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Microwave assisted pyrolysis of kraft lignin at reduce pressure in a multimode oven

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MICROWAVE ASSISTED PYROLYSIS OF KRAFT LIGNIN AT REDUCE PRESSURE IN A MULTIMODE BATCH OVEN

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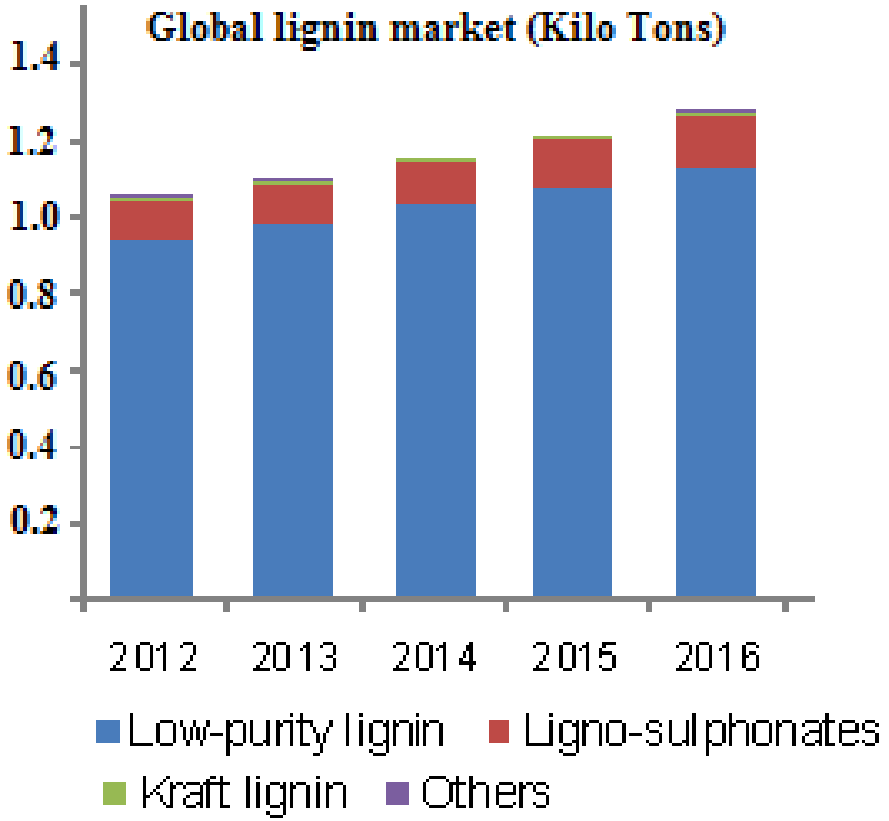
LIGNIN AND KRAFT LIGNIN



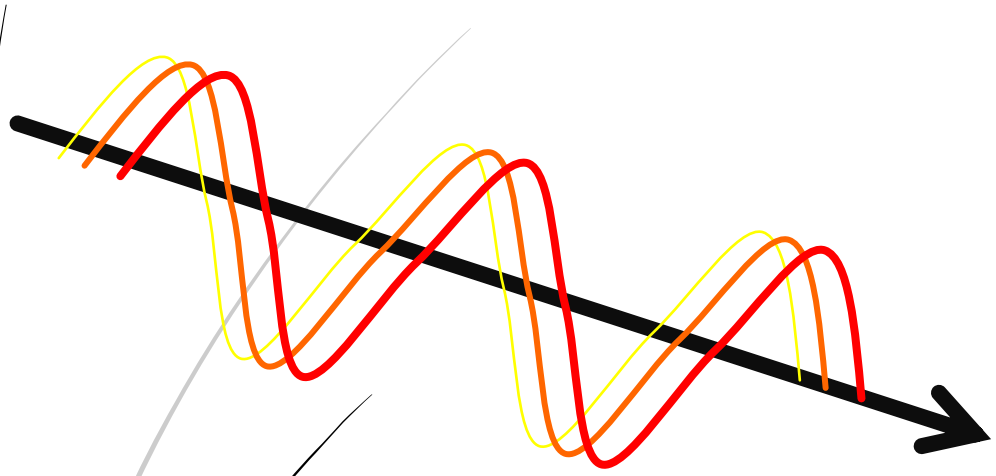
from "*Grand view research report*"

- Lignin is the second most abundant natural polymer (up to 30%).
- It is the only aromatic natural polymer.
- It is raised in economical relevance year by year.
- Kraft lignin gained neglectable global market.
- It is used like energy solid fuels, dispersant in high performance conglomerate, for water treatment and for chemicals productions

RESEARCH AIMS

- Use of Microwave based approach to process Kraft lignin at reduce pressure
- Improve the recovery of aromatics from lignin

MICROWAVES AND THEIR INTERACTION WITH MATERIALS



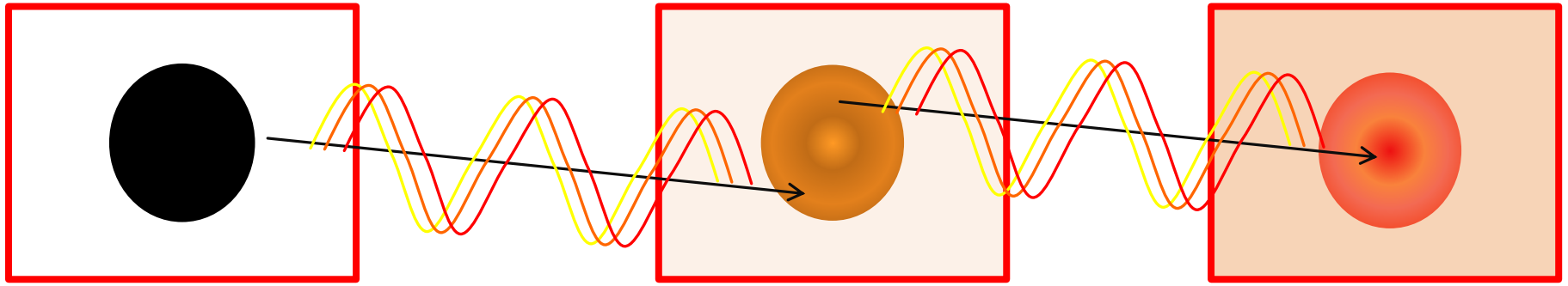
Three interaction mechanisms:

1. Dipole reorientation
2. Interfacial or Maxwell-Wagner polarization (multicomponent systems)
3. Conduction (metals and conducting materials)

The heating occurs when dipolar molecules exposed to an electromagnetic field try to rotate in phase with the alternating electric current. Resistance to this rotation on molecular level results in friction between molecules and heat is generated.

