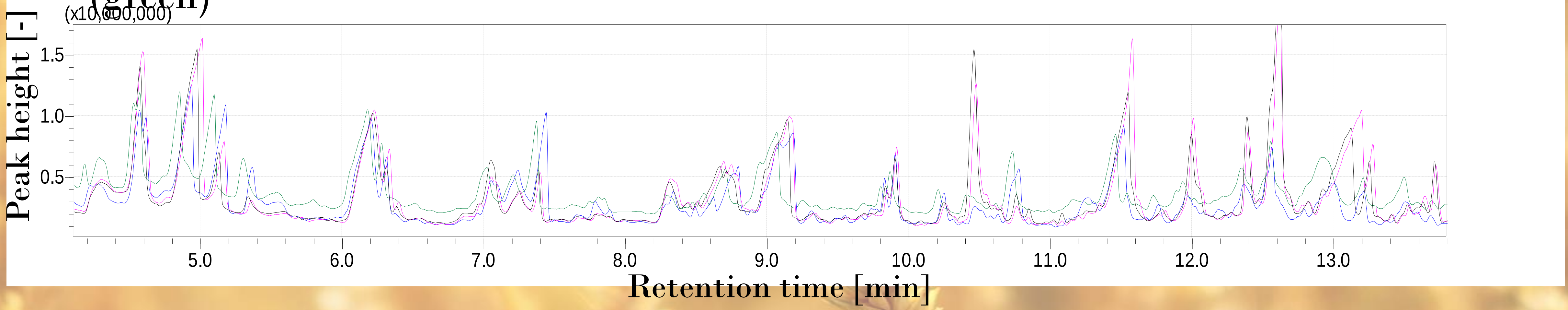
Effect of temperature on the composition of pyrolysis products



Part of the chromatogram showing the peaks of furfural and cyclopentenone as a function of temperature

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

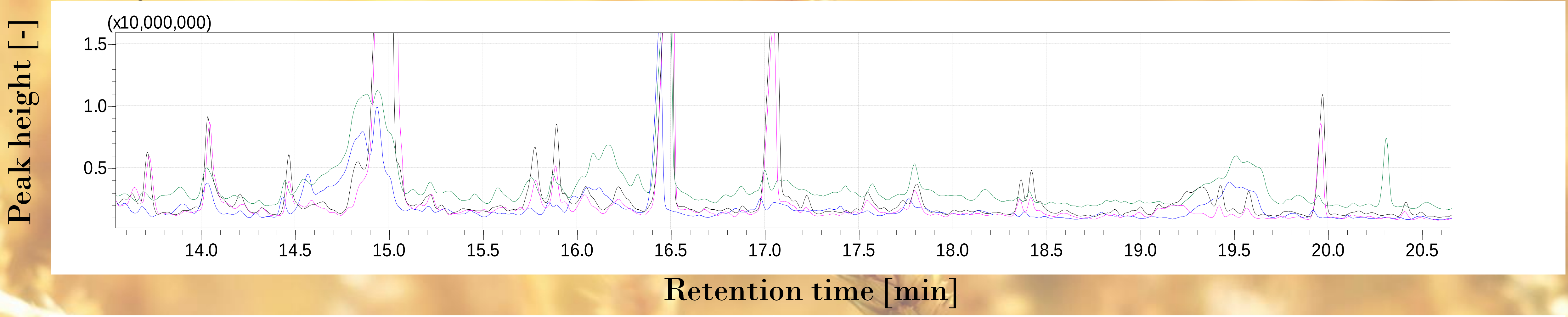
Glossy surface of stem (black); interior (pink); outer part of stem (blue) and leaf (green)



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)

Glossy surface of stem (black); interior (pink); outer part of stem (blue) and leaf (green)

