Thermal behaviour/treatment of some vegetable residues. Gas chromatographic analysis of pyrolysis products from pine cone

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Municipal Solid Waste (MSW):

~ 65 wt% lignocellulosic / cellulosic waste
~ 15 wt% synthetic polymer materials
~ 20 wt% inorganic materials

Lignocellulosic materials:

- polymeric composites
- laminates with plastics for packaging
- upgrading by co-pyrolysis / co-gasification

Co-pyrolysis:

- biomass: ~ 47-51 wt% C; 42-46 wt% O;
  lower thermal stability
- plastics: ~ 84 wt% C; 1.5 wt% O;
  source of H

Pine cone:

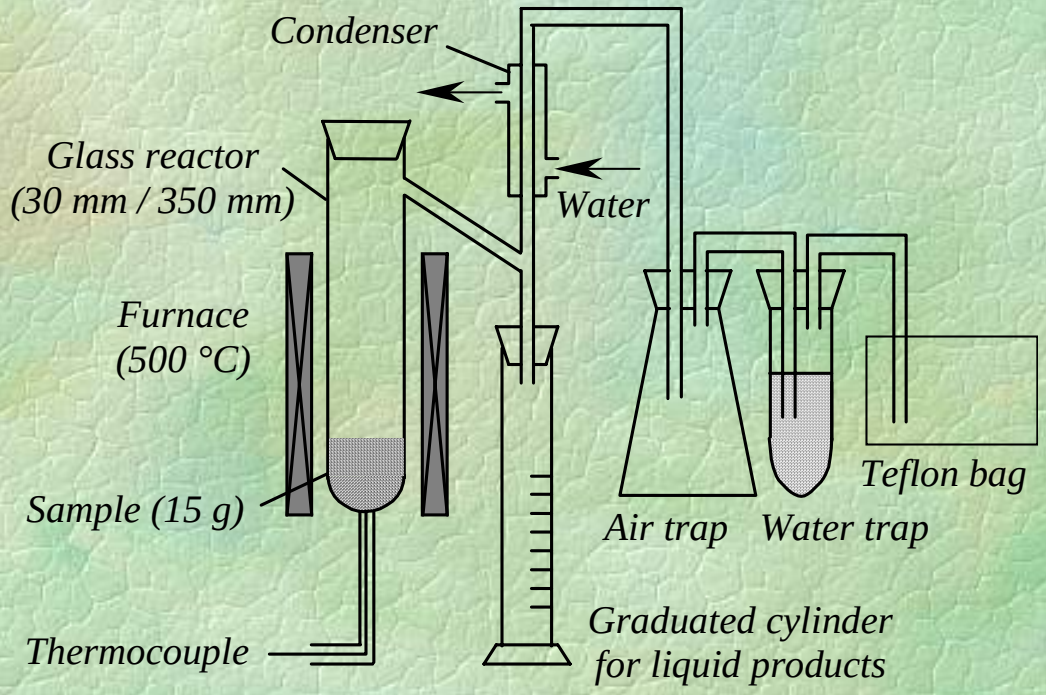
- low ash content;

Materials

- pine cones of *Pinus pinea L* (**Pc**):

