Evaluating the suitability of co-processing gardening residues and the organic fraction of municipal solid wastes via thermal and catalytic pyrolysis

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WHAT IS A URBAN BIOWASTE?

GARDEN AND PARK WASTES

FOOD WASTES

RESIDUES FROM FOOD PROCESSING PLANTS

SEWAGE SLUDGE

MORE THAN 1,100,000 TONS OF URBAN BIO-WASTES ARE GENERATED EVERY YEAR[1]

URBAN BIOWASTES DISPOSAL

URBAN MANAGEMENT AND TREAMENT OPTIONS

↓

TO EXPLOTE THE POTENTIAL RESOURCES CONTAINED IN THOSE BIORESIDUES

[1]Estrategia de la Gestión Sostenible de Residuos en la Comunidad de Madrid (2017-2024)

URBAN BIORESIDUES

- FOOD WASTES
- GARDEN RESIDUES
- SEWAGE SLUGDE
- PAPER

→ HIGH HETEROGENEITY

FAST PYROLYSIS

DECOMPOSITION IN THE ABSENCE OF OXYGEN

REACTION CONDITIONS:

- ✓ TEMPERATURE: 400-500 ºC
- ✓ HEATING RATE: 10^3-10^4 K/s
- ✓ VAPORS RESIDENCE TIME: 1-2s

GAS (10-30 %) — CO CO_2 H_2 C_1-C_3

BIOCHAR (10-35 %)

BIO-OIL (10-75 %)

BIOFUEL PRECURSOR
SOURCE OF CHEMICAL COMPOUNDS

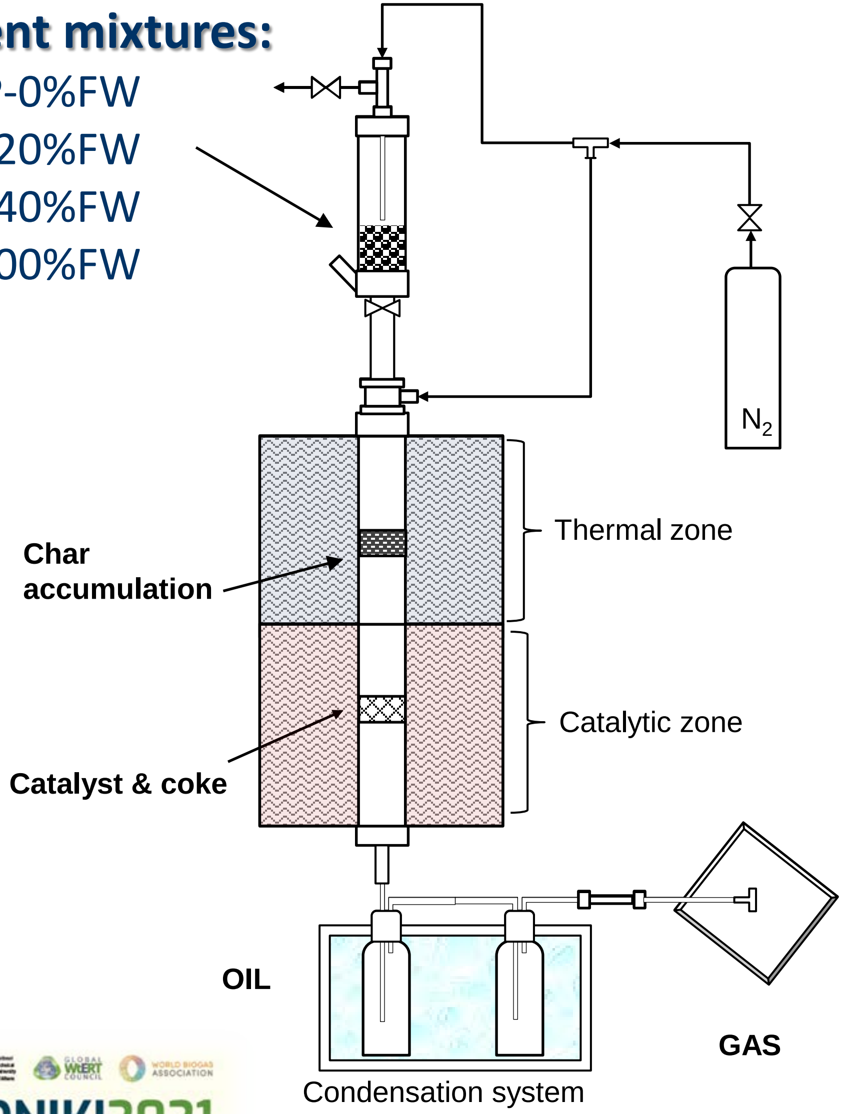
STUDY ABOUT THE CO-PYROLYSIS OF MIXTURES OF TWO BIO-WASTES: GARDENING PRUNING RESIDUES (GP) AND FOOD WASTES (FW)

THERMAL PYROLYSIS

CATALYTIC PYROLYSIS

Four different mixtures:

100%GP-0%FW
80%GP-20%FW
60%GP-40%FW
0%GP-100%FW



Reaction conditions:

- Thermal zone: 500 ˚C
- Catalytic zone: 450 ºC
- Pressure: 1 atm
- N_2 flow: 100 Nml/min
- Feed: 5 g of biowaste mixture
- Catalyst/feedstock: 0.4

Analytical techniques:

- **ICP-OES:** Metal content
- **Karl-Fisher:** water content
- **Elemental analysis**: CHNS/O
- **GC-MS**: molecular composition bio-oil
- **GC**: Gas composition

