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Bio-oils from microwave assisted pyrolysis of cellulose using a multi mode batch reactor

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MICROWAVE ASSISTED PYROLYSIS OF α-CELLULOSE IN A MULTIMODE BATCH OVEN

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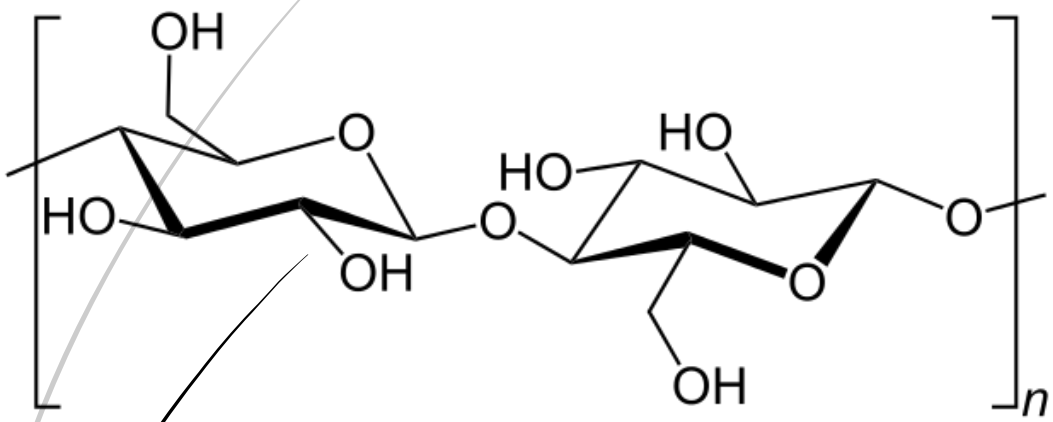
CELLULOSE HIGHLIGHTS



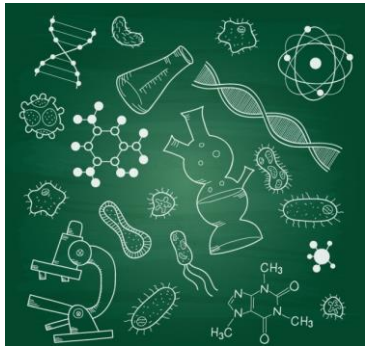
- CELLULOSE IS THE MOST ABUNDANT NATURAL POLYMER
- IT COMPOSES ABOUT THE 35-45% OF LIGNOCELLULOSIC MATERIALS
- IT IS GENERALLY COMPOSED BY 3000-5000 GLUCOSE UNITS BONDED EACH OTHER THROUGH β 1-4 BOND
-

MAIN USES OF CELLULOSE

- ***PAPER INDUSTRY***
- ***TEXTILES PRODUCTION***
- ***FILLER FOR POLYMERIC MATERIALS AND DRUGS***
- ***EXPLOSIVES***

FROM CELLULOSE TO CHEMICALS: ROUTES AND TECHNOLOGIES

SUGAR AND SUGAR DERIVATIVES RECOVERY



❖ **BIOTRANSFORMATION**

❖ **CHEMICAL TREATMENTS**

❖ **THERMOCHEMICAL APPROACHES**

PYROLYSIS

- ❖ TORREFACTION
- ❖ SLOW PYROLYSIS
- ❖ FAST PYROLYSIS
- ❖ ULTRAFAST PYROLYSIS
- ❖ PLASMA INDUCED PYROLYSIS
- ❖ MICROWAVE ASSISTED PYROLYSIS (MAP)

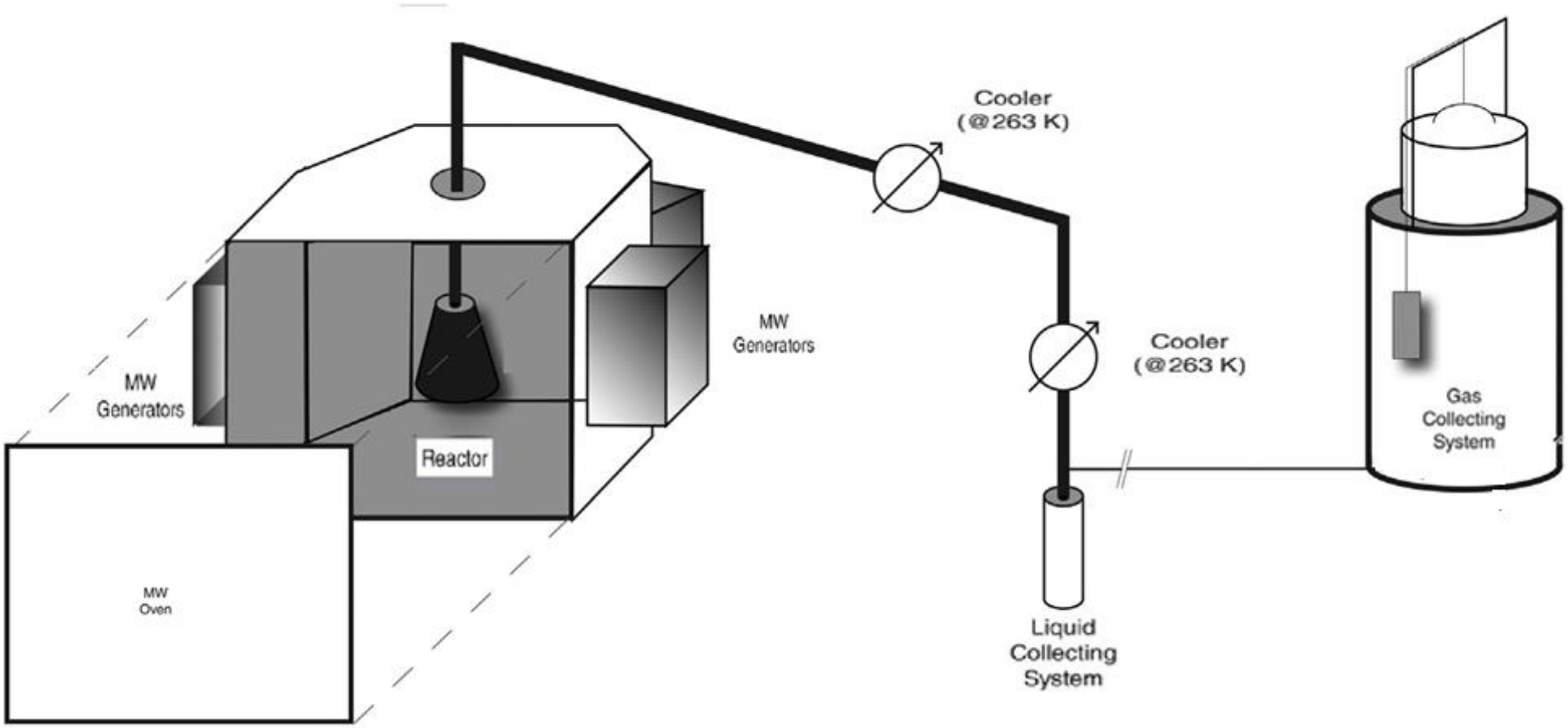
MICROWAVE OVEN PLANT: TEMPERATURE MEASUMERMENT