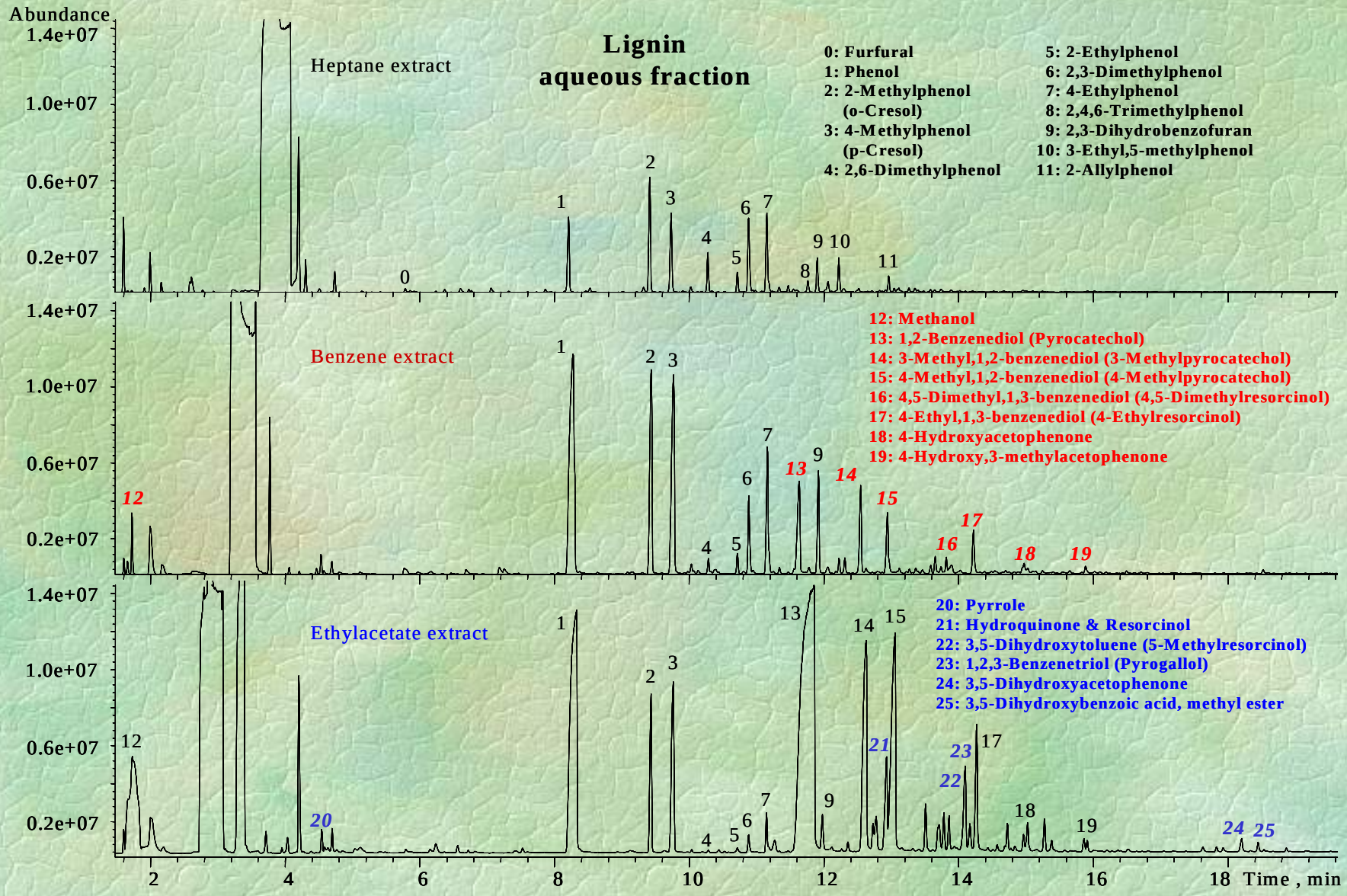
- proximate analysis:
  moisture: 9.6%; ash: 0.9%; volatiles: 77.8%
- elemental analysis:
  C: 42.62%; H: 5.56%; N: 0.76%; S: 0.05%: O: 51.01%
- main constituents:
  cellulose: 32.7%; hemicellulose: 37.6 %; lignin: 24.9%, extractives: 4.8%

- polyethylene (**PE**)
- polypropylene (**PP**)
- polystyrene (**PS**)
- cellulose (**Cell**)