FW AND GP CHARACTERIZATION

CHEMICAL AND STRUCTURAL PROPERTIES

	FOOD WASTES	GARDEN PRUNING
MOISTURE (WT.%)	1.1	1.2
PROXIMATE ANALYSES (WT.% DB)		
VOLATILE MATTER	70.5	82.5
ASH	5.6	3.3
FIXED CARBON	24.0	14.2
ELEMENTAL ANALYSES (WT.% DAF)		
C	51.5	50.1
H	6.3	6.1
N	1.3	1.4
O	40.9	42.4
HHV (MJ/KG)	19.9	19.5
STRUCTURAL COMPONENTS (WT.%)		
EXTRACTIVES	**60.2**	9.3
CELLULOSE	9.2	**37.2**
HEMICELLULOSE	6.7	**14.0**
LIGNIN	15.6	**29.1**
ACETYL GROUPS	1.6	4.8
OTHERS	1.1	2.3

[a] db: dry basis [b] daf: dry and ash-free basis

IMPORTANT EFFECT IN BIO-OIL YIELD

GP: MAINLY COMPOSED BY CELLULOSE, HEMICELLULOSE AND LIGNIN

FW: SIGNIFICANT EXTRACTIVES CONTENT (WAX/FAT, PROTEINS, AMINO ACIDS AND PECTIN)

FW AND GP CHARACTERIZATION

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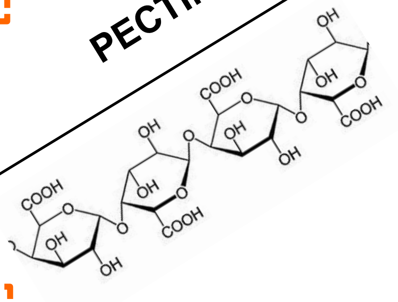
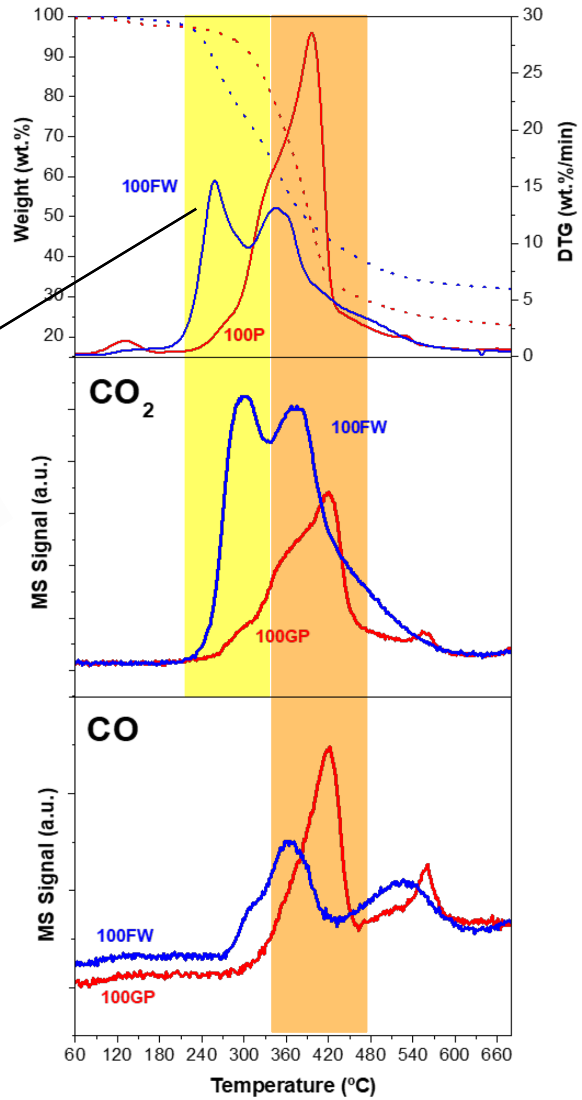
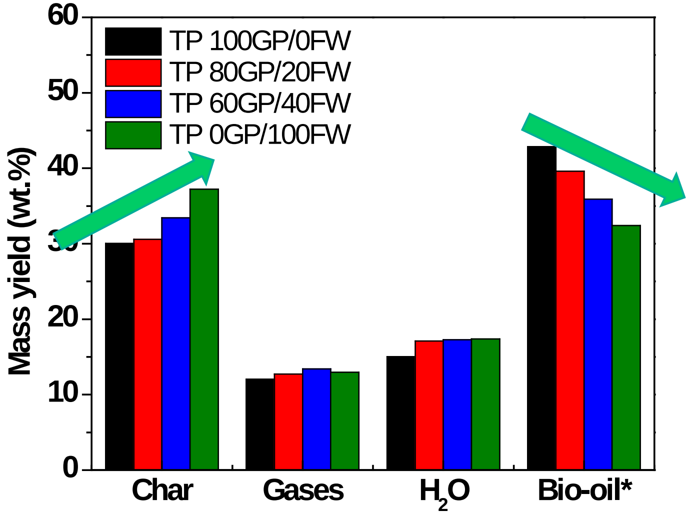
PECTIN