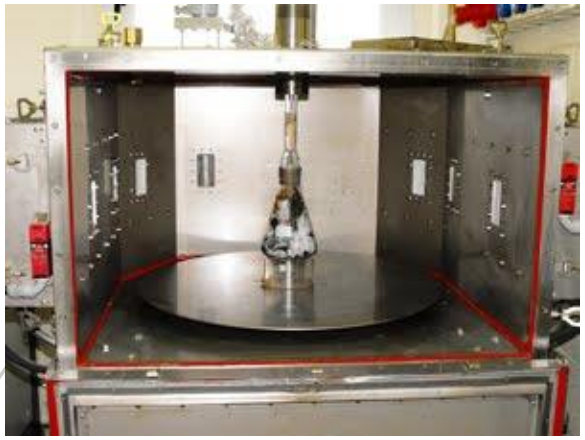
MICROWAVES AND THEIR INTERACTION WITH MATERIALS

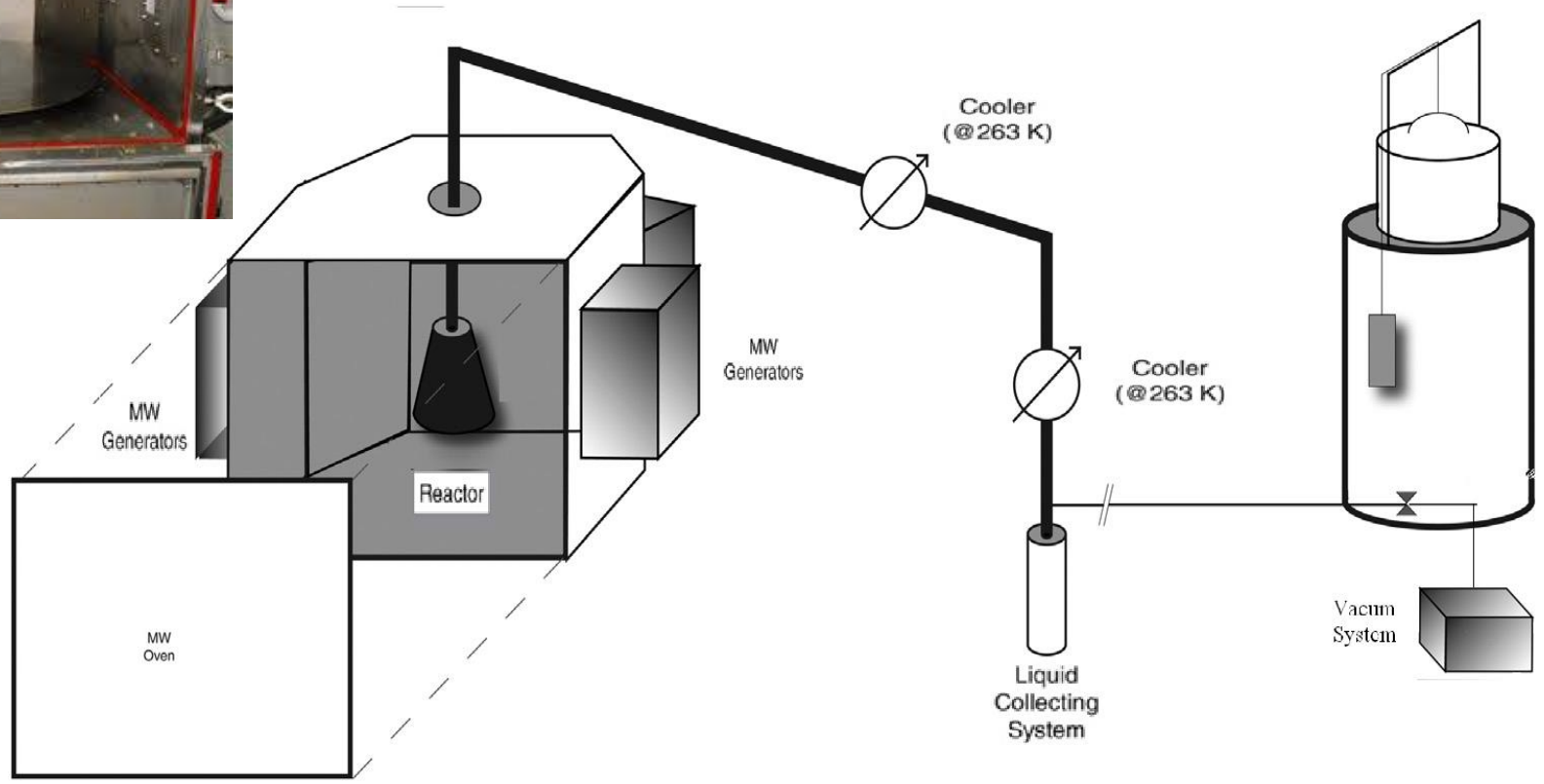
The energy absorbed is function of the intensity of electromagnetic field and the loss-factor



In dielectric multi materials MW absorption is different point by point, depending on their characteristics as MW absorber.

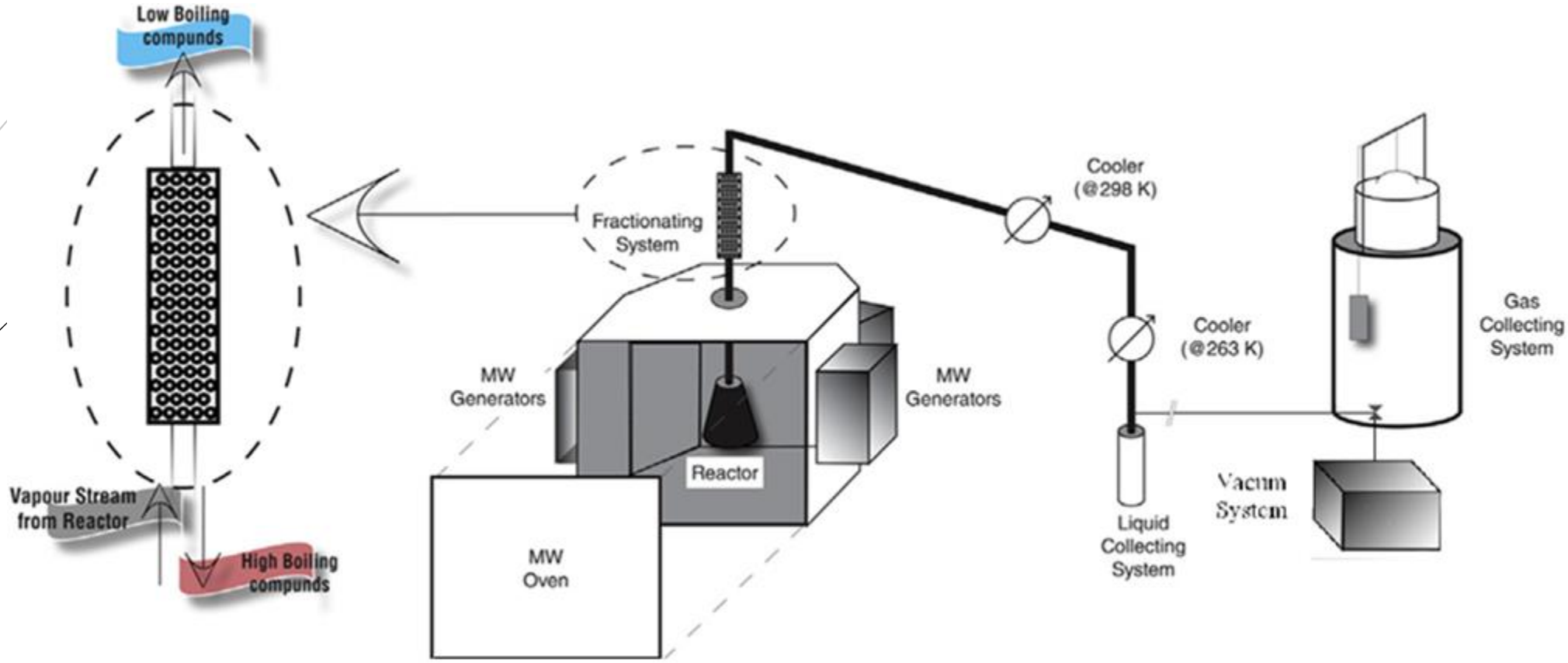
MICROWAVE OVEN PLANT: SET UP A





- A. Undri, S. Meini, L. Rosi, M. Frediani, P. Frediani, Microwave pyrolysis of polymeric materials: Waste tires treatment and characterization of the value-added products, Journal of Analytical and Applied Pyrolysis, 103 (2013) 149-158.