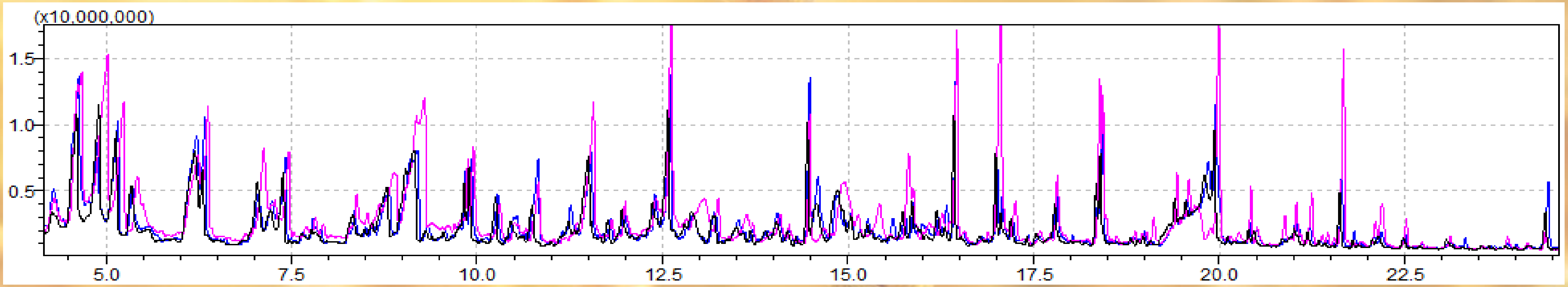


Retention time [min]	Part of the plant	Substance
13,73	glossy surface of stem, interior	2,6-dimethylphenol
14,9	glossy surface of stem, interior	benzofuran
16,16	leaf	2-deoxy-D-galactose
17,1	glossy surface of stem, interior	syringol
19,5	leaf, outer part of stem	levoglucosane

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

Glossy surface of stem (black); interior (pink); outer part of stem (blue) and leaf (green)

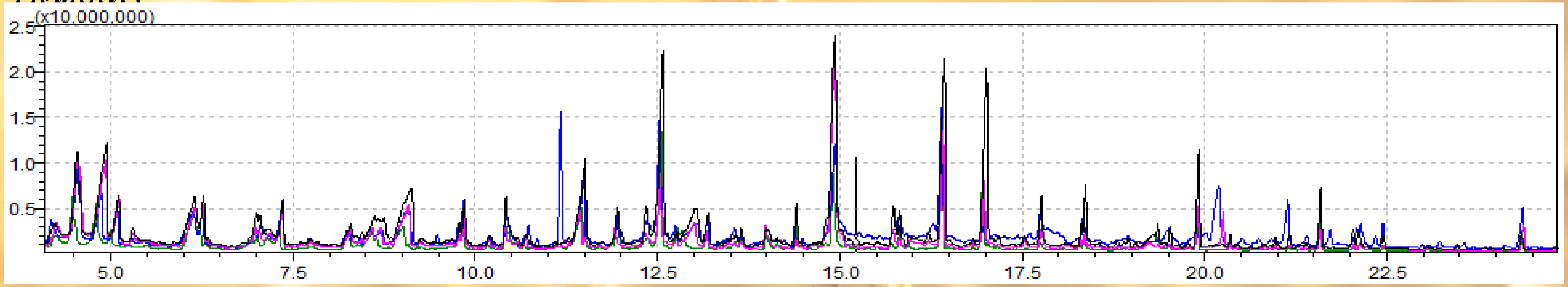
Peak height [-]



Retention time [min]

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

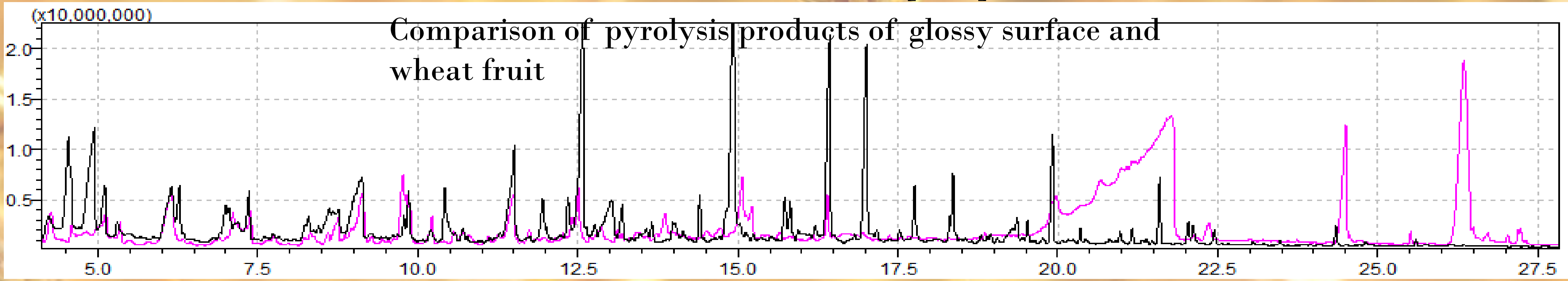
Glossy surface of stem (black); interior (pink); outer part of stem (blue) and leaf (green)