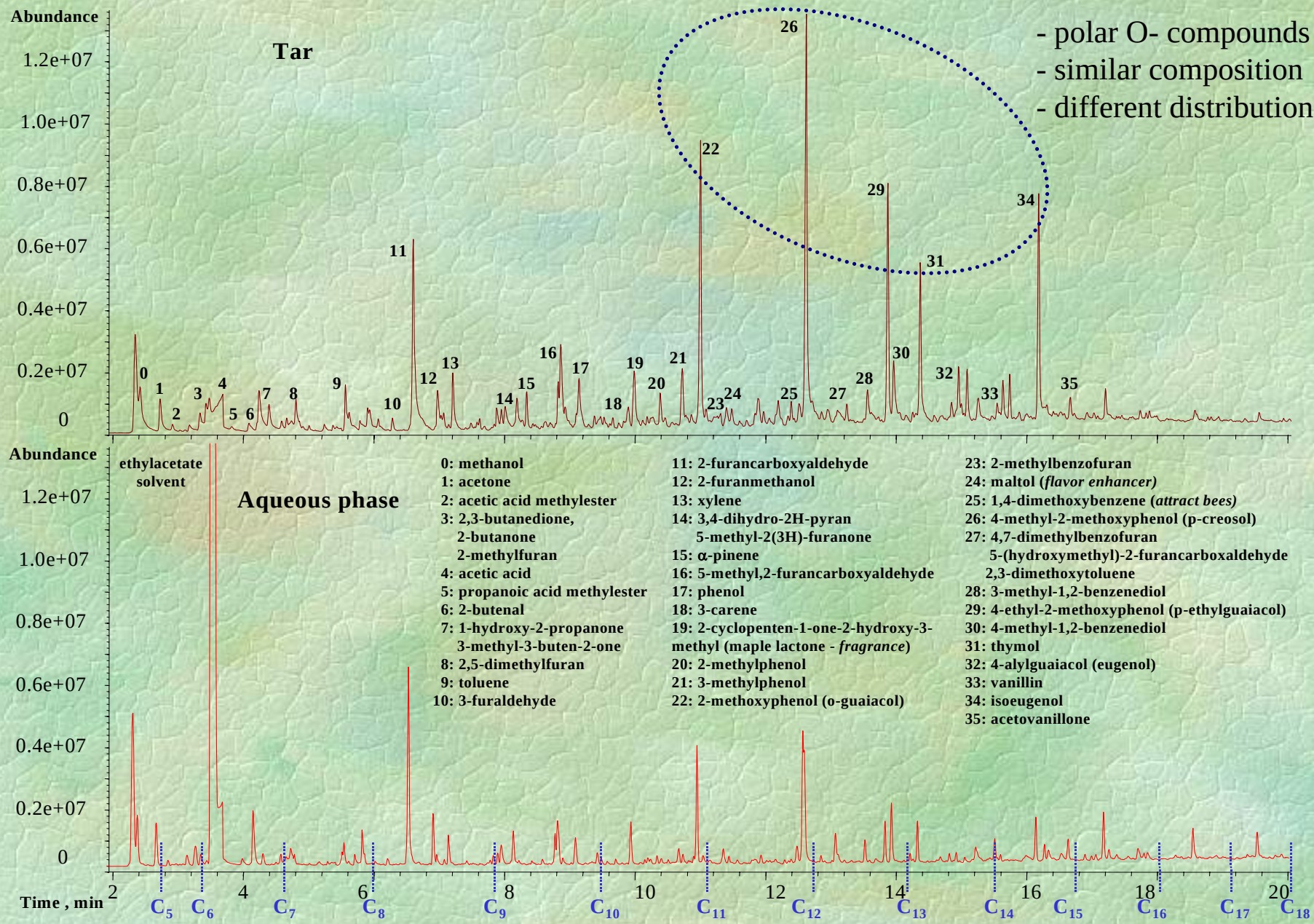
Pyrolysis set-up

Extraction of compounds from aqueous phase



- Ethylacetate is suitable solvent

GC-MSD analysis of Pine cone pyrolysis products



0: methanol
1: acetone
2: acetic acid methylester
3: 2,3-butanedione, 2-butanone 2-methylfuran
4: acetic acid
5: propanoic acid methylester
6: 2-butenal
7: 1-hydroxy-2-propanone 3-methyl-3-buten-2-one
8: 2,5-dimethylfuran
9: toluene
10: 3-furaldehyde
11: 2-furancarboxyaldehyde
12: 2-furanmethanol
13: xylene
14: 3,4-dihydro-2H-pyran 5-methyl-2(3H)-furanone
15: α-pinene
16: 5-methyl,2-furancarboxyaldehyde
17: phenol
18: 3-carene
19: 2-cyclopenten-1-one-2-hydroxy-3-methyl (maple lactone - *fragrance*)
20: 2-methylphenol
21: 3-methylphenol
22: 2-methoxyphenol (o-guaiacol)
23: 2-methylbenzofuran
24: maltol (*flavor enhancer)*
25: 1,4-dimethoxybenzene (*attract bees)*
26: 4-methyl-2-methoxyphenol (p-creosol)
27: 4,7-dimethylbenzofuran 5-(hydroxymethyl)-2-furancarboxaldehyde 2,3-dimethoxytoluene
28: 3-methyl-1,2-benzenediol
29: 4-ethyl-2-methoxyphenol (p-ethylguaiacol)
30: 4-methyl-1,2-benzenediol
31: thymol
32: 4-alylguaiacol (eugenol)
33: vanillin
34: isoeugenol
35: acetovanillone

