Aristotle University of
Thessaloniki
Department of Chemistry

Valorization of hazardous organic solid wastes towards fuels and chemicals via pyrolysis

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Project Pyrolwaste
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AQUILA ATLANTIS HOTEL Heraklion, Crete Island, Greece

26 – 29 June 2019

Pyrolysis: Thermal decomposition in inert atmosphere

Typical product weight yields (dry wood basis)

obtained by different modes of wood pyrolysis

Mode	Conditions	Liquid	Solid	Gas
Fast	~500^{o}C, short hot vapour residence time ~1 s	75%	12% char	13%
Intermediate	~500^{o}C, hot vapour residence time ~10-30 s	50%	25% char	25%
Carbonisation (slow)	~400^{o}C, long vapour residence hours days	30%	35% char	35%
Gasification	~750-900^{o}C	5%	10% char	85%
Torrefaction (slow)	~290^{o}C, solids residence time ~10-60 min	0% unless condensed, then up to 5%	80% solid	20%

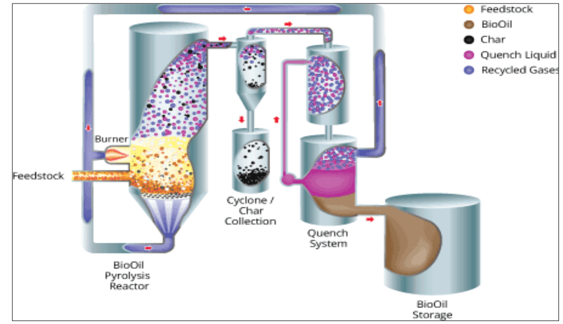
Bridgwater, A.V. (2012) Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy, **38**, 68–94.

E.F. Iliopoulou, P.A. Lazaridis, K.S. Triantafyllidis, “Nanocatalysis in the Fast Pyrolysis of Lignocellulosic Biomass”, in “Nanotechnology in Catalysis - Applications in the Chemical Industry, Energy Development, and Environment Protection”, Eds. Bert Sels, Marcel Van de Voorde, Wiley, 2017

Biomass Fast Pyrolysis (BFP)

Main process characteristics:

- small particles of biomass (< 3 mm)
- inert solid heat carriers (silica sand) & inert carrier gas (i.e. N_2)
- atmospheric pressure
- high heating rates and moderate temperatures (400-600°C)
- low residence time (0.5 – 2 sec)
- rapid cooling of pyrolysis vapours to enhance bio-oil



Bubbling or circulating-riser fluidized-bed reactors

BFP products:

Pyrolyis oil (bio-oil)	up to 75 wt.% (including water, 15-30 %)
Gases	10-25 wt.%, CO, CO_2; also H_2,C_1-C_6
Char/ coke	10-20 wt.%

Pilot unit Circulating Fluidized Bed reactor (1 kg/h) CPERI/CERTH, Greece

Additional process characteristics:

- Flexibility with regard to biomass feedstock
- Autothermal (gas & solid/char products can cover energy requirements)

E. Iliopoulou, S. Stefanidis, K. Kalogiannis, A. Psarras, A. Delimitis, K. Triantafyllidis, A. Lappas, Green Chem. 16 (2014) 662–674

Characteristics of fast pyrolysis oil (bio-oil)

- ✓ **Dark brown, low viscosity, relatively acidic with 15-30 wt.% water**

Composition	**Origin**
Acetic acid	Hemicellulose
Ketones	Hemicellulose, cellulose & lignin
Ethers	Hemicellulose, lignin
Furans	Hemicellulose & cellulose
Phenolics	Lignin & hemicellulose
Minor: Esters, aldehydes, alcohols, sugars, N-comp, heavy	

Bio-oil characteristics (e.g. from wood pyrolysis):	
Density	1150 - 1250 kg/m^3
Energy density	**15-25 GJ/m^3 *(biomass: 9 GJ/m^3)***
Water content	15 - 30 wt.%
Acidity	(pH) 2.5 - 3
Viscosity	25 - 1000 cP
Ash	< 0.1 wt.%