Peak height [-]

Retention time [min]

Comparison of pyrolysis products of glossy surface and wheat fruit

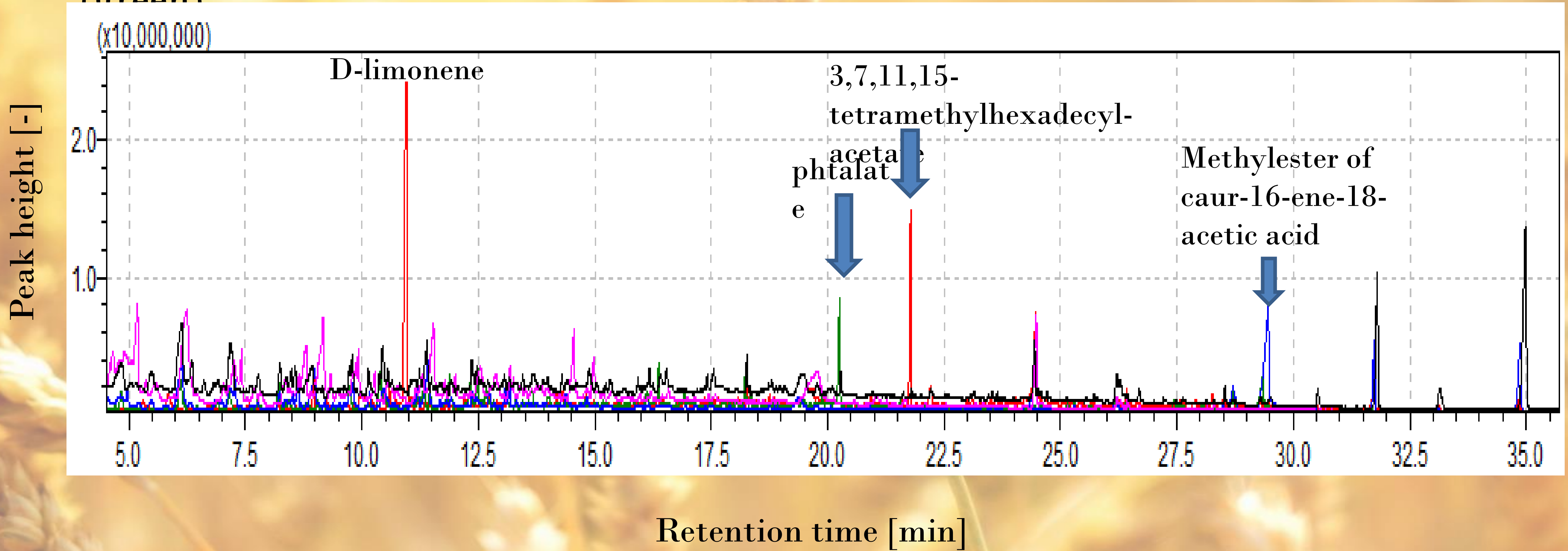


Peak height [-]

Retention time [min]

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

Glossy surface of stem (black); interior (pink); outer part of stem (blue) and leaf (green)



Conclusion

- Comparison of the composition of pyrolysis products of agricultural residues: practically identical products, the difference is in the amount and presence of some compounds characteristic of the plant. Residues of agrochemicals are also visible.
- Different morphological parts of the plants supported the formation of different amounts of pyrolysis products, specific also for the cover and the grains themselves.
- The temperature of pyrolysis: up to 300°C only volatile components are separated; at higher temperatures up to 500°C the largest amount of liquid products are formed by retrocondensation reactions; above 550°C bond cleavage - cracking occurs, consecutive reactions of primary decomposition products takes place

Plans

- Complete analyzes (new samples)
- Evaluate chromatograms
- Compare by plant and place of origin
- Repeat in the presence of catalysts

Thank you for your attention!

Acknowledgement

European Regional Development Fund (Interreg, SKHU/1902/4.1/001/Bioeconomy)

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