Thermocouples	Interact with MW, no suited
IR Thermometer	Only surface/gas temperature
Fiber Optic Thermometer	Only a spot point temperature
Estimation	Correlation with silicon oil with a volume similar to the sample
Chemical probe	Formation of compounds stable in specific temperature range

- 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.

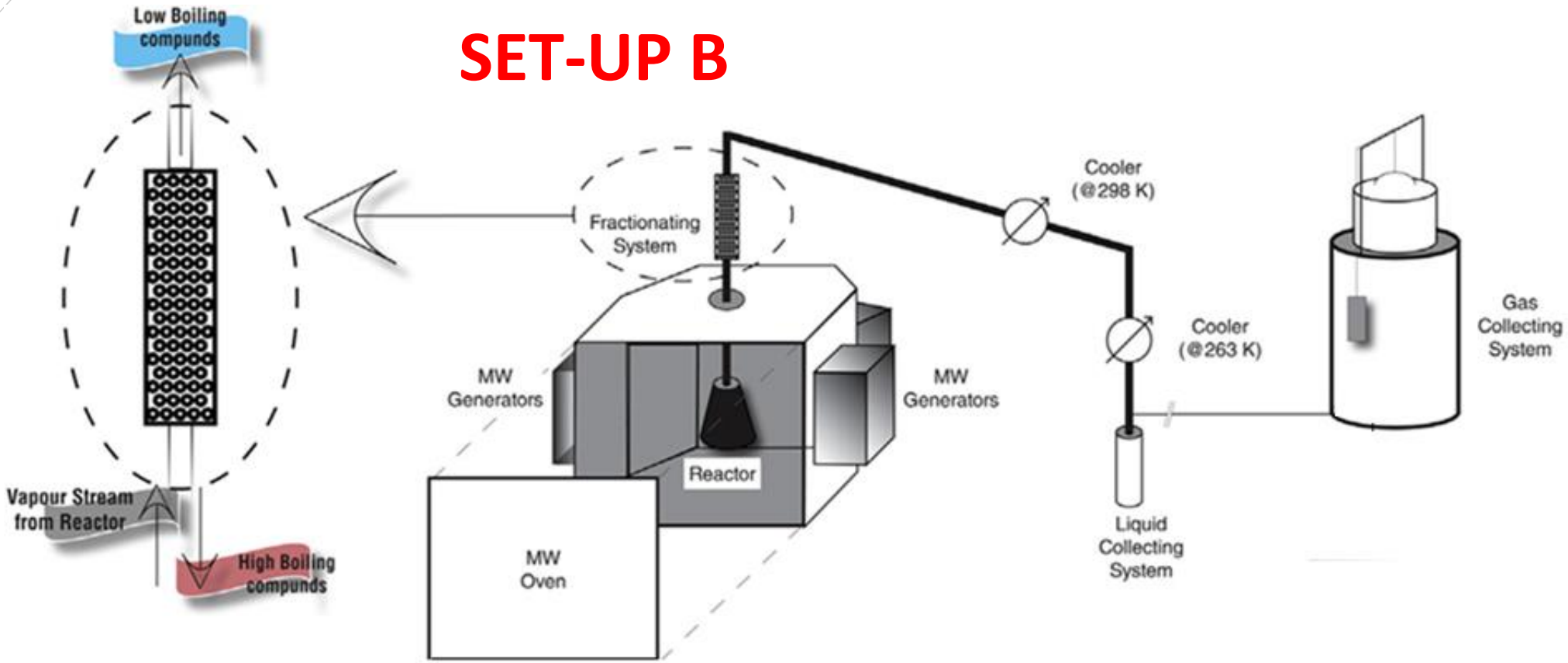
THE UNIT : SET-UPS

SET-UP A

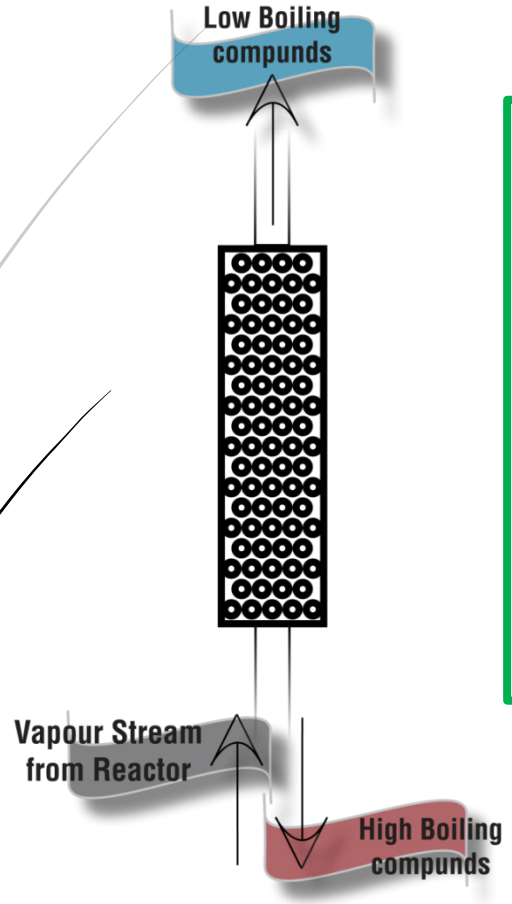


THE UNIT : SET-UPS

SET-UP B



THE UNIT : INSIDE THE SET-UP B



Fractionating system is a distillation apparatus

- ***Avoids heavy mass transportation***
- ***Avoids particles transportation***
- ***Reduces «mist» formation***
- ***Increases the pyrolysis efficiency***

- Frediani, P.; Frediani, M.; P.; Rosi, L.; Undri, A.; Occhialini, S.; Meini, S.; WO/2012/110991 A1.
- Frediani, P.; Frediani, M.; Rosi, L; Undri, A.; Occhialini, S.; WO/2012/110990 A1.

INSIDE THE EXPERIMENTS: SET-UPS & YIELDS

	Set-up	Time [min]	Power [KW]	Absorber		α-Cellulose [g]	α-Cellulose /Absorber (wt/wt)	T [K][a]	Products (%)		
				Type	Dissipation factor				Bio-char	Bio-oil	Gas
ID1	A	20	3	Carbon	0.57-0.80	100.2	2.0	723	15.7	32.6	51.7
ID2	A	33	3	Fe	2.70	100.2	2.0	702	27.2	37.0	35.8
ID3	B	20	3	Carbon	0.57-0.80	100.0	2.0	745	16.2	30.0	53.8
ID4	B	37	3	Fe	2.70	100.2	2.0	681	23.6	37.6	38.8
ID5	A	40	3	SiC	5.15	102.0	2.0	659	58.3	29.9	11.8
ID6	A	33	3	SiO_2	0.40	99.9	1.9	481	62.9	35.1	2.0
ID7	A	32	3	Al_2O_3	0.86	100.6	2.0	455	64.1	32.9	3.0
ID8	A	18	3	Graphite	0.57-0.80	149.6	2.1	532	26.7	28.5	44.7