Undesirable properties:

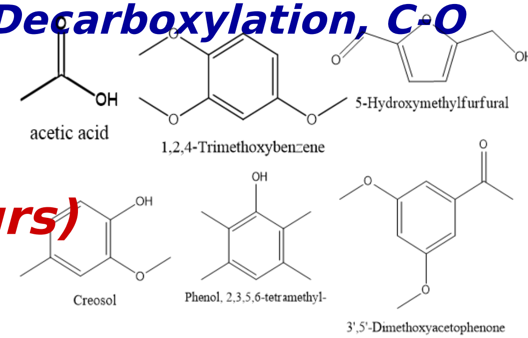
- **Acidic - corrosive**
- **Unstable (polymerizes)**
- **Not miscible with petroleum fuels**
- **Low Higher heating value (HHV)**

In situ upgrading of bio-oil via Catalytic Fast Pyrolysis (CFP)

Lignocellulosic biomass

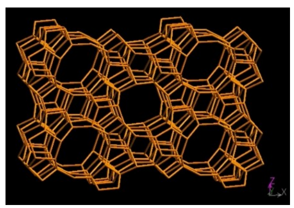
Initial degradation reactions: thermal / non-catalytic

Depolymerization, Hydrolysis, Dehydration, Decarbonylation, Decarboxylation, C-O cleavage



Smaller oligomers and monomers
(non-catalytic biomass pyrolysis vapours)

Catalytic Effect: Porosity morphology active sites



MFI (ZSM-5)
5.1x5.5 & 5.3x5.6 Å

dehydration, decarbonylation, decarboxylation, ketonization, esterification, cracking, aromatization, condensation, coke formation

De-oxygenated, aromatic bio-oil

Gaseous products: **CO, CO_2, H_2, light hydrocarbons**
Solid products: **Char and reaction-coke on catalyst**

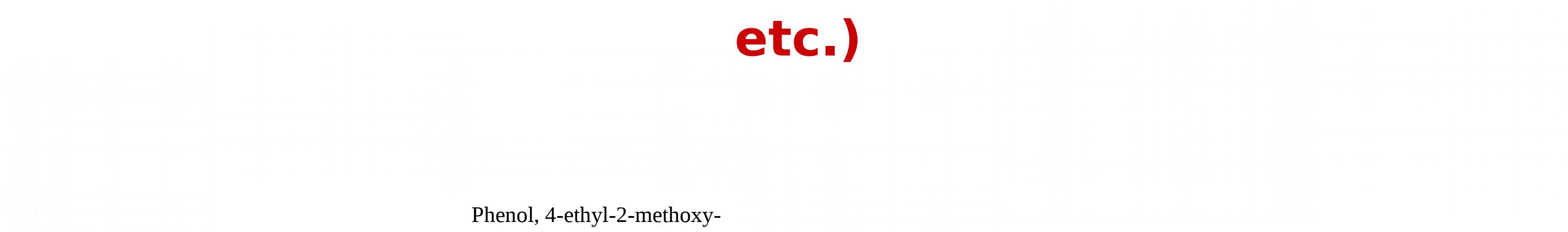
E.F. Iliopoulou et al, Appl. Catal. B: Environ. 127 (2012) 281–290; E.F. Iliopoulou et al., Green Chem. 16 (2014) 662–674

Biomass fractionation & fast pyrolysis

Fast pyrolysis of lignocellulosic biomass

Bio-oil : Complex mixture of various oxygenated compounds

Fast pyrolysis of lignin (Kraft lignin, hydrolysis lignin, etc.)