MICROWAVE OVEN PLANT: SET UP B

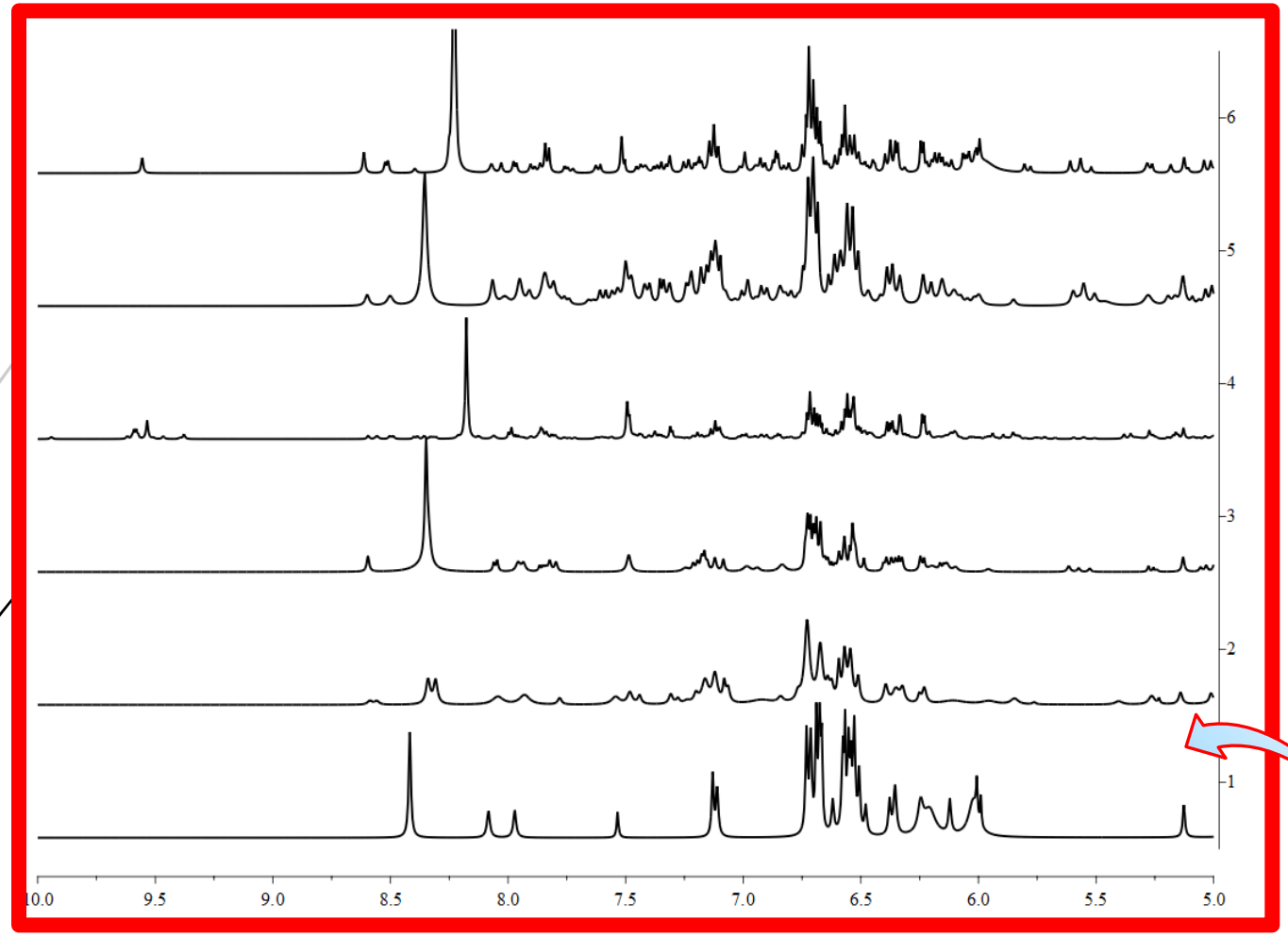


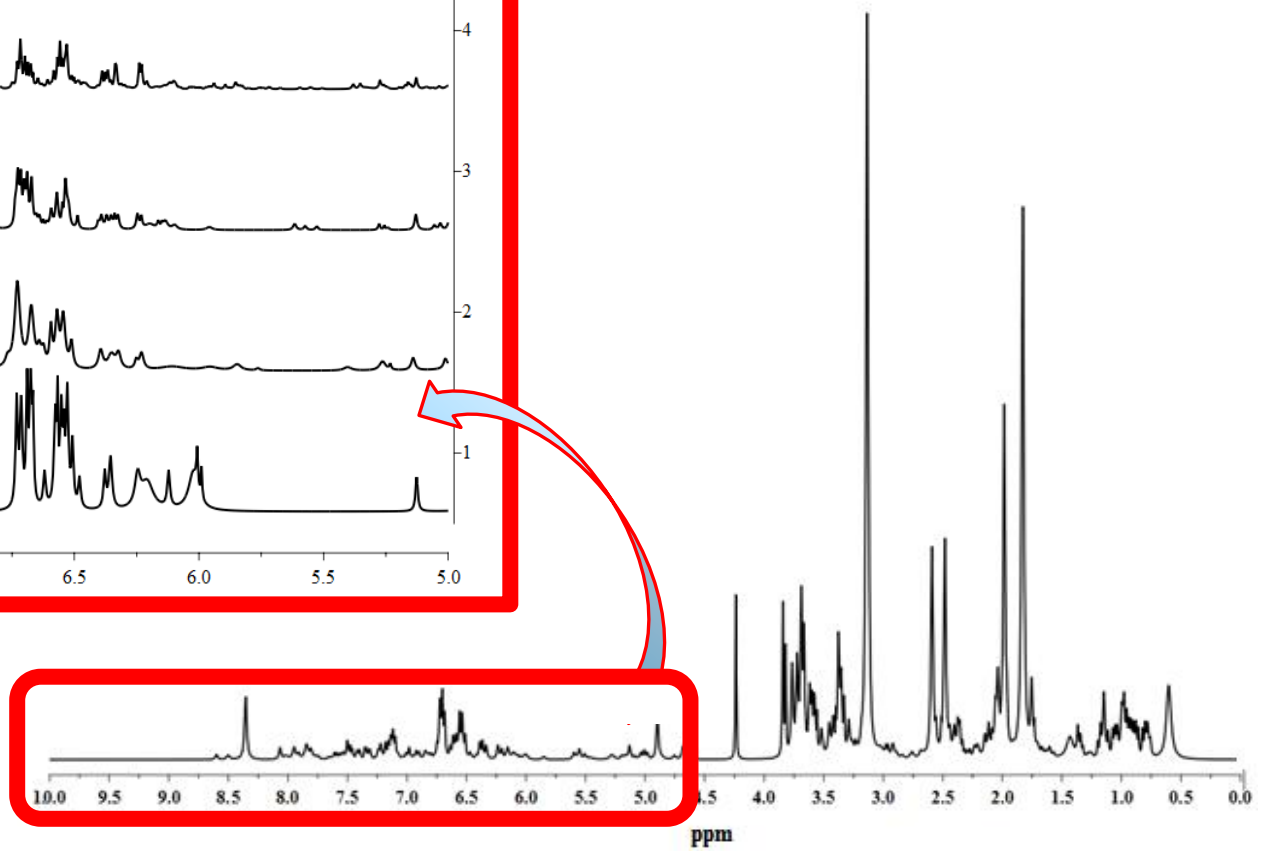
- A. Undri, L. Rosi, M. Frediani, P. Frediani, Upgraded fuel from microwave assisted pyrolysis of waste tire, Fuel, 115 (2014) 600-608.