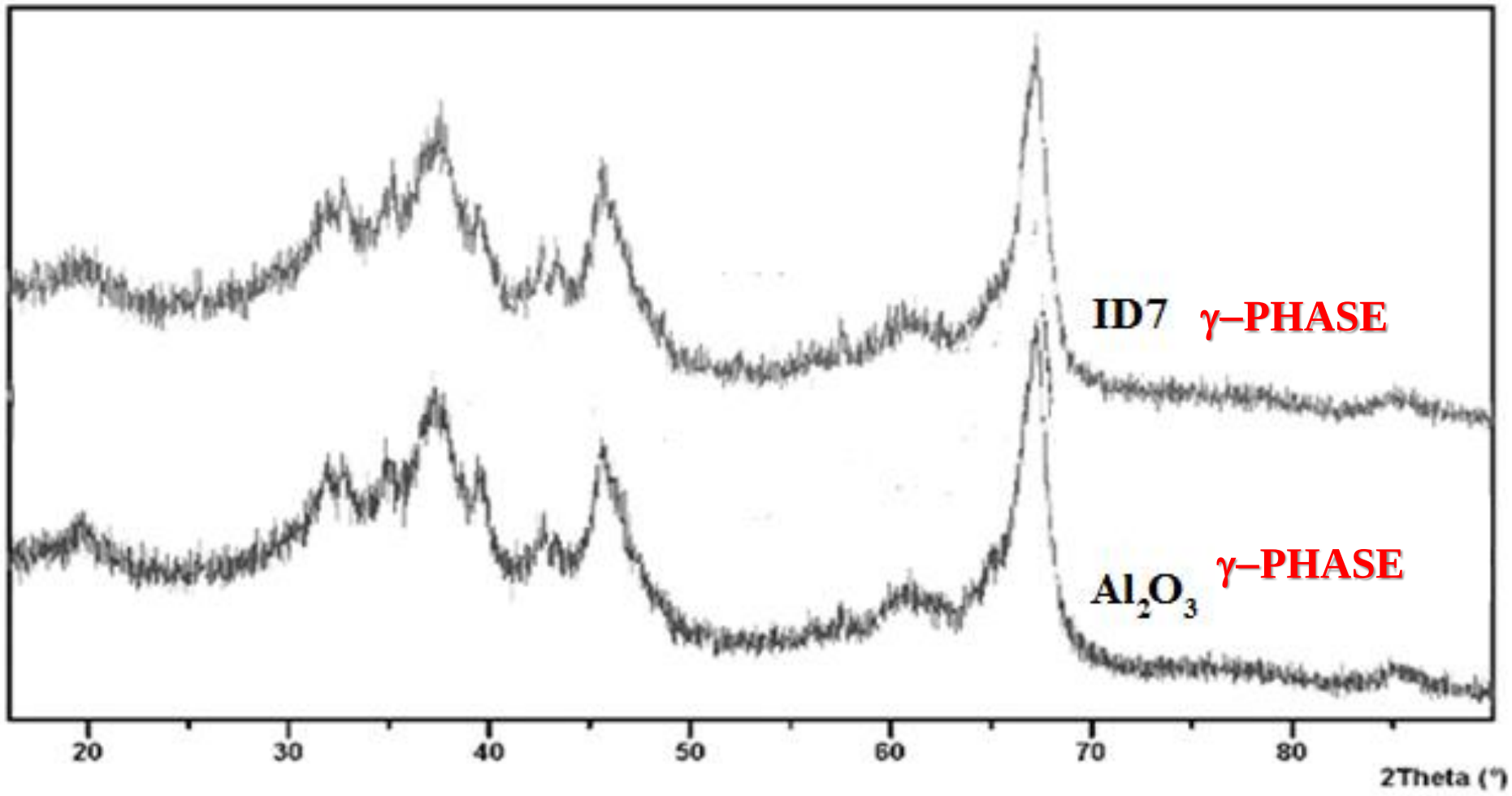
BIO-CHAR: A LOOK TO THE SOLID FRACTION

	Ultimate Analysis[a] (%)			*O/C*	*H/C*	EHC
	C	*H*	*O*[b]	*molar ratio*	*molar ratio*	[MJ/Kg]
ID1	84.7	1.4	13.9	0.1	0.02	29.6
ID2	79.8	1.4	18.8	0.2	0.02	27.9
ID3	88.5	0.6	10.9	0.1	>0.01	30.9
ID4	79.0	0.2	20.8	0.2	>0.01	27.6
ID5	78.3	0.6	21.1	0.2	0.01	27.4
ID6	74.1	1.8	24.1	0.3	0.02	25.9
ID7	74.3	1.2	24.5	0.3	0.01	26.0
ID8	83.5	1.6	14.9	0.2	0.02	29.2

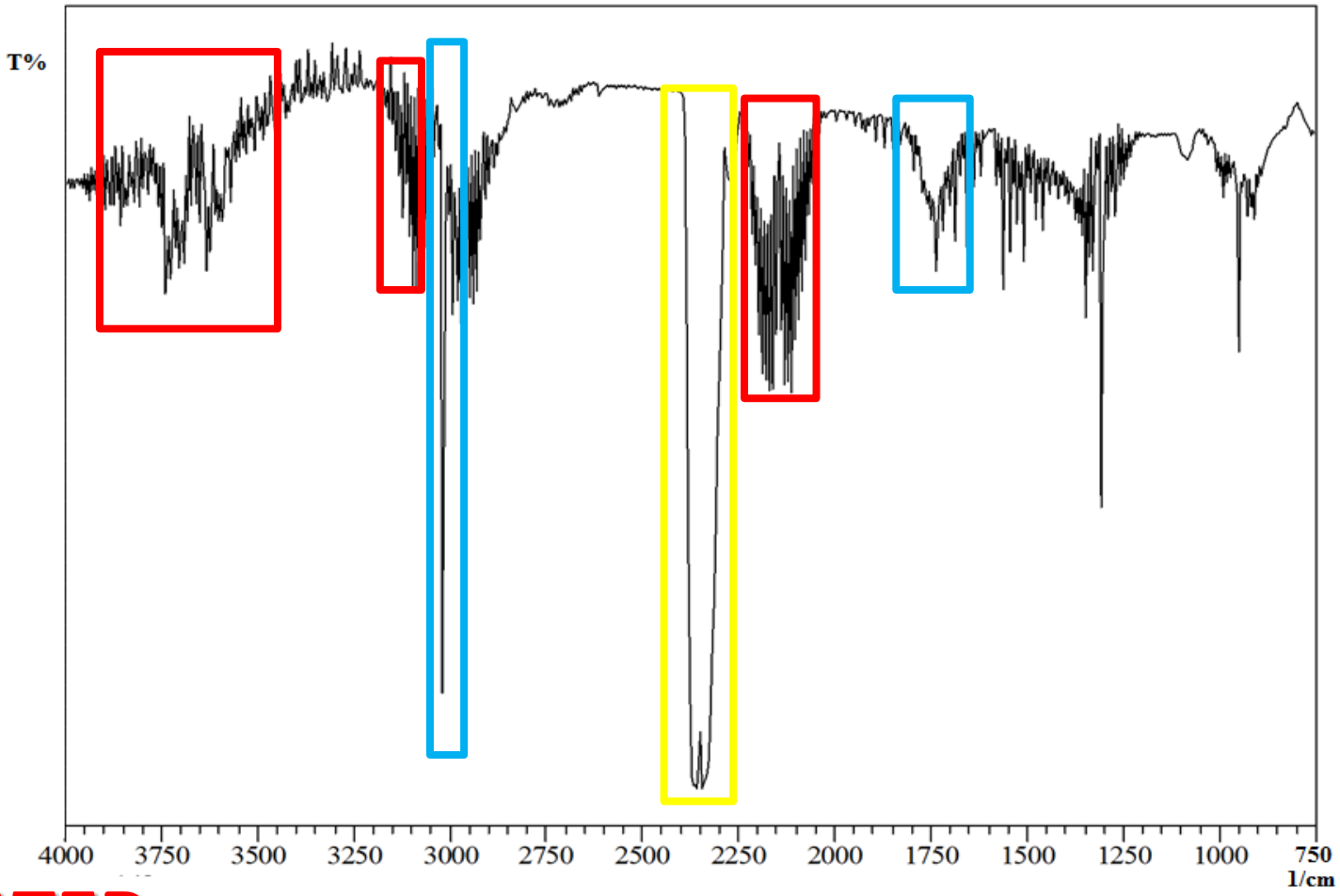
- **High content of carbon, up to 74%**
- **O/C and H/C are compatible with their use like solid fuel**