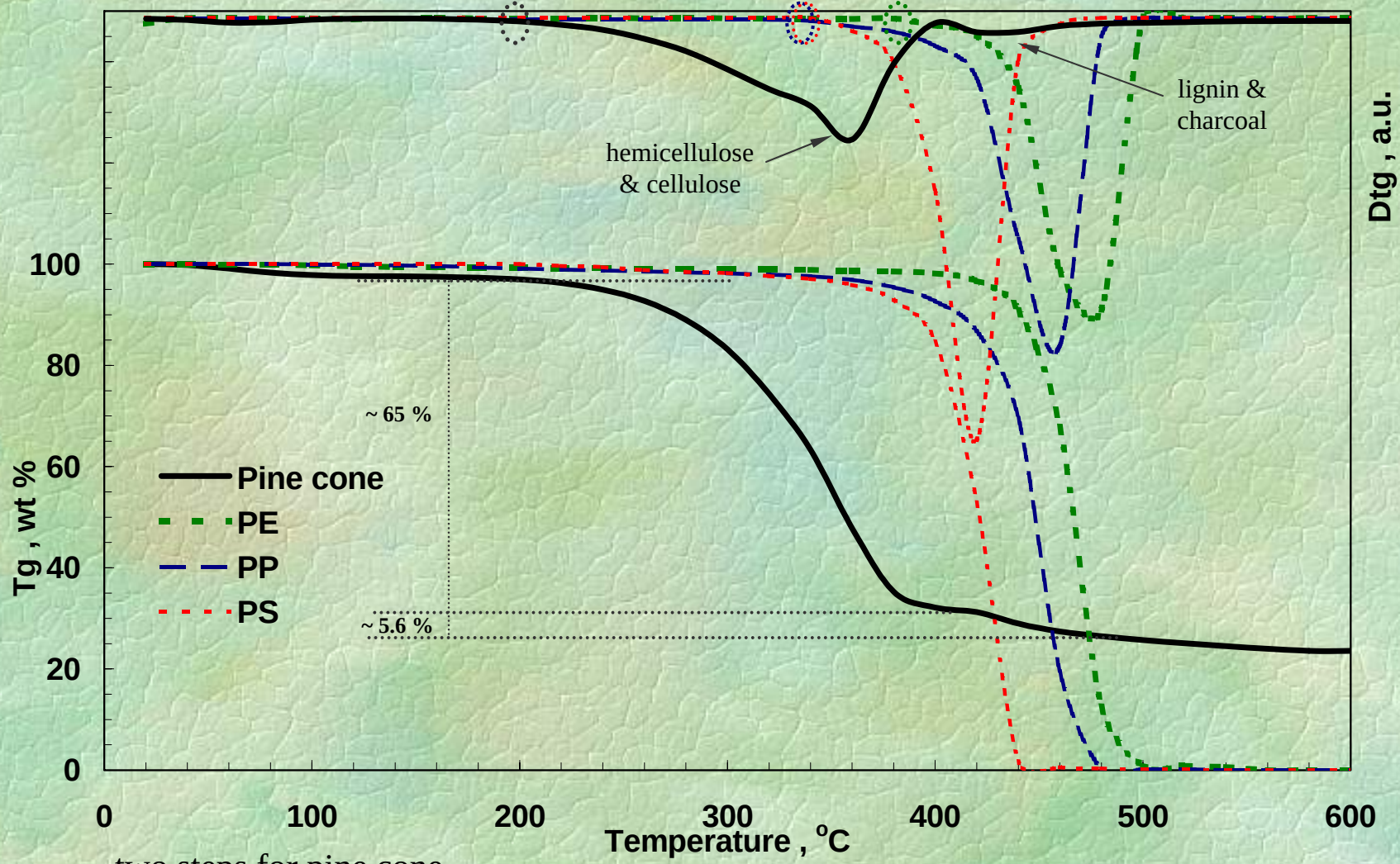
Main compounds by GC-MSD

	Rt (min)	*Pc tar*	Pc aq. ph.
Alcohols		***1.58***	**2.25**
Methanol	2.40	*1.58*	2.13
Acids		***3.67***	**7.90**
Formic acid	3.06	-	-
Acetic acid	3.71	*2.46*	5.06
Propanoic acid	4.70	*0.34*	1.47
2-Propenoic acid	4.80	-	0.30
Aldehydes		***1.21***	**1.7**
Hydroxyacetaldehyde	3.17	*0.30*	0.51
2-Propenal, 2-methyl-	4.01	*0.30*	0.41
2-Butenal, 2-methyl-	5.64	*0.12*	0.18
Propanal	5.73	*0.31*	0.39
Benzeneacetaldehyde	10.23	*0.17*	0.21
Non aromatic ketones		***11.51***	**13.99**
Furans		***11.68***	**14.52**
Furan, 2-methyl-	5.32	*0.89*	0.11
2-Furaldehyde	6.24	*0.22*	0.23
2-Furancarboxaldehyde	6.56	*4.85*	6.80
2-Furfuryl alcohol	6.94	*0.77*	1.54
Furan, 2-ethyl-	7.11	*0.10*	0.16
2-Acetylfuran	7.93	*0.35*	0.35
2(5H)-Furanone	7.98	*0.34*	0.90
2(5H)-Furanone, 5-methyl-	8.50	*0.08*	0.37
5-Methylfurfural	8.84	*1.77*	1.86
Hydroxymethylfurfural	13.10	*0.89*	1.40
5-acetoxymethyl-2-furaldehyde	14.24	*0.23*	0.25