EXPERIMENTAL CONDITIONS

	Set-up	Lignin [g]	Absorber [g]	Lignin/ Absorber	t [min]	T [K]	Pressure [bar]	Yields [wt%]		
								Bio-char	Bio-oil	Gas
ID1	A	118.8	60.0	1.98	20	723	1.0	36.8	43.6	19.5
ID2	B	100.5	50.2	2.00	16	681	1.0	47.6	26.4	26.1
ID3	A	101.2	50.6	2.00	13	638	$1.3*10^{-1}$	45.0	27.5	27.6
ID4	B	100.0	50.1	2.00	19	721	$1.3*10^{-1}$	41.4	25.5	33.1
ID5	A	100.0	50.3	1.99	9	720	$1.3*10^{-2}$	33.2	37.7	29.1
ID6	B	100.1	50.1	2.00	15	618	$1.3*10^{-2}$	58.4	27.1	14.5

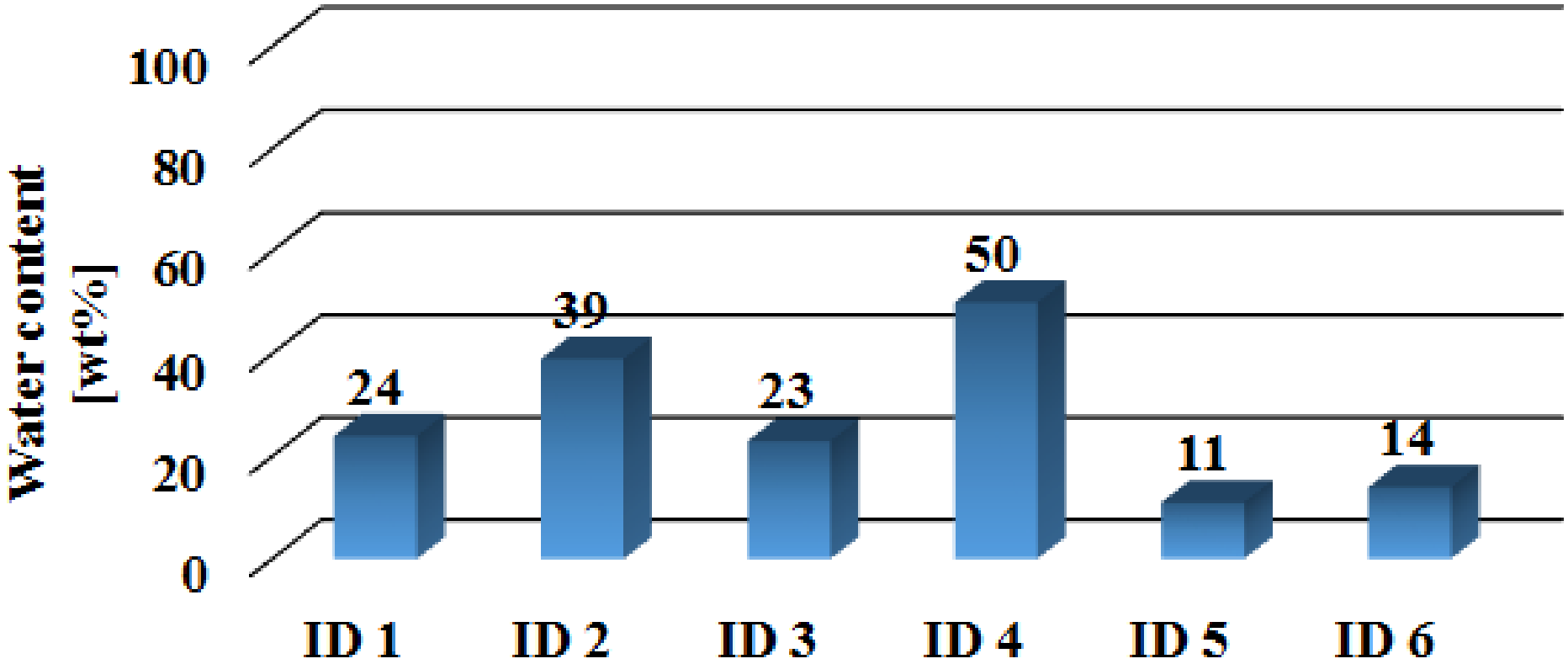
PRELIMINARY CHARACHTERIZATIONS: ^{1}H-NMR