EHC ≈ carbon from MAP of plastic materials

SOLID RESIDUE: AN ALTERNATIVE TEMPERATURE MEASUREMENT

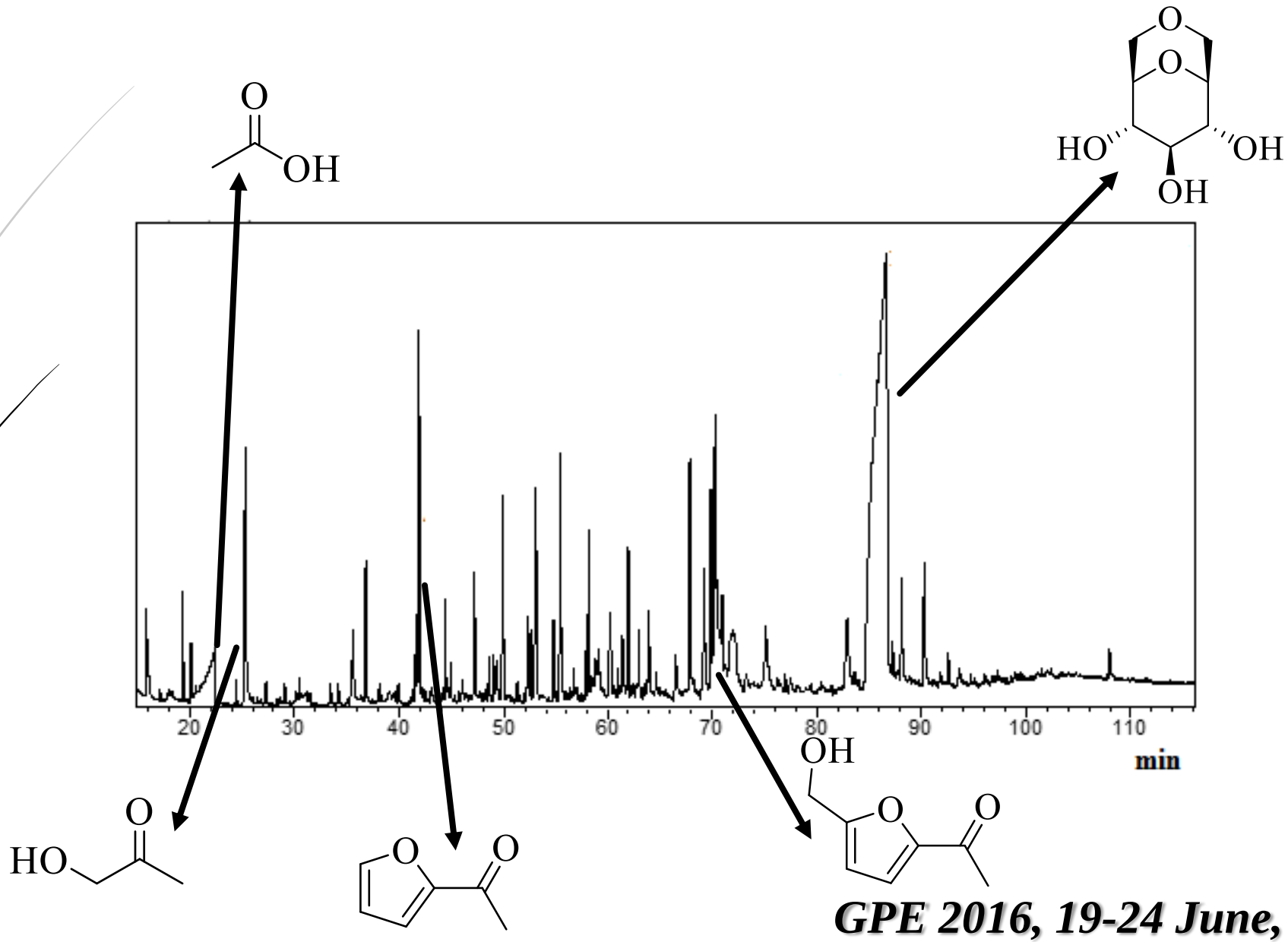


GAS FRACTION: FT-IR ANALYSIS