	Rt (min)	*Pc tar*	Pc aq. ph.
Phenols		***5.76***	**2.61**
Phenol	9.12	*1.46*	1.08
Phenol, 2-methyl-	10.37	*0.68*	0.28
Phenol, 3-methyl-	10.70	*1.21*	0.67
Phenol, 2,4-dimethyl-	11.87	*0.17*	0.30
Phenol, 2,3-dimethyl-	12.18	*0.21*	0.27
Guaiacols		***25.05***	**15.99**
Guaiacol	10.98	*5.00*	3.39
Phenol, 2-methoxy-4-methyl-	12.60	*7.89*	7.33
Phenol, 4-ethyl-2-methoxy-	13.86	*3.89*	1.22
Eugenol	14.95	*1.16*	0.30
Phenol, 2-methoxy-4-propyl-	15.08	*0.12*	0.19
Vanilin	15.54	*0.68*	0.90
Phenol, 2-methoxy-4-(1-propenyl)-	15.63	*0.88*	0.23
Phenol, 2-methoxy-4-(1-propenyl)-	16.17	*3.81*	1.31
Catechols		***5.05***	**4.84**
1,2-Benzenediol, 3-methyl-	13.55	*0.77*	0.78
1,2-Benzenediol, 3-methoxy-	13.62	*0.45*	0.11
Hydroquinone	13.72	-	0.23
1,2-Benzenediol, 4-methyl-	13.96	*1.92*	1.95
3,5-Dihydroxytoluene	14.03	-	0.09
Hydroquinone, methyl-	14.70	*0.38*	0.28
1,3-Benzenediol, 4,5-dimethyl-	14.84	*0.59*	0.28
1,3-Benzenediol, 4-ethyl-	15.25	-	1.12
1,3-Benzenediol, 4-propyl-	16.44	-	-

- phenols and quaiacols remain in tar
- smaller molecules go to aqueous phase

Aplication: co-pyrolysis with PE, PP, PS



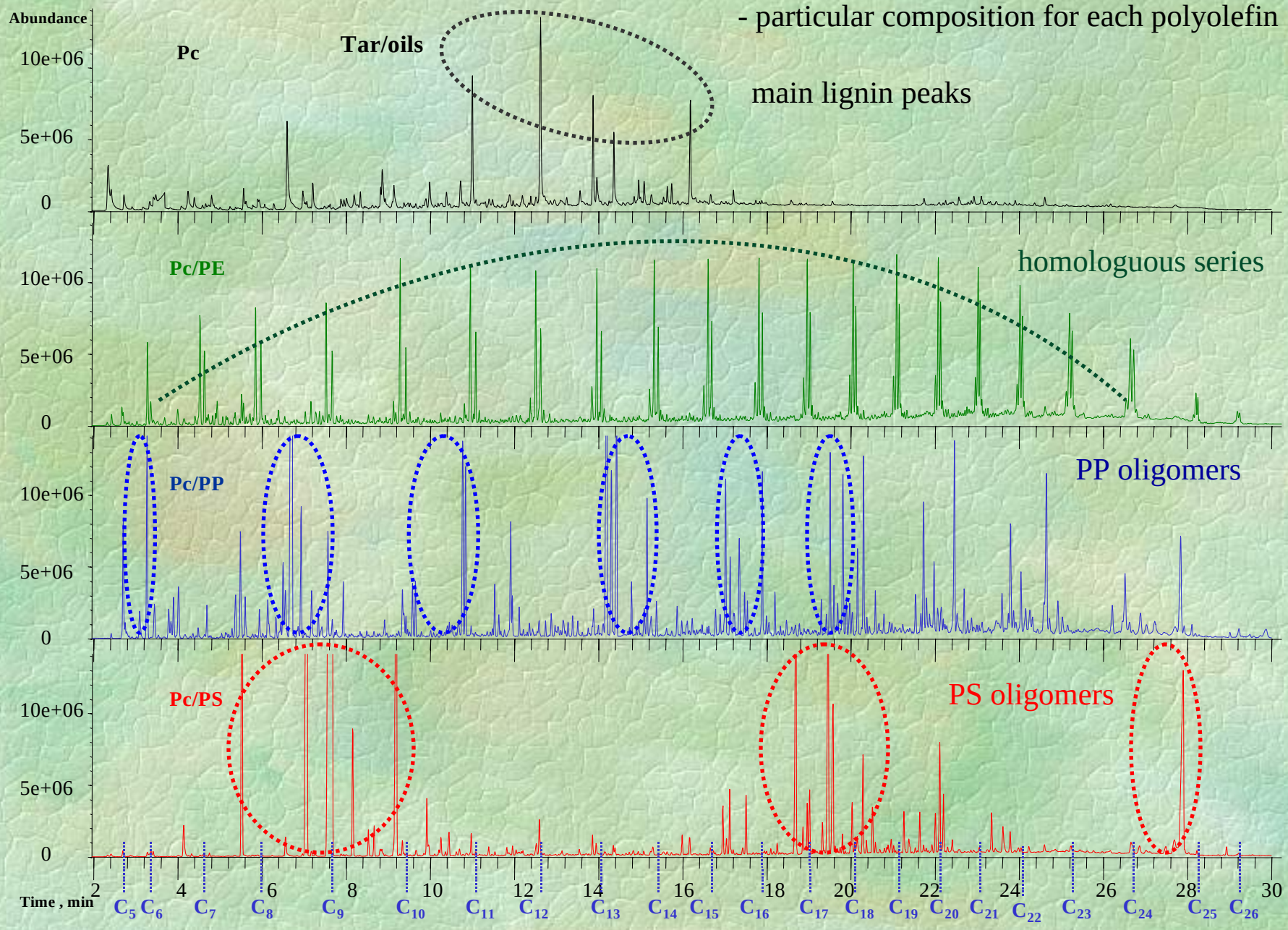
- two steps for pine cone
- one step for PE, PP and PS
- possible interactions between Pc an polyolefins due to overlapping of degradation steps