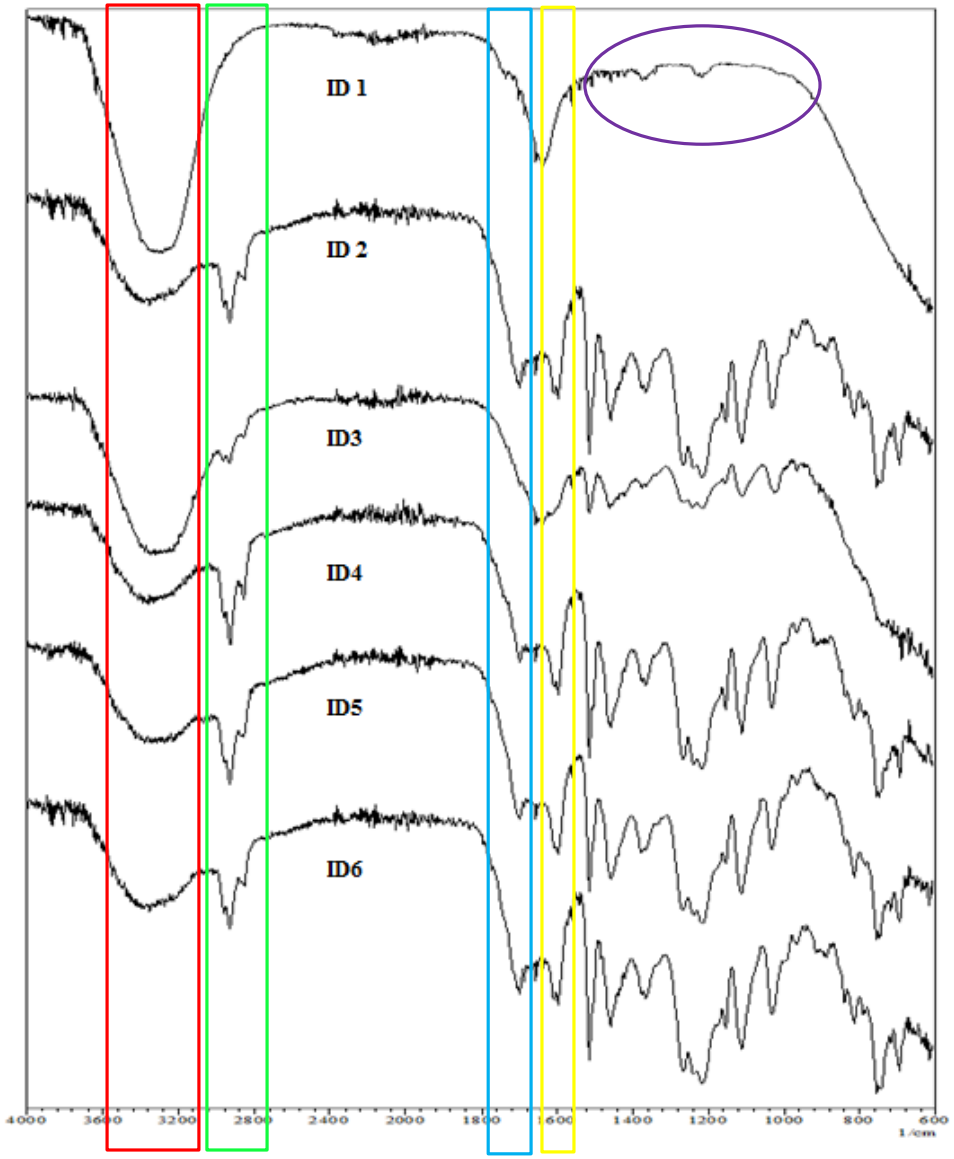


^{1}H-NMR OF ID 5 WITHOUT WATER SIGNAL

^{1}H-NMR ANALYSIS: ALTERNATIVE WAY TO WATER WATER ESTIMATIOON

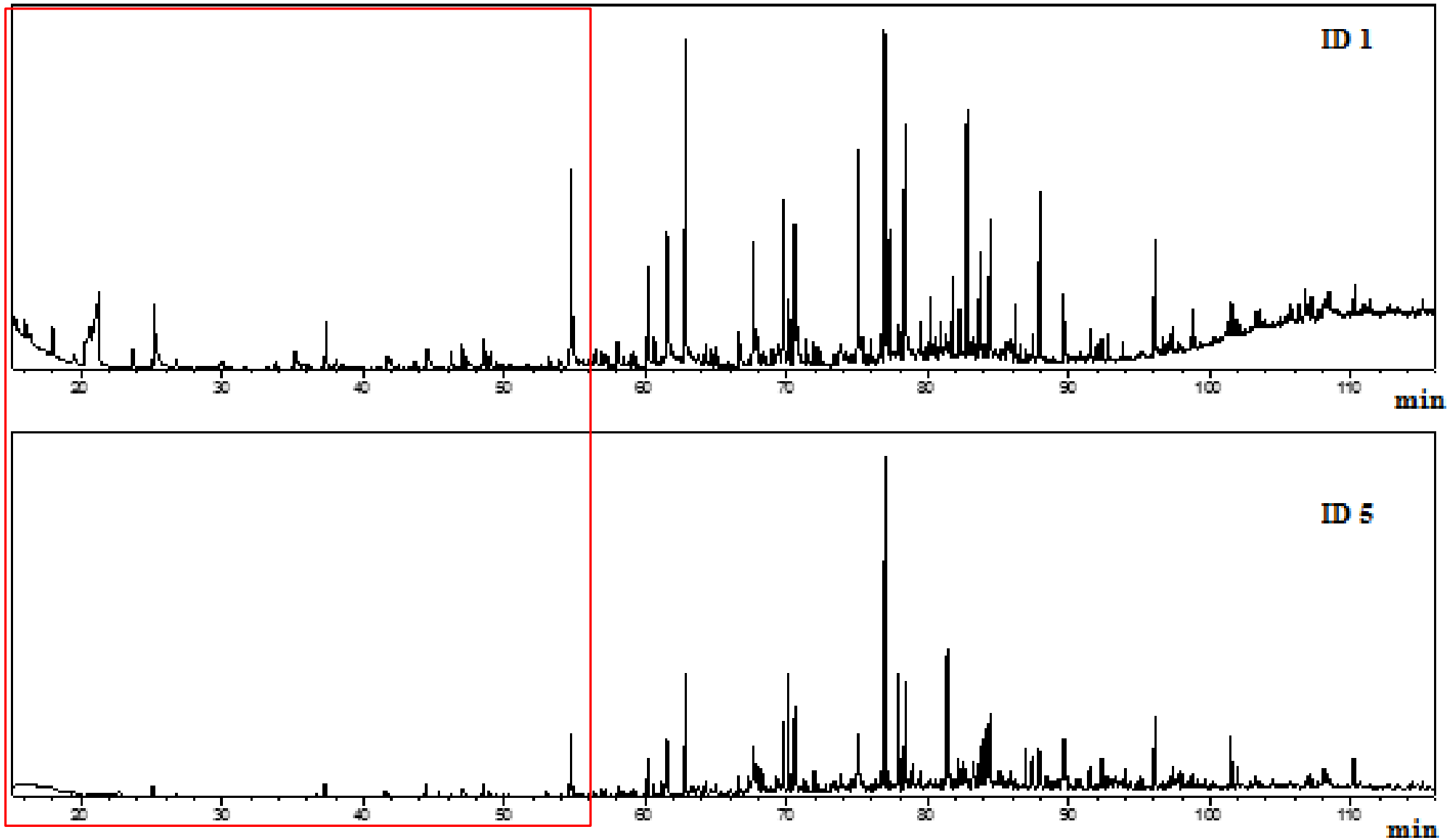


PRELIMINARY CHARACHTERIZATIONS: FT-IR ATR



- ν_{O-H} due to water and carboxylic acid (mainly acetic acid)
- ν_{C-H} due to the presence of alkyl groups (CH_3-, R-CH_2-Ar, ecc.)
- $\nu_{C=O}$ due to the presence of carbonyl and carboxylic compounds
- $\nu_{C=C}$ due to the presence of aromatic ring (ring breathing)

BIO-OILS CHALLENGE: THE COMPOSITION



CHARACTERIZATION OF BIO-OILS: QUANTITATIVE GC-MS METHOD

- ***Bio-oils contains up to several hundreds of compounds.***
- ***Difficult evaluation of concentrations of different bio-oils components.***
- ***A theorical method to calculate relative response factors (RRF) and concetrations of compounds inside the bio-oils was developed and improved for GC-MS and GC-MS/FID***
- ***Concentration was calculated using the RRF referred to DIPHENILE as standard:***

$$RRF_i = \frac{MW_i \cdot A_i \cdot C_S}{MW_S \cdot A_S \cdot C_i}$$

where i is referred to compound and s to internal standard

- ***When RRF were not available they were predicted using the contribution factors following the equation:***

$$RRF_{calc\ i} = \frac{rt_S \cdot MW_i \cdot \sum_k (P_k \cdot n_{kS}^{Z_k} + Q)}{rt_i \cdot MW_S \cdot \sum_k (P_k \cdot n_{ki}^{Z_k} + Q)}$$

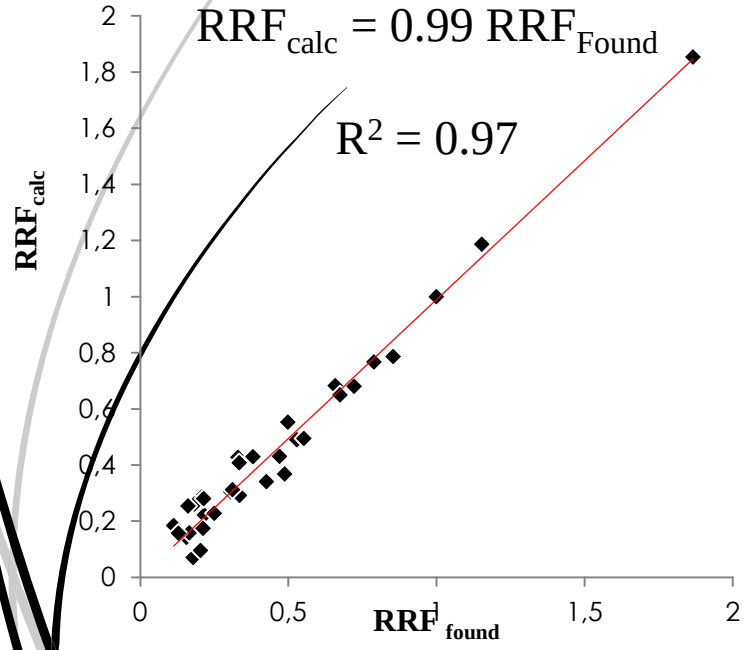
rt, retention time; MW, molecular weight; P and Z, parameters to be refined for each group; n number of atoms of carbon, hydrogen, oxygen, aromatic rings, double bonds, ketone groups, carboxylic groups (in acids, esters, anhydride), alcoholic groups, aldehydic groups, and ether groups , Q a constant.