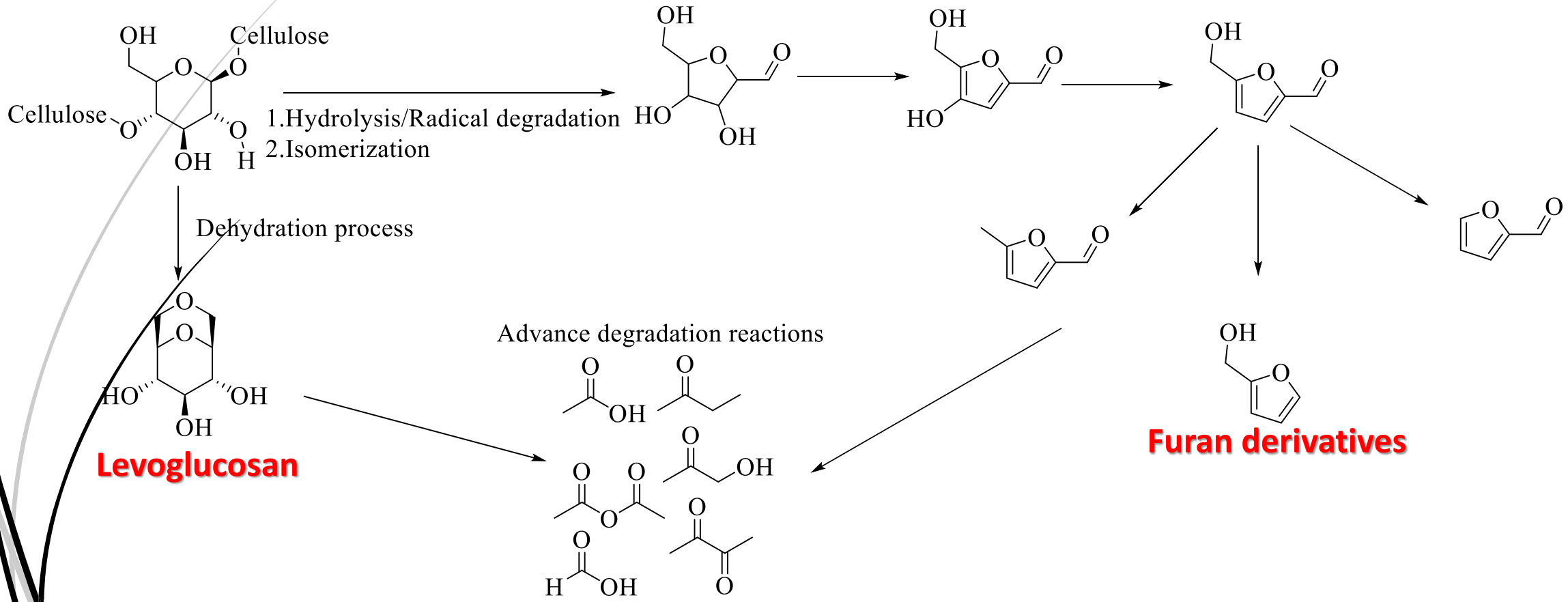


- WATER
- CO_2
- LIGHT ORGANIC MOLECULES

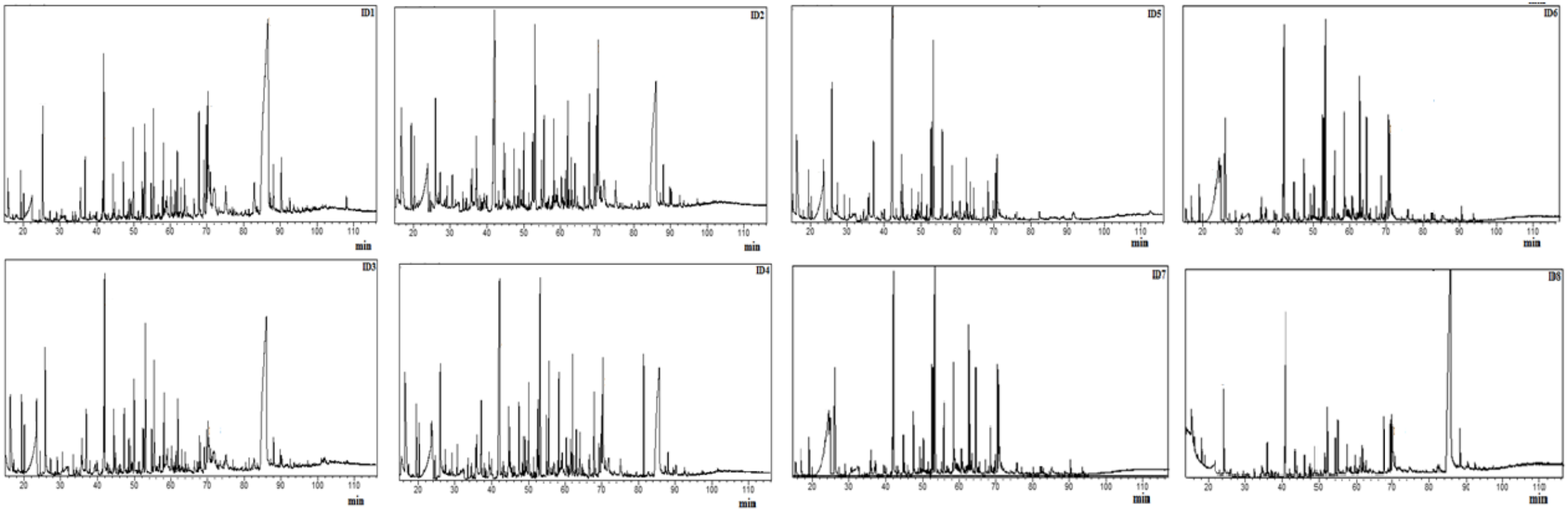
BIO-OILS CHARCTERIZATION : GC-MS APPROACH