Pyrolysis mass balance

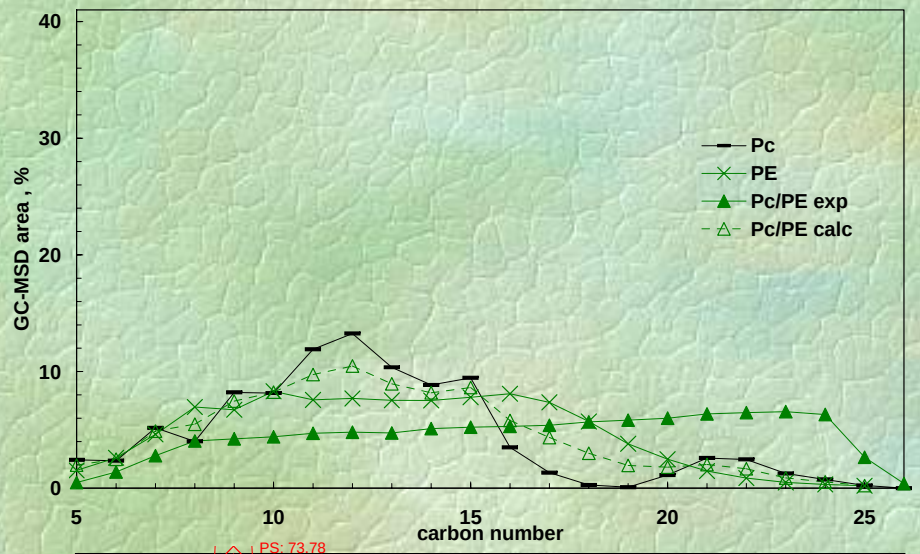
Feed	Gas	Aqueous phase	Tar/Oil	Residue
Pc	15.9	38.6	8.9	36.6
PE	14.4	-	68.2	16.8
PP	12.7	-	72.6	14.7
PS	1.0	-	85.2	13.8
Pc/PE (1/1)	16.5	18.9	45.0	19.6
Pc/PP (1/1)	16.8	18.4	45.7	19.1
Pc/PS (1/1)	8.8	17.4	52.3	21.5
Pc/PE/PP/PS (3/4/2/1)	11.3	11.9	64.1	12.7
Cell/PE/PP/PS (3/4/2/1)	21.5	14.0	54.9	9.6

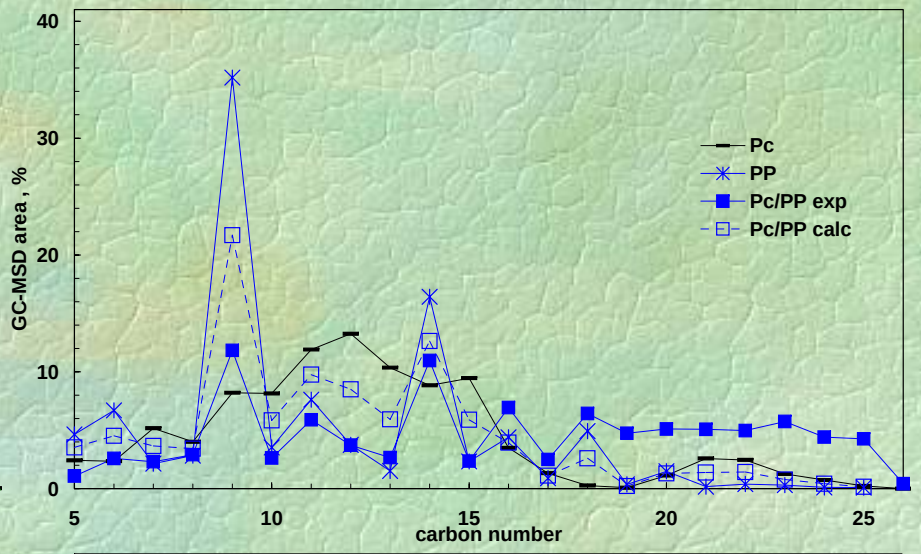
- increased gas and oils
- decreased residue
- polyolefins act as source of H
- particular behaviour for Cell