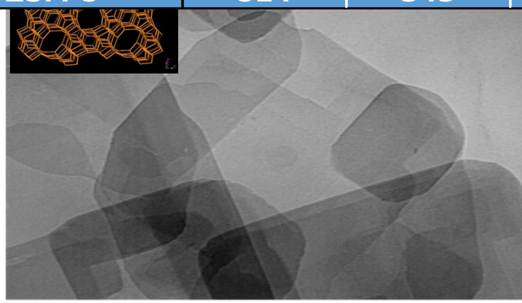
Bio-oil : Homogeneous mixture of alkoxy-phenolics

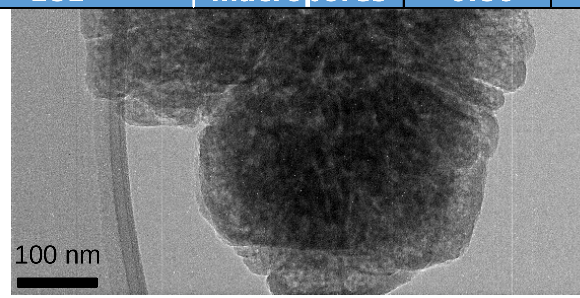
- **Production of “phenol”-formaldehyde resins replacing petroleum phenol**
- **Homogeneous substrate for catalytic upgrading**

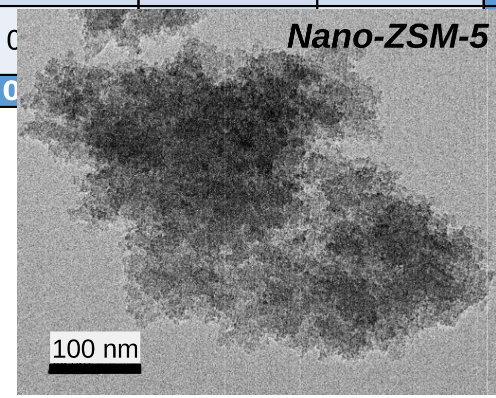
ZSM-5 zeolite catalysts in fast pyrolysis

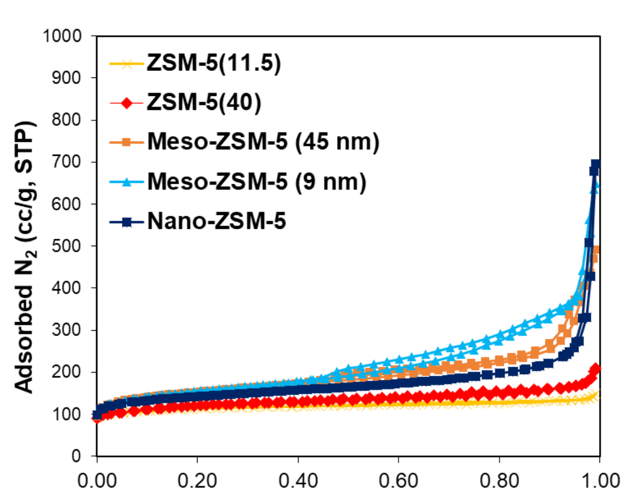
Catalyst	Total SSA [a] (m²/g)	Micropore area [b] (m²/g)	Meso/macropore and external area[c] (ml/g)	Average mesopore diameter [e] (nm)	Chemical composition		Acidity		
					Al	Na	FT-IR/pyridine (μmol Pyr/g)		
					(wt.%)		Brønsted	Lewis	B/L
ZSM-5 (40)	437	332	105	-	0.91	0.03	190	26	**7.3**
ZSM-5 (11.5)	424	349	75	-	3.20	0.06	430	123	**3.5**
Meso-ZSM-5 (9nm)	560	259	301	~ 9 & 90	0.82	0.05	192	21	**9.1**
Meso-ZSM-5 (45nm)	556	289	267	~ 45	3.00	[illegible]	[illegible]	[illegible]	**5.0**
Nano-ZSM-5	**524**	**343**	**181[d]**	**macropores**	**0.86**	[illegible]	[illegible]	[illegible]	**1.9**

[a] Multi-point BET method; [b] t-plot method; [c] Difference of total SSA minus micropore area; [d] Attributed mainly to macropores and external surface area; [e] BJH analysis using adsorption data.