BIO-OILS CHARCTERIZATION : A LOOK TO CELLULOSE THERMOCHEMICAL DEGRADATION PROCESS



BIO-OILS CHARCTERIZATION : GC-MS APPROACH

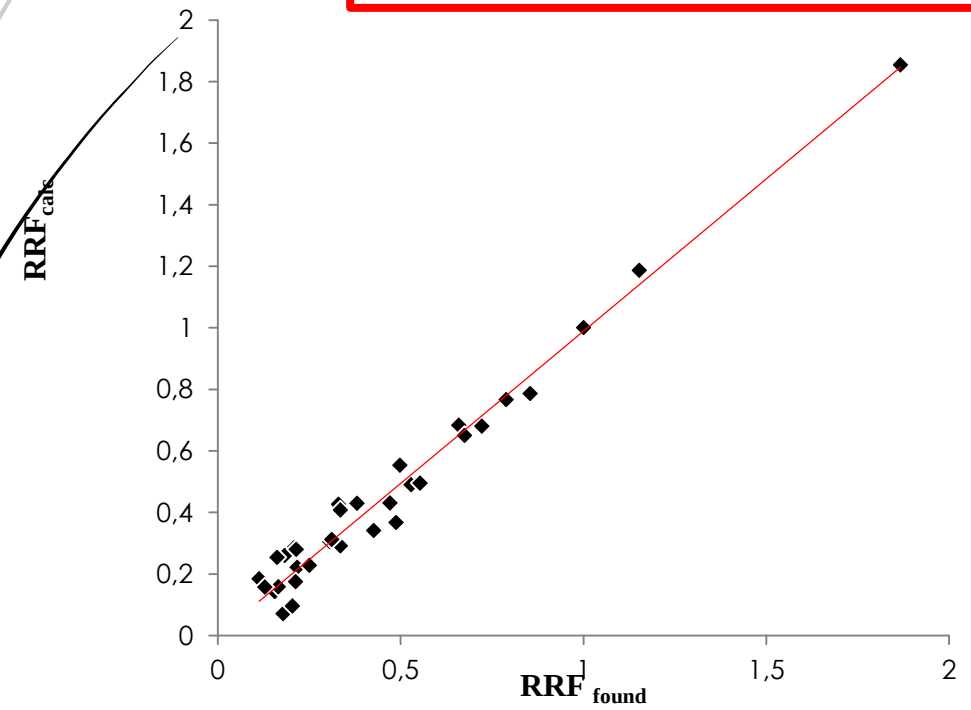


MICROWAVE ASSITED PYROLYSIS: CHARACTERIZATION OF LIQUID FRACTIONS

✓ *QUANTITATIVE GC-MS METHOD DEVELOPMENT*

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

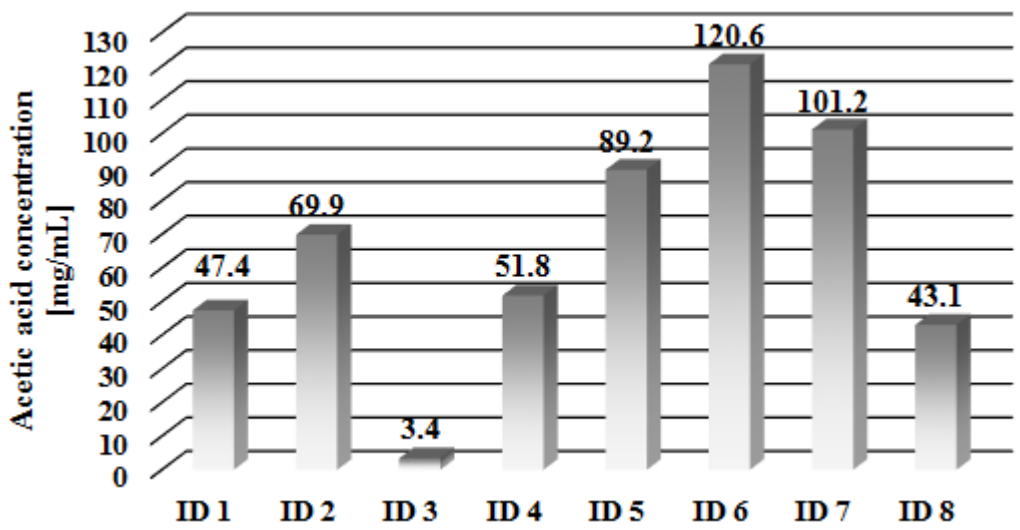
$$RRF_{calc\,i} = \frac{rt_S \cdot MW_i \cdot \sum_k (P_k \cdot n_{kS}^{z_k} + Q)}{rt_i \cdot MW_S \cdot \sum_k (P_k \cdot n_{ki}^{z_k} + Q)} \qquad \text{Eq.2}$$