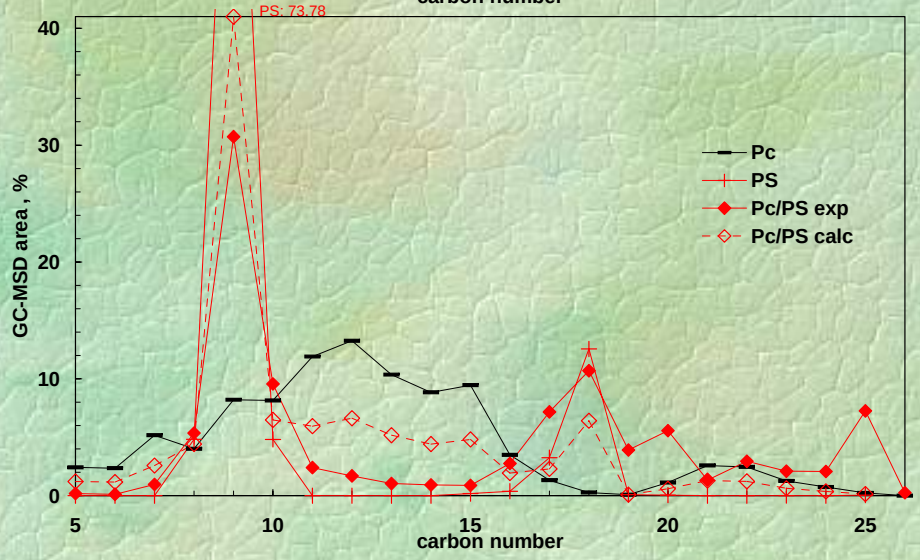
GC-MSD analysis

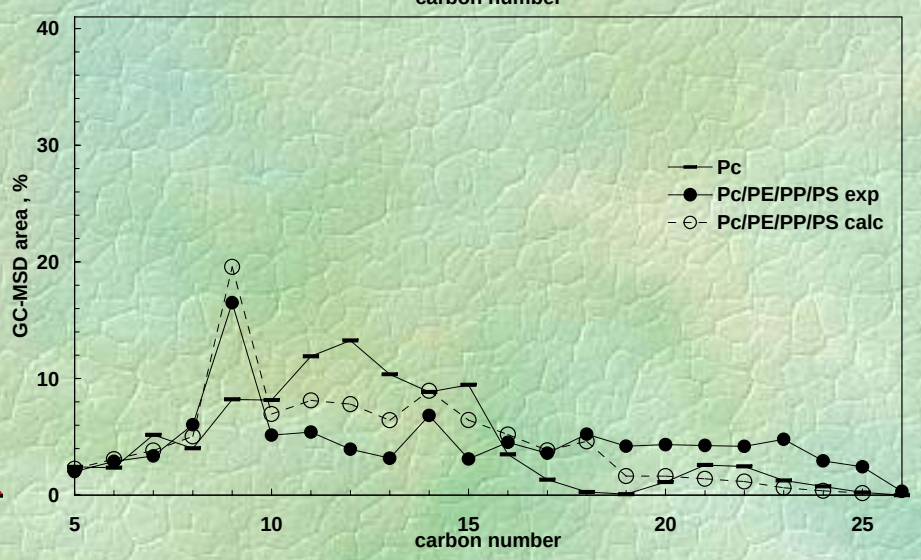


C-NP grams









- particular distribution for each pine cone / polyolefin mixture
- interactions between pine cone and polyolefins

Main compounds by GC-MSD

	Pc/PE	Pc/PP	Pc/PS	Pc/PE/PP/PS	Cell/PE/PP/PS
Alcohols	**4.64**	**3.19**	**2.61**	**4.66**	**2.25**
Methanol	3.26	2.42	1.94	3.30	0.97
Acids	**11.38**	**9.05**	**7.99**	**7.51**	**3.79**
Formic acid	0.23	0.20	-	0.20	0.27
Acetic acid	8.80	7.05	6.07	5.46	-
Propanoic acid	0.88	0.73	0.70	0.69	1.98
2-Propenoic acid	0.86	0.73	0.57	1.17	0.19
Aldehydes	**1.87**	**1.18**	**1.64**	**2.08**	**2.72**
Hydroxyacetaldehyde	0.63	0.60	0.62	0.64	1.52
2-Propenal, 2-methyl-	0.72	0.57	0.40	0.74	0.41
2-Butenal, 2-methyl-	-	-	-	-	0.27
Propanal	0.52	0.42	0.40	0.45	0.52
Benzeneacetaldehyde	-	0.18	0.25	0.25	-
Non aromatic ketones	**19.77**	**19.65**	**16.05**	**18.28**	**22.44**
Furans	**17.46**	**16.20**	**13.91**	**15.14**	**36.21**
Furan, 2-methyl-	0.09	0.09	0.08	0.09	0.10
2-Furaldehyde	0.23	0.22	0.16	0.17	0.17
2-Furancarboxaldehyde	8.17	7.32	6.45	7.27	15.35
2-Furfuryl alcohol	1.27	1.47	1.62	1.69	0.82
Furan, 2-ethyl-	0.16	0.13	0.14	0.15	
2-Acetylfuran	0.45	0.38	0.29	0.37	0.08
2(5H)-Furanone	1.20	1.01	0.91	1.19	0.70
2(5H)-Furanone, 5-methyl-	0.45	0.40	0.24	0.47	1.09
5-Methylfurfural	2.25	2.02	1.69	1.86	6.07
Hydroxymethylfurfural	1.54	1.76	1.88	1.29	11.07
5-acetoxymethyl-2-furaldehyde	0.25	0.31	0.37	0.35	0.49