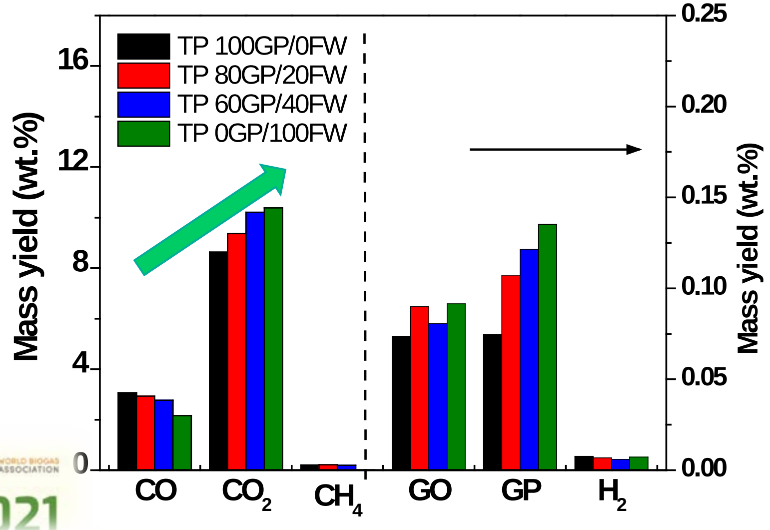


THERMAL PYROLYSIS

Products Distribution



Gaseous Products Distribution



- LOWER BIO-OIL YIELD AND HIGHER BIOCHAR PRODUCTION WITH INCREASING FW AMOUNT → LOWER VOLATILE MATTER.
- SLIGHT INCREASE IN WATER AND GAS FRACTION YIELDS.
- FW FAVOURS THE DEOXYGENATION OF THE PYROLYSIS VAPOURS VIA DECARBOXYLATION → PREFERRED TO DECARBONYLATION IN TERMS OF MASS AND ENERGY EFFICIENCY

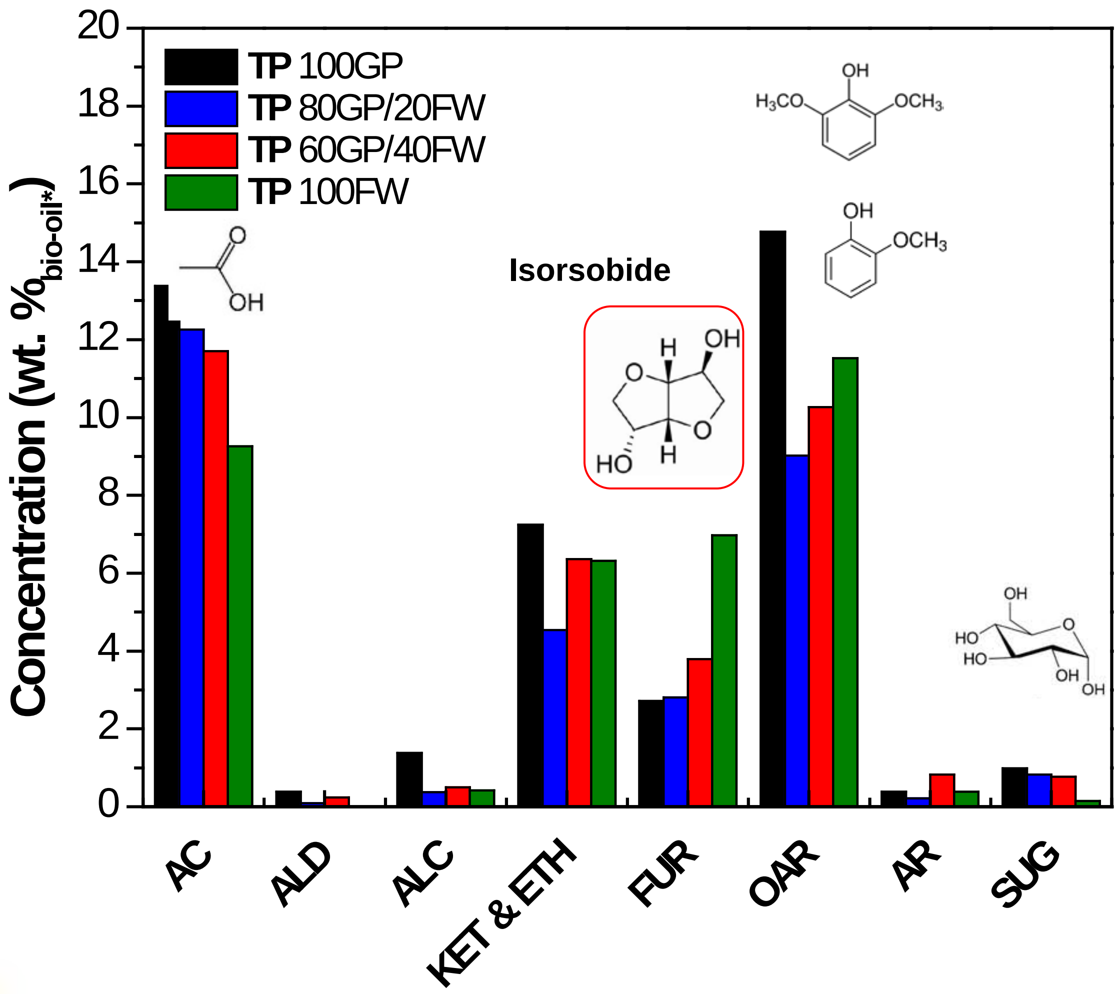
Bio-oil* chemical composition

Experiment	Water content (wt.% $_{\text{liquid fraction}}$)	Elemental composition (wt.% $_{\text{bio-oil}}$ db)					HHV (MJ/kg$_{\text{bio-oil}}$ db)
		C	H	N	S	O	
TP 100GP	27.2	57.6	7.3	1.1	0.0	34.0	25.2
TP 80GP/20FW	29.7	60.2	7.4	1.5	0.0	31.0	26.5
TP 60GP/40FW	31.8	60.9	7.7	1.9	0.0	29.5	27.3
TP 100FW	35.7	66.5	8.3	2.8	0.0	22.4	30.7