- A. Undri, M. Abou-Zahid, C. Briens, F. Berruti, L. Rosi, M. Frediani, M. Bartoli, P. Frediani, A simple procedure for chromatographic analysis of pyrolysis bio-oils, Journal of Analytical and Applied Pyrolysis, (2015), 114, 208-221.

CHARACTERIZATION OF BIO-OILS: QUANTITATIVE GC-MS METHOD

$$RRF_{found\,i} = \frac{MW_i \cdot A_i \cdot C_S}{MW_S \cdot A_S \cdot C_i} \qquad \text{Eq.1}$$

$$RRF_{calc\,i} = \frac{rt_S \cdot MW_i \cdot \sum_k (P_k \cdot n_{kS}^{Z_k} + Q)}{rt_i \cdot MW_S \cdot \sum_k (P_k \cdot n_{ki}^{Z_k} + Q)} \qquad \text{Eq.2}$$



- M. Bartoli, L. Rosi, M. Frediani, P. Frediani, An improvement on the calculation of relative response factors for chromatographic analysis of bio-oils, Journal of European Mass Spectroscopy, submitted

Sample preparation:

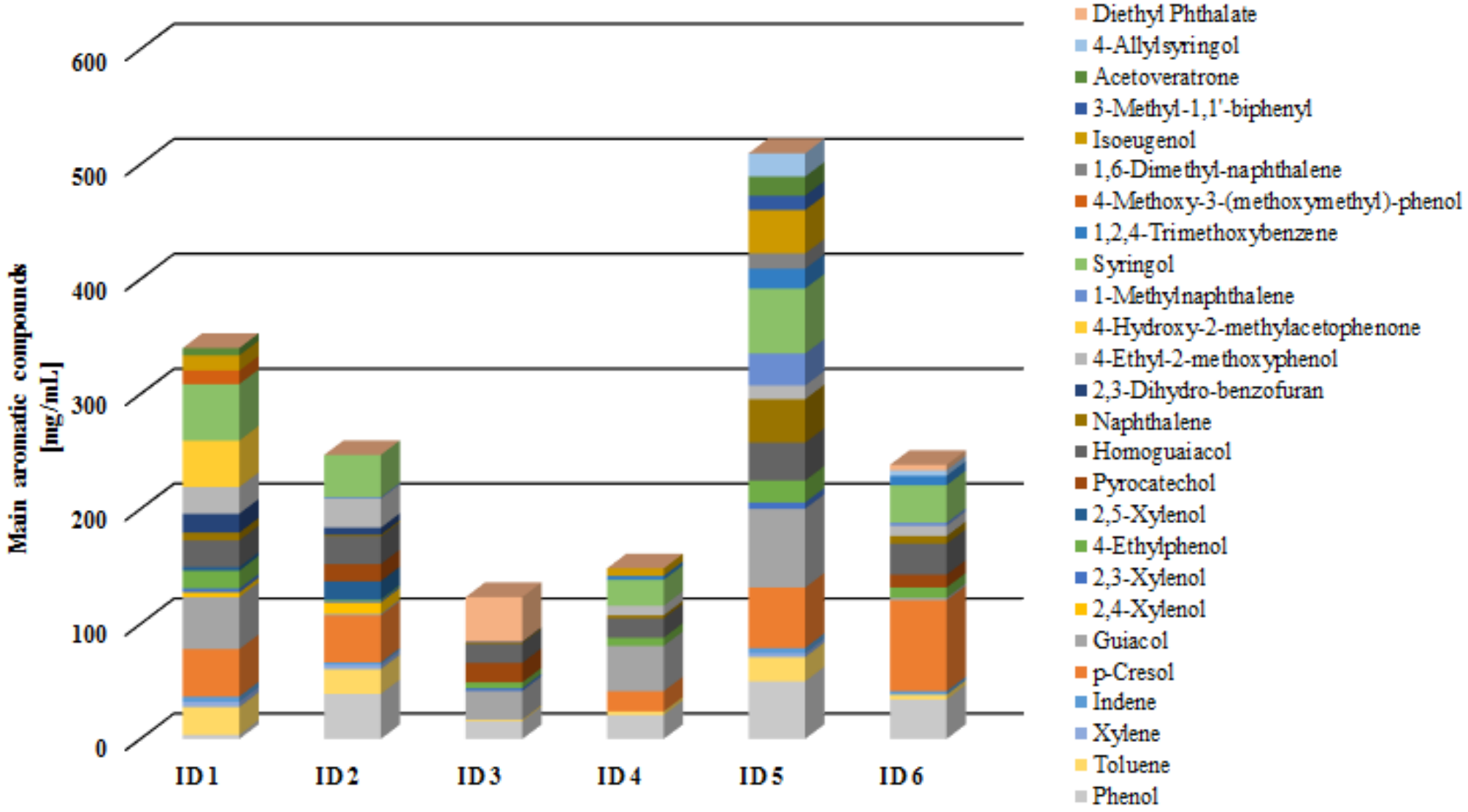
- *100 mg of bio-oil or 1 mg of standard compound in 1 mL of acetonitrile*
- *1 mg of diphenile*
- *Mix with ultrasound bath for 5 min*
- *filtered onto PTFE filter (0.4 mm)*

GC-MS set-up:

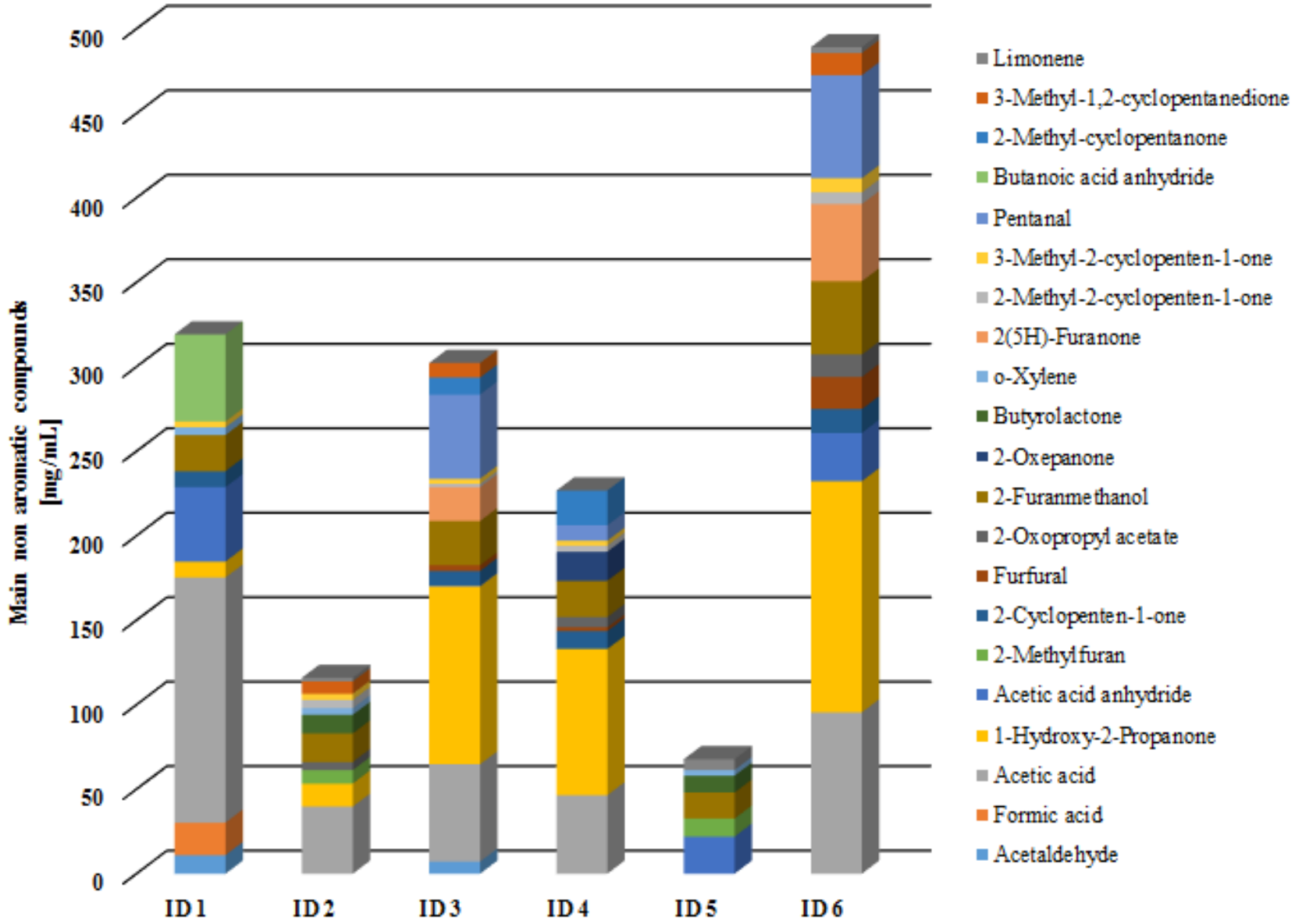
- *capillary column Petrocol™ DH 24160-U, (100 m length, 0.25 mm diameter, 0.5 µm stationary phase)*
- *detector quadrupole (EI 70 eV)*
- *split ratio 1:30*
- *298 K for 15 min then heated at 2.5 K/min up to 523 K and kept at this temperature for 15 min*

	Standard compounds	RRF found	RRF calc
1	3-Penten-2-one	0.11	0.18
2	Furfural	0.13	0.16
3	Pyridine	0.16	0.14
4	Toluene	0.16	0.25
5	3-Methyl-2-butanone	0.17	0.16
6	Acetic acid	0.18	0.07
7	2.4-Pentandiol	0.18	0.26
8	3.3-Dimethyl-2-butanol	0.19	0.26
9	Butyraldehyde	0.20	0.10
10	Valerolactone	0.21	0.29
11	2-Pentanone	0.21	0.17
12	Anilin	0.21	0.28
13	p-Benzoquinon	0.22	0.22
14	Cyclopentanol	0.25	0.23
15	Salicylaldehyde	0.31	0.30
16	Cyclohexanone	0.31	0.31
17	1-Hydroxy-1-methylcyclohexane	0.33	0.43
18	Vanillin	0.33	0.41
19	Phenol	0.34	0.29
20	Sesamol	0.38	0.43
21	Guaiacol	0.43	0.34
22	Acetophenone	0.47	0.43
23	p-Xylene	0.49	0.37
24	Cinnamaldehyde	0.50	0.55
25	1,3,5-Trimethylbenzene	0.53	0.49
26	7-Methyloctadiene	0.55	0.49
27	(-) Carvone	0.66	0.69
28	Benzilidenaceton	0.66	0.68
29	4-Phenyl-2-butanone	0.67	0.65
30	4-Phenyl-2-butanol	0.72	0.68
31	Menthol	0.79	0.77
32	Endo (-) borneol	0.85	0.79
33	2.6-Ditertbutyl-4-methylphenol	1.15	1.19
34	Phenantrene	1.82	1.85