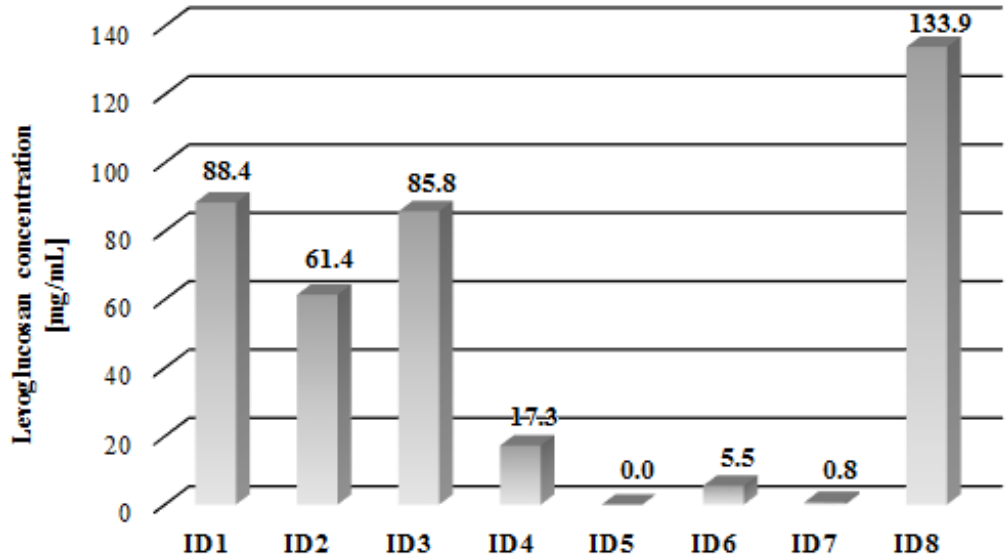


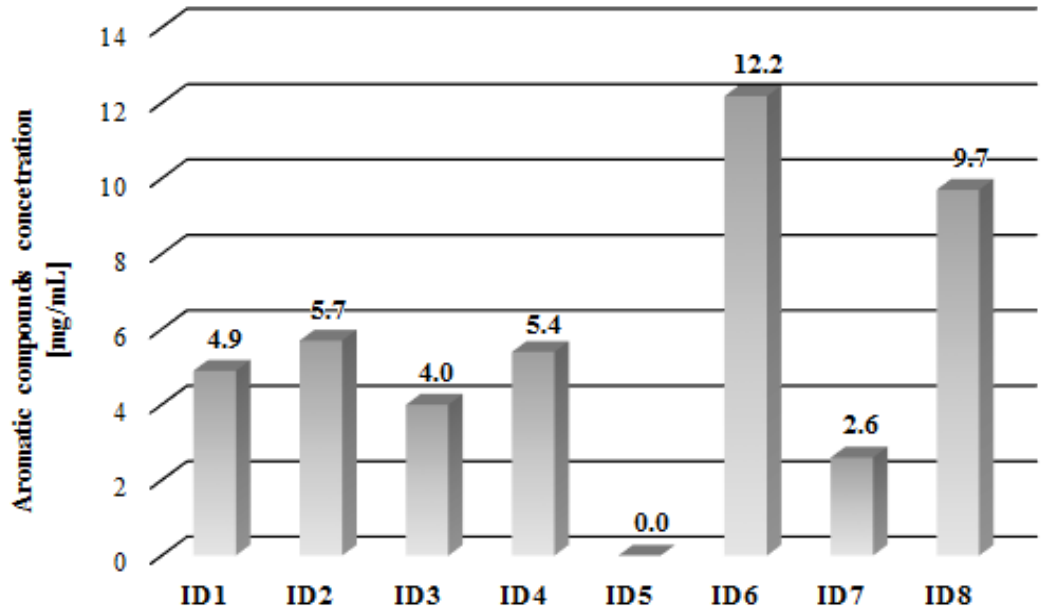
	Standard compounds	RRF found	RRF calc
1	3-Penten-2-one	0.11	0.18
2	Furfural	0.13	0.16
3	Pyridine	0.16	0.14
4	Toluene	0.16	0.25
5	3-Methyl-2-butanone	0.17	0.16
6	Acetic acid	0.18	0.07
7	2.4-Pentandiol	0.18	0.26
8	3.3-Dimethyl-2-butanol	0.19	0.26
9	Butyraldehyde	0.20	0.10
10	Valerolactone	0.21	0.29
11	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

➢ 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

CHARACTERIZATION OF BIO-OILS: QUANTITATIVE GC-MS METHOD

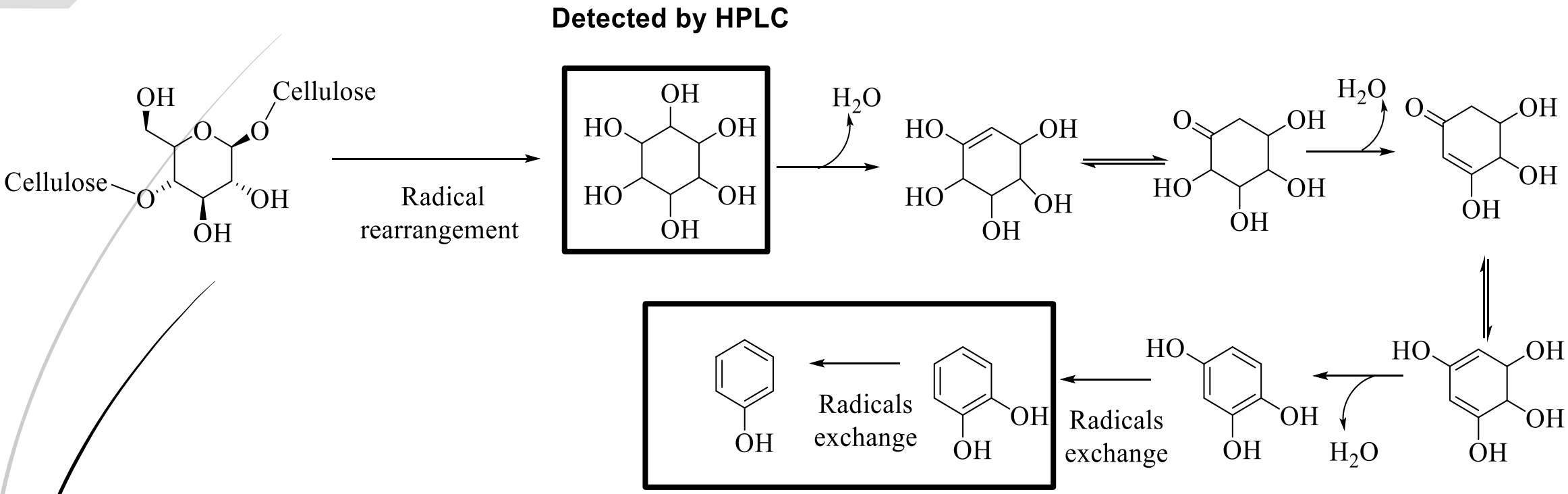






- Levoglucosan is a high valuable compound (110 €/g).
- Acetic acid was produced in a very attractive concetration.
- Furans were produced in appreciable concentration and variety.
- Surprisingly aromatic compounds like phenol, resorcinol, orcinol, guaicol toluene and benzene were detect in not neglectable concentrations.

CHARACTERIZATION OF BIO-OILS: AROMATIC COMPOUNDS FORMATION PATHWAY