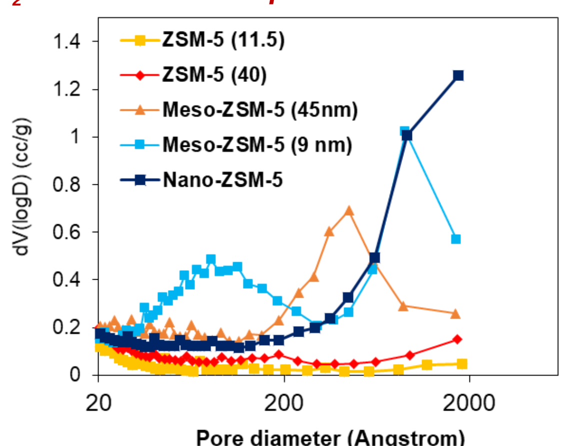




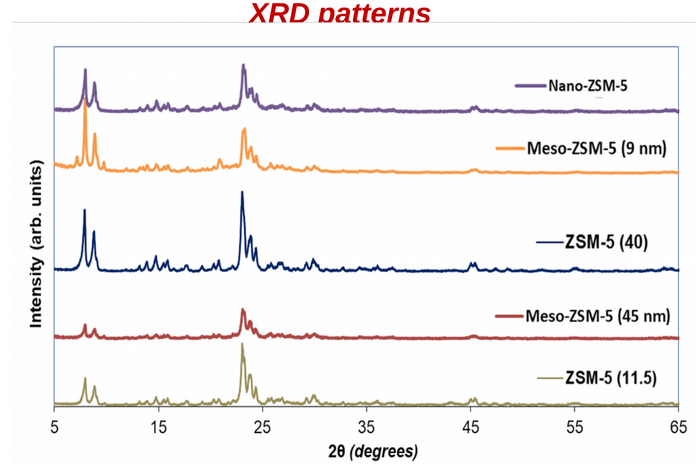




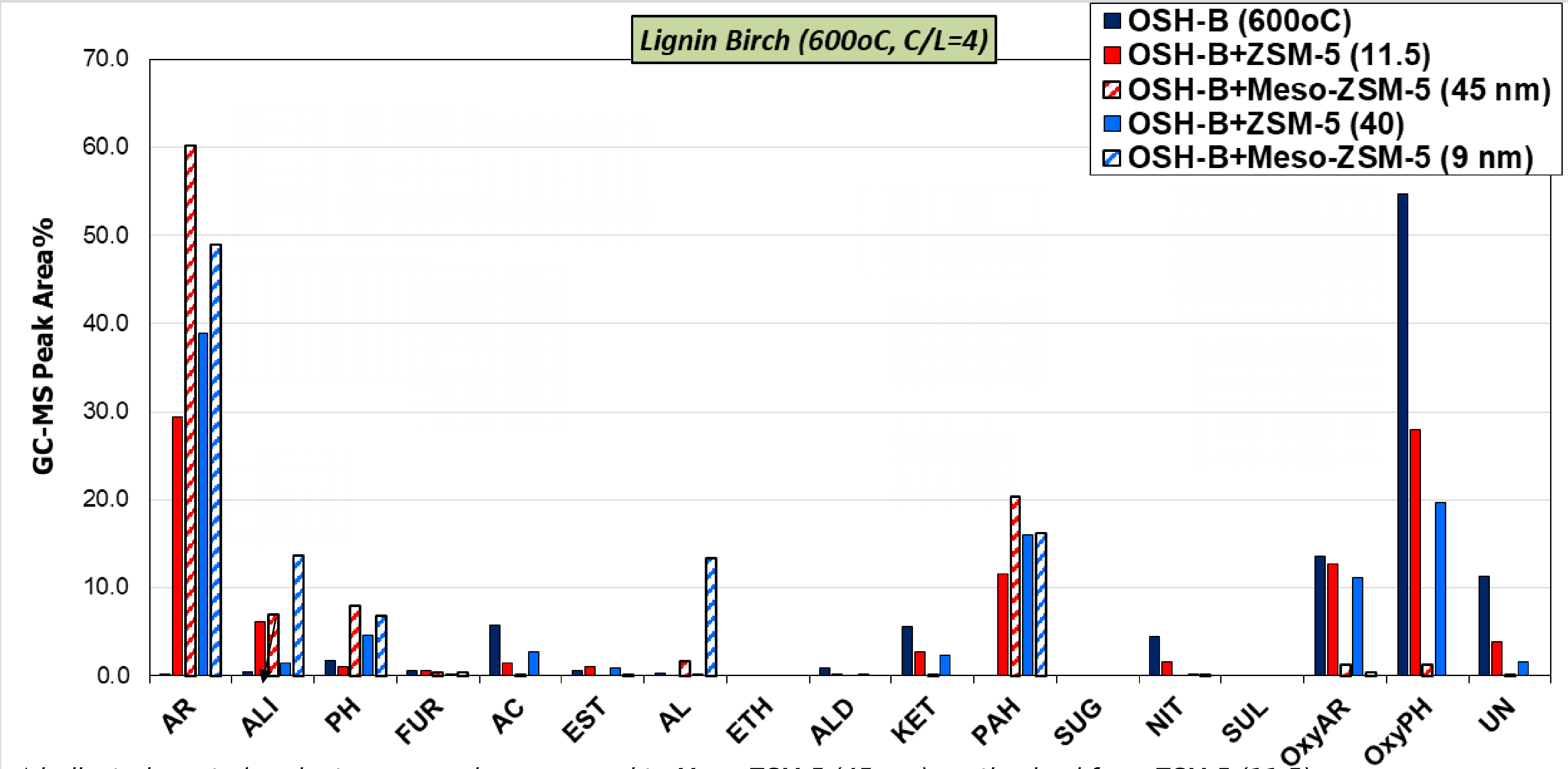
N_2 isotherms & BJH pore size distribution