C, H: + O: - HHV: +

THERMAL PYROLYSIS

Bio-oil* molecular composition (GC-MS)



CATALYTIC PYROLYSIS

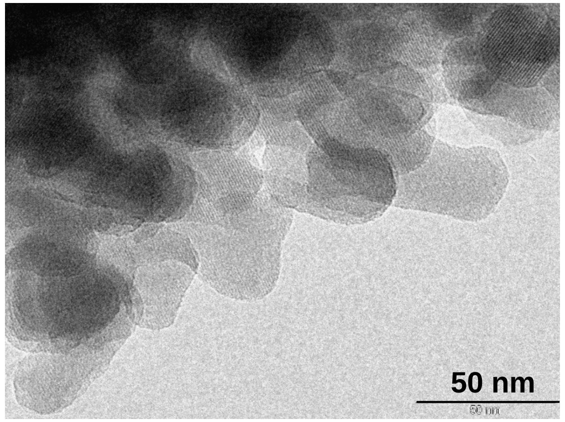
CATALYST: nanocystalline ZMS-5 zeolite

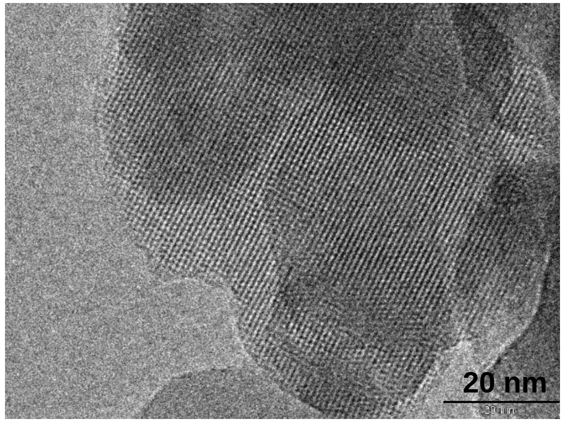
Physicochemical properties of n-ZSM-5 zeolite

Catalyst	$[Si/Al]_{MOL}$ [a]	S_{BET} [b] (m^2/g)	S_{MIC} [c] (m^2/g)	S_{EXT} [c] (m^2/g)	V_T [d] (cm^3/g)	Acidity[e] (mmol/g)
n-ZSM-5	42	445	312	133	0.512	0.28

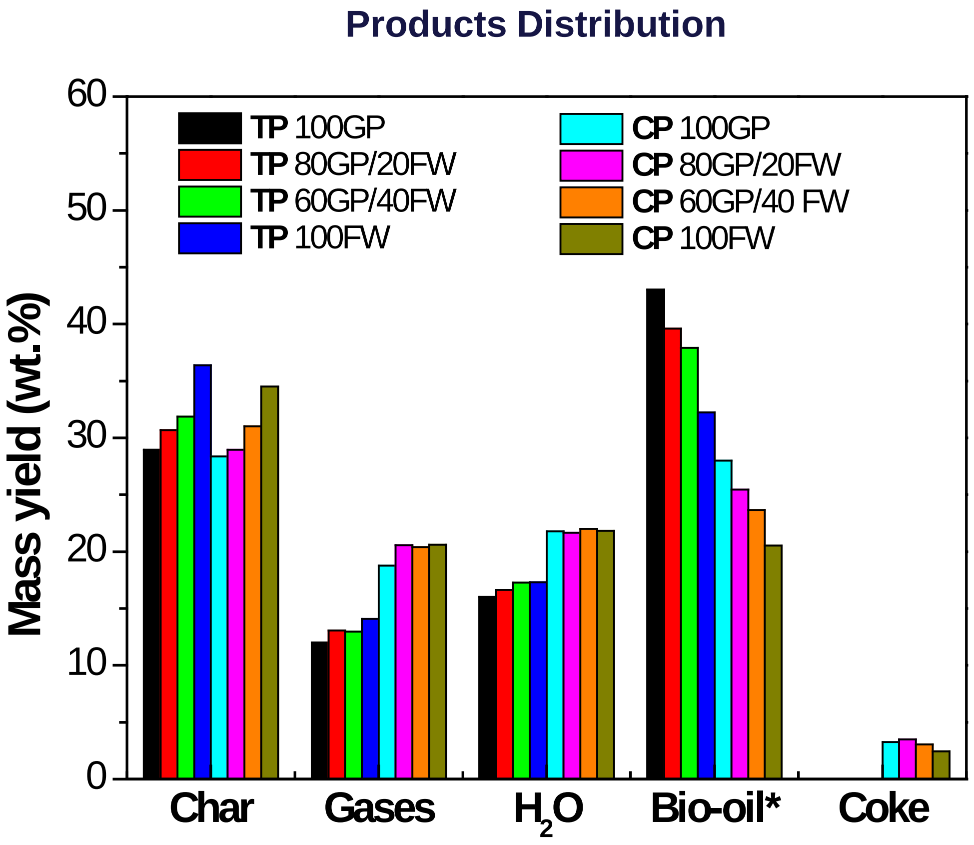
.
[a] Measured by ICP-OES., [b] BET surface area. [c] Micropore surface area (S_{MIC}) and External surface area (S_{EXT}), calculated from NL-DFT., [d] Total pore volume at $P/P_0 \approx 0.98$.[f] Measured by TPD-NH_3.