	ID1 [mg/mL]	ID2 [mg/mL]	ID3 [mg/mL]	ID4 [mg/mL]	ID5 [mg/mL]	ID6 [mg/mL]	ID7 [mg/mL]	ID8 [mg/mL]
Sorbitol	2.61	1.14	1.31	2.02	0.00	3.07	4.31	5.22
Mannitol	1.50	0.70	0.49	0.87	0.00	0.75	0.82	1.09
Galactitol	1.02	0.43	0.32	0.48	0.00	0.00	0.00	0.00
Fructose	4.76	2.08	2.37	3.68	2.01	5.49	7.84	9.49
Glucose	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00

CONCLUSIONS

- *MAP OF CELLULOSE WAS PERFORMED IN A MULTIMODE BATCH OVEN*
- *DIFFERENT MW ABSORBERS WERE TESTED*
- *BIO-OILS WERE DEEPLY ANALYZED AND MAIN COMPONENTS WERE IDENTIFIED*
- *A QUANTITATIVE METHOD FOR GC-MS WAS TESTED FOR EVALUATION OF BIO-OILS COMPOSITION*
- *A NEW PATHWAYS FOR THE FORMATION OF AROMATIC MOIETIES DURING MAP OF CELLULOSE WAS PROPOSED*

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ENTE CASSA DI RISPARMIO DI FIRENZE

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…ANY QUESTIONS?

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