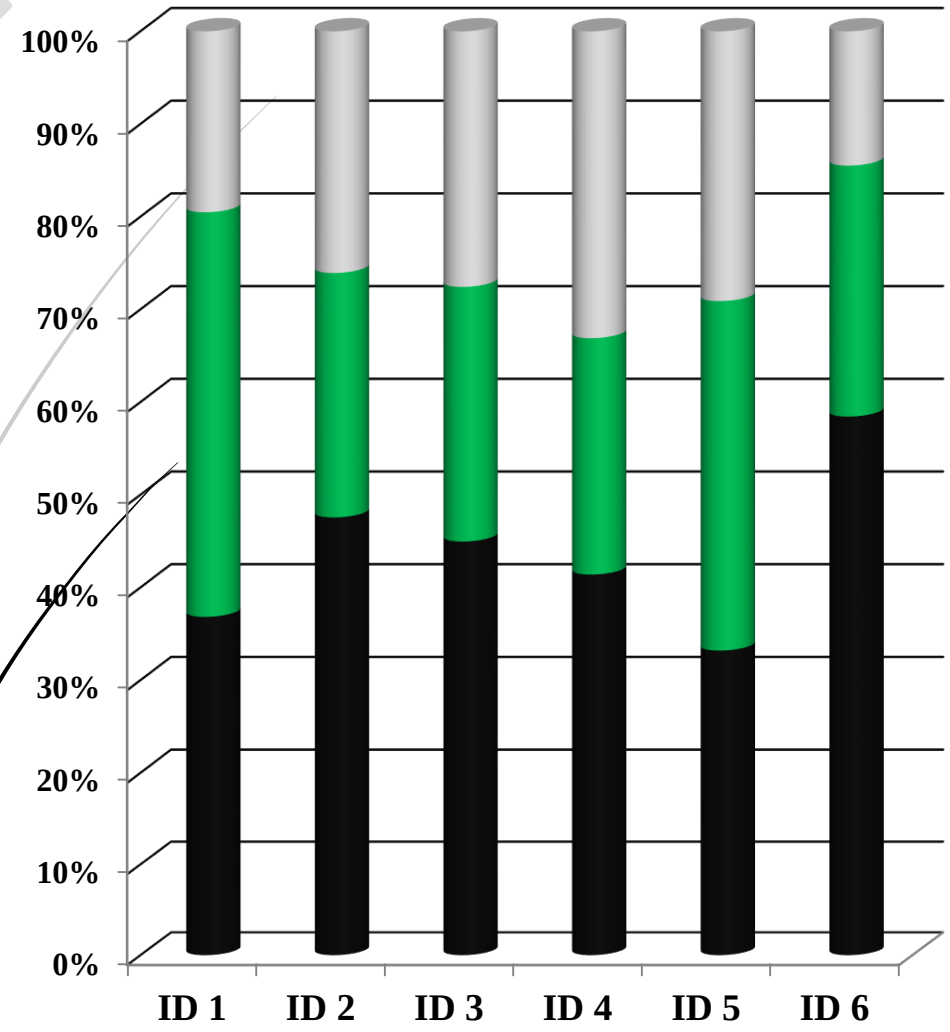
BIO-OILS CHALLENGE: THE COMPOSITION



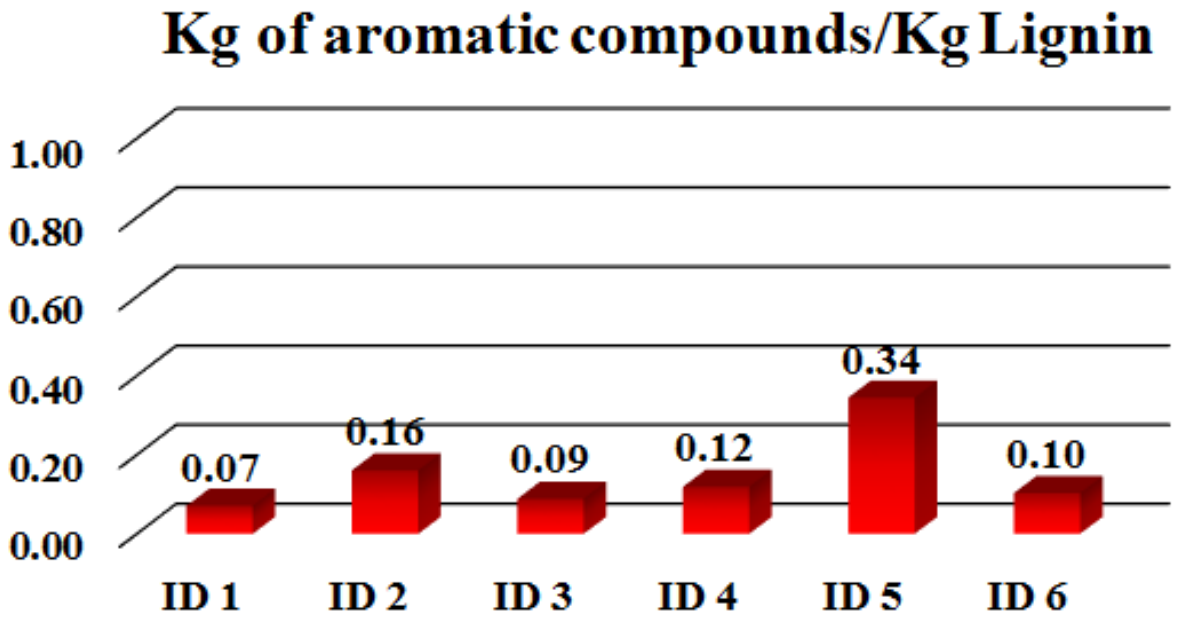
BIO-OILS CHALLENGE: THE COMPOSITION



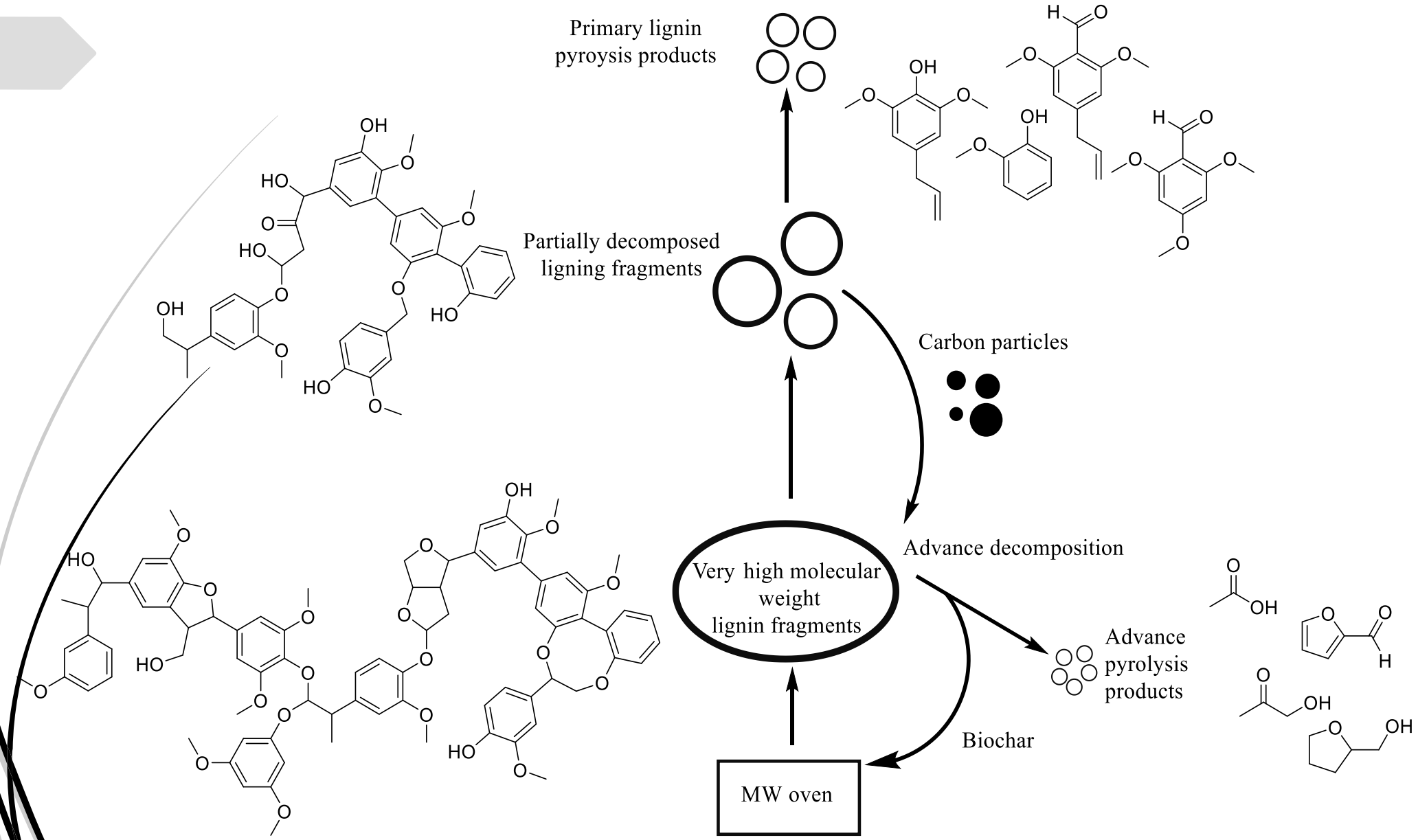
BIO-OILS FROM LIGNIN: RESIDENCE TIME EFFECT



Gas fraction
Liquid Fraction
Biochar



BIO-OILS FROM LIGNIN: CHEMICAL PATHWAYS



CONCLUSIONS

- **Bio-oils obtained were dark brown liquids and showed a low viscosity and density (close to 1cP and 1 g/mL respectively).**
- **MAP was carried out in 9 min.**
- **Maximum yield (37%) was obtained at residual pressure of 0.013 kPa with set-up A.**
- **and at the same pressure with fractionating when process was carried out in 9 min. Analysis showed the presence multisubstituited aromatic ring and few light hydrocarbons/organic acids from advanced thermal degradation of lignin structure. A degradation mechanism was proposed to explain the result observed**

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…ANY QUESTIONS?