TEM





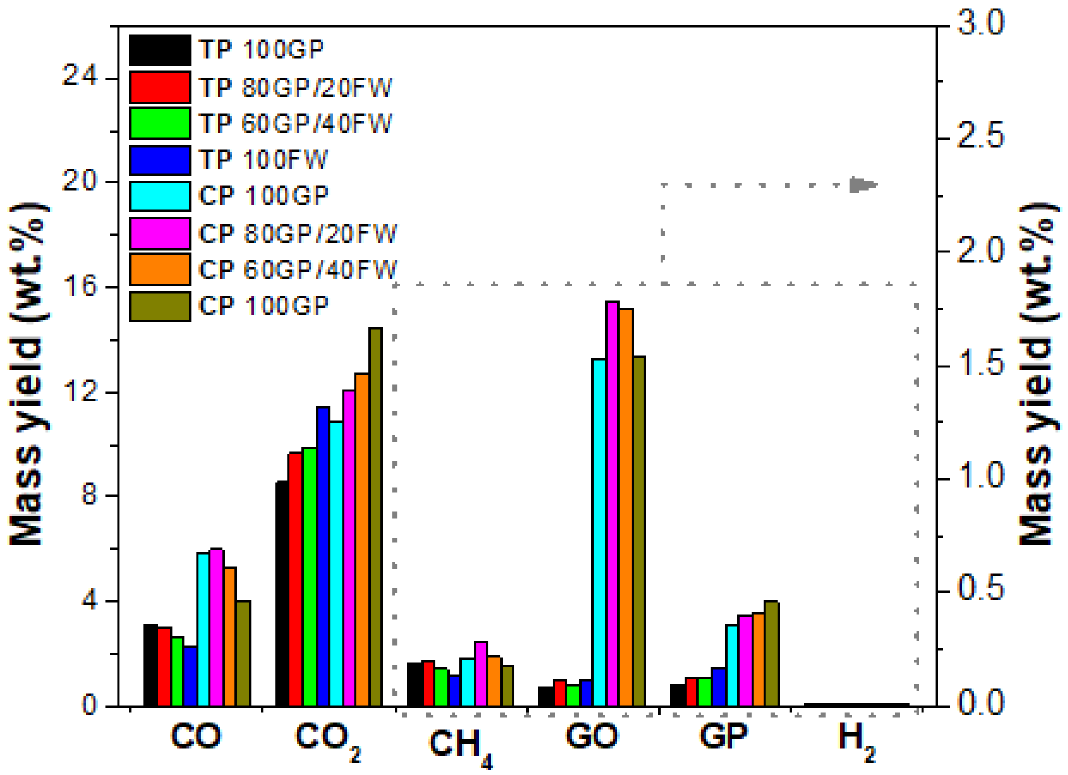
CATALYTIC PYROLYSIS



- SIMILAR CHAR YIELDS TO THOSE OBTAINED FOR THERMAL TESTS.
- A CARBONACEOUS RESIDUE (COKE) IS DEPOSITED OVER THE CATALYST SURFACE.
- SIGNIFICANT INCREASE OF GASES PRODUCTION
- HIGHER WATER PRODUCTION → OXYGEN REMOVAL VIA DEHYDRATION AND CONDENSATION REACTIONS.

CATALYTIC PYROLYSIS

Gaseous Products Distribution



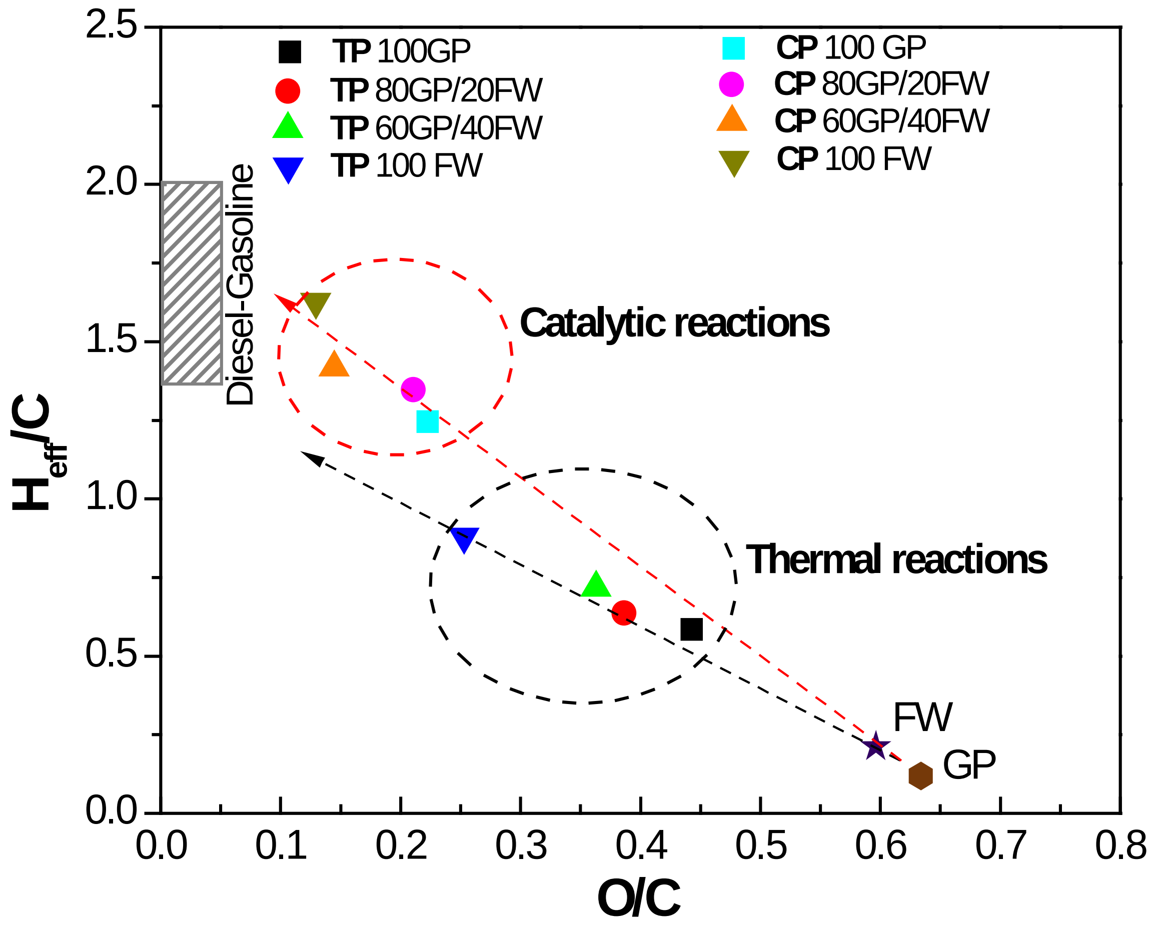
- INCREASE OF CO_2 and CO YIELDS → PROMOTION OF DECARBOXYLATION AND DECARBONYLATION.
- HIGHER PRODUCTION OF GO AND GP → DEOXYGENATION AND CRACKING REACTIONS.