	Pc/PE	Pc/PP	Pc/PS	Pc/PE/PP/PS	Cell/PE/PP/PS
Phenols	**8.75**	**11.10**	**12.96**	**12.05**	**5.51**
Phenol	1.31	1.25	0.84	1.31	-
Phenol, 2-methyl-	0.43	0.31	0.16	0.22	0.29
Phenol, 3-methyl-	0.97	0.97	0.48	0.69	0.35
Phenol, 2,4-dimethyl-	0.50	0.40	0.16	0.32	-
Phenol, 2,3-dimethyl-	0.25	0.37	-	-	-
Guaiacols	**11.83**	**11.21**	**6.96**	**5.11**	**-**
Guaiacol	4.00	3.43	2.74	2.58	-
Phenol, 2-methoxy-4-methyl-	4.52	3.49	-	-	-
Phenol, 4-ethyl-2-methoxy-	1.31	1.30	1.05	0.77	-
Eugenol	0.25	0.27	0.33	0.17	-
Phenol, 2-methoxy-4-propyl-	0.14	0.26	0.11	-	-
Vanilin	0.70	0.92	1.13	0.87	-
Phenol, 2-methoxy-4-(1-propenyl)-	0.18	0.24	0.24	-	-
Phenol, 2-methoxy-4-(1-propenyl)-	0.77	1.14	1.35	0.72	-
Catechols	**5.04**	**8.68**	**7.91**	**10.41**	**-**
1,2-Benzenediol, 3-methyl-	1.27	1.96	1.19	1.76	-
1,2-Benzenediol, 3-methoxy-	0.18	0.22	0.19	0.20	-
Hydroquinone	0.29	0.42	0.48	0.47	-
1,2-Benzenediol, 4-methyl-	2.96	4.42	3.98	4.91	-
3,5-Dihydroxytoluene	0.34	0.09	0.19	-	-
Hydroquinone, methyl-	-	0.81	-	-	-
1,3-Benzenediol, 4,5-dimethyl-	-	0.75	0.49	0.77	-
1,3-Benzenediol, 4-ethyl-	-	-	1.10	1.46	-
1,3-Benzenediol, 4-propyl-	-	0.27	0.29	0.22	-

- composition depends on system, due to interactions
- PS decresases low Mw compounds and guaiacols; increases phenols
- Cell increases furans and kerones; decreases phenols; no lignin compounds

Properties of tar/oils and of chars

	Tar/oils						Chars		
Sample	Pc	Pc/PE	Pc/PP	Pc/PS	Pc/PE/PP/PS	Cell/PE/PP/PS	Pc	Pc/PE/PP/PS	Cell/PE/PP/PS
Elemental composition,wt%									
C	23.55	81.00	84.65	80.49	81.56	80.59	70.33	79.79	93.19
H	7.68	12.94	13.17	12.53	7.94	12.09	3.98	3.60	3.45
N	0.84	0.43	0.57	0.40	0.64	0.48	0.98	0.94	0.72
S	0.14	0.02	0.06	0.04	0.05	0.02	0.08	0.07	0.06
O[a]	67.79	5.61	1.55	6.54	9.81	6.82	24.36	15.6	2.58
Water amount , wt%	66.0	0.09	0.45	0.02	0.13	0.04	-	-	-
GCV[b] , kcal/kg	n.d.	46.33	45.58	46.43	41.33	45.71	27.35	31.64	34.76

[a] by difference; [b] gross calorific value

- Pc tar: high content of water
- Pc char: lower GCV
- polyolefin oils: N and S traces
- polyolefin chars: higher GCV ; low S

Conclusions

- **Gc: suitable method for qualitative/quantitative characterisation of pyrolysis products**
- **pine cone tar: mainly lignin- derived compounds**
- **pine cone aqueous phase: mainly carbohydrates- derived compounds**
- **synergistic effect at co-pyrolysis of biomass and synthetic polymers**
- **composition of aqueous phase depends on the lignin/cellulose ratio in biomass**
- **composition of oils depends on the type of synthetic polymer**

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