Bio-oil* chemical composition

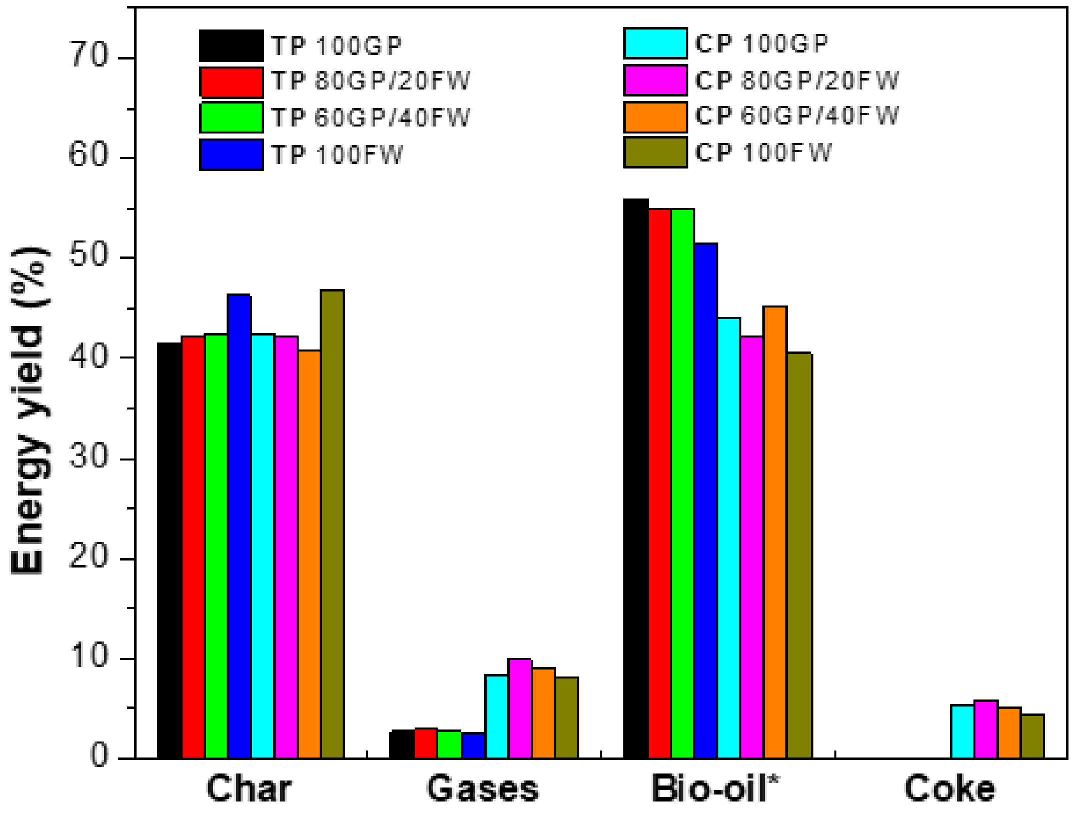
Experiment	Water content (wt.% liquid fraction)	Elemental composition (wt.% bio.oil db)					HHV (MJ/kg bio-oil db)
		C	H	N	S	O	
TP 100GP	27.2	57.6	7.3	1.1	0.0	34.0	25.2
TP 80GP/20FW	29.7	60.2	7.4	1.5	0.0	31.0	26.5
TP 60GP/40FW	31.8	60.9	7.7	1.9	0.0	29.5	27.3
TP 100FW	35.7	66.5	8.3	2.8	0.0	22.4	30.7
CP 100GP	43.9	69.4	8.3	1.7	0.0	20.6	31.9
CP 80GP/20FW	46.5	69.4	8.8	2.4	0.0	19.5	32.5
CP 60GP/40FW	47.2	74.8	8.9	2.0	0.0	14.4	35.0
CP 100FW	51.2	74.5	9.8	3.0	0.0	12.7	36.2

+ - +

Van Krevelen Graph



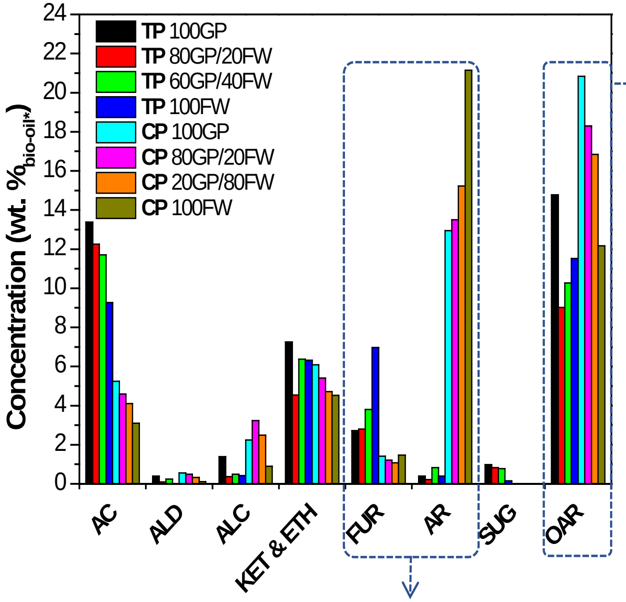
Energy yield

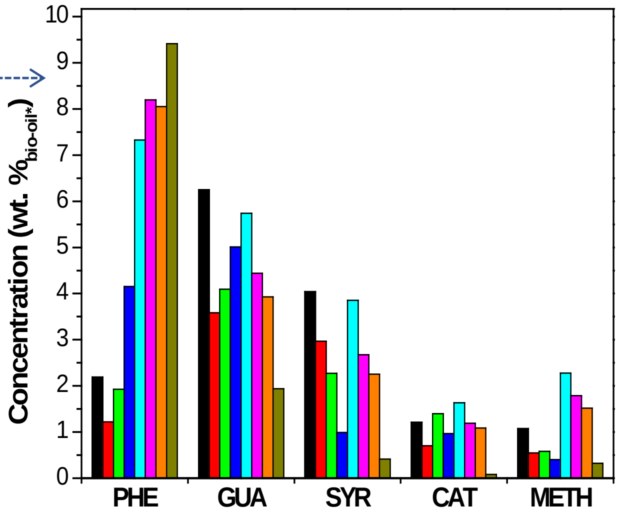


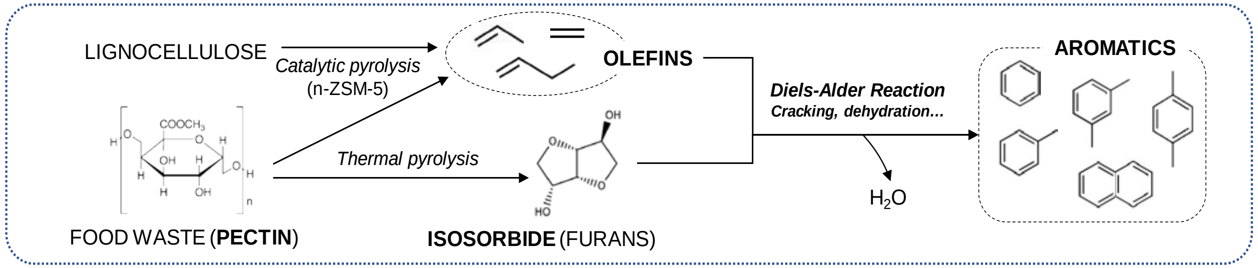
THE ENERGY YIELD REDUCTION IS LESS MARKED THAN THAT PRODUCED IN THE BIO-OIL* MASS YIELDS → LOWER OXYGEN CONTENT EXHIBITED IN THE CATALYTIC BIO-OIL.

CATALYTIC PYROLYSIS

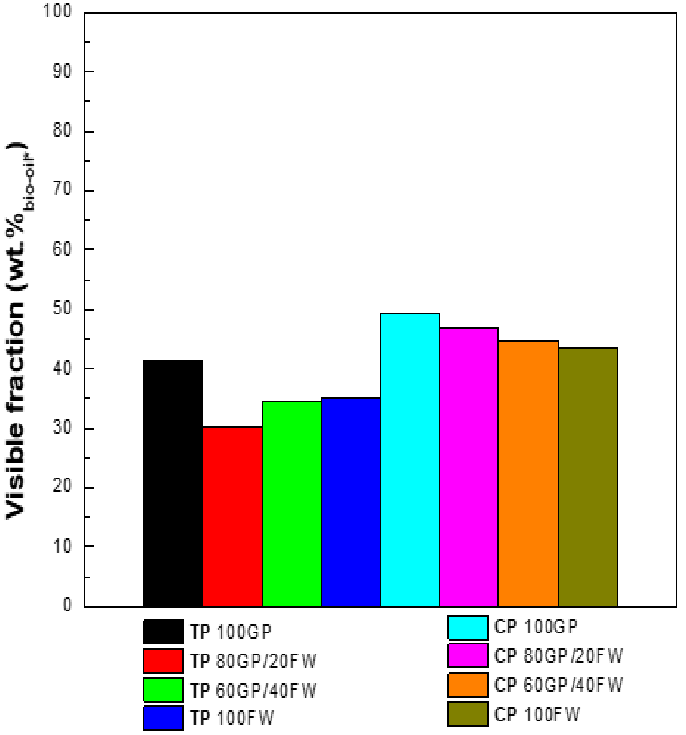
Bio-oil* molecular composition (GC-MS)







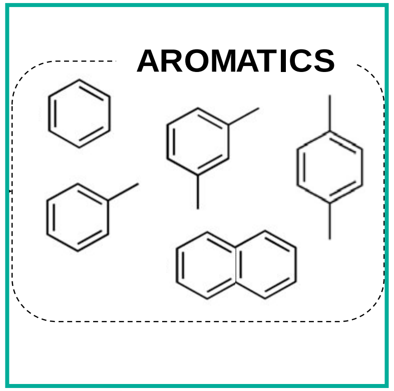
Percentage of mass detected by GC–MS in bio-oil*



- CO-PROCESSING OF **GARDEN PRUNING** AND **FOOD** BIO- RESIDUES VIA CATALYTIC PYROLYSIS IS A PROMISING VALORISATION ROUTE TO AVOID INCINERATION OR LANDFILL DISPOSAL.

- THE CO-UTILISATION OF **FOOD WASTES** WITH **GARDEN PRUNING RESIDUES** FACILITATES THE BIO-OIL* DEOXYGENATION, ENHANCING ITS QUALITY.

- THIS EFFECT IS BOOSTED IN PRESENCE OF n-ZSM-5 ZEOLITE.



- THE SIGNIFICANT FORMATION OF VALUABLE **AROMATIC HYDROCARBONS** (ESPECIALLY BENZENE AND ALKYLBENZENES) BY CATALYTIC PYROLYSIS INCREASE THE **COMMERCIAL VALUE** OF THIS PROCESS.

ACKNOWLEDGEMENTS

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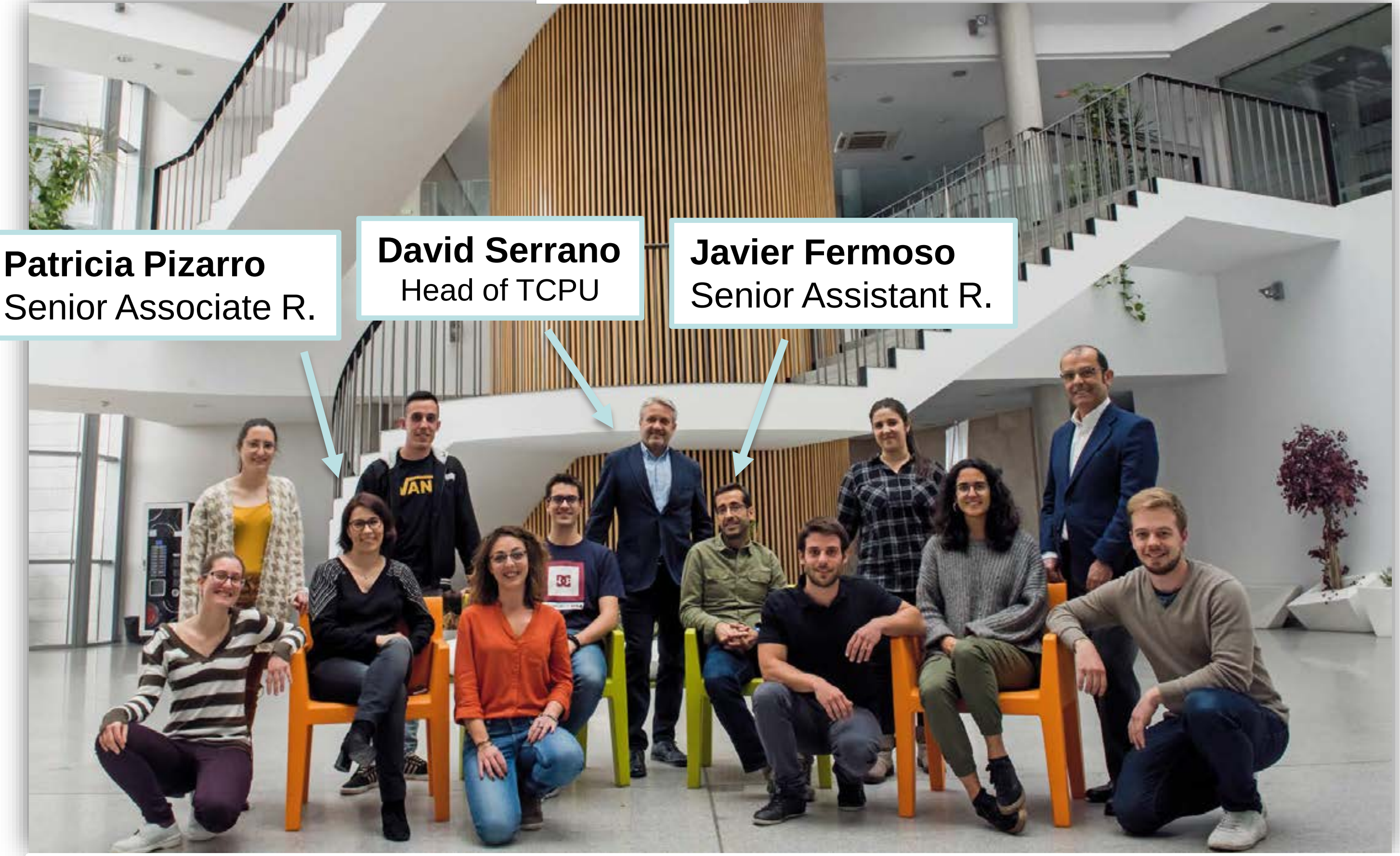

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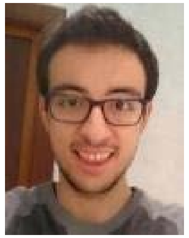

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