XRD patterns



CFP of Birch Organosolv lignin with conventional and mesoporous ZSM-5 zeolite (C/B ratio=4 at 600°C)



** indicated most abundant compounds correspond to Meso-ZSM-5 (45 nm) synthesized from ZSM-5 (11.5)*

- Enhanced conversion of syringol compounds with 2 methoxy-groups on the mesoporous ZSM-5 zeolites

Hazardous organic solid wastes

Wood containing creosote preservatives

Paint Residues on Scrap Metal

Petroleum Sludges and Sediments

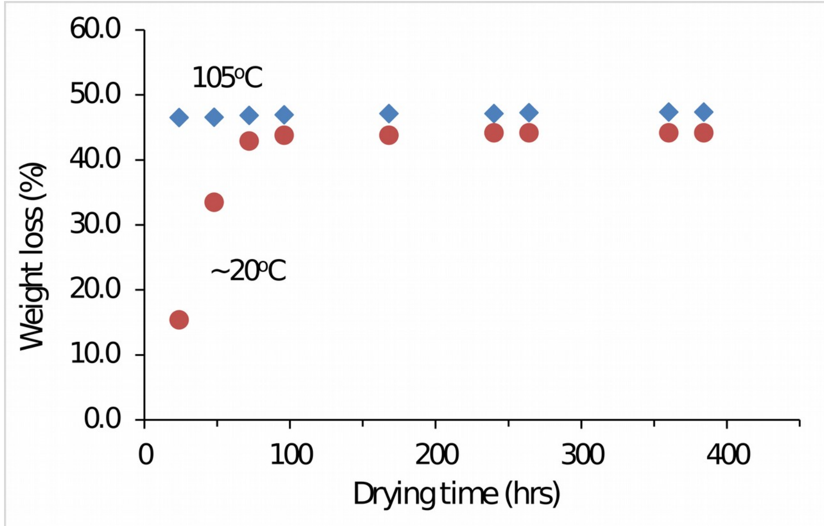
Conventional Management Process

Incineration to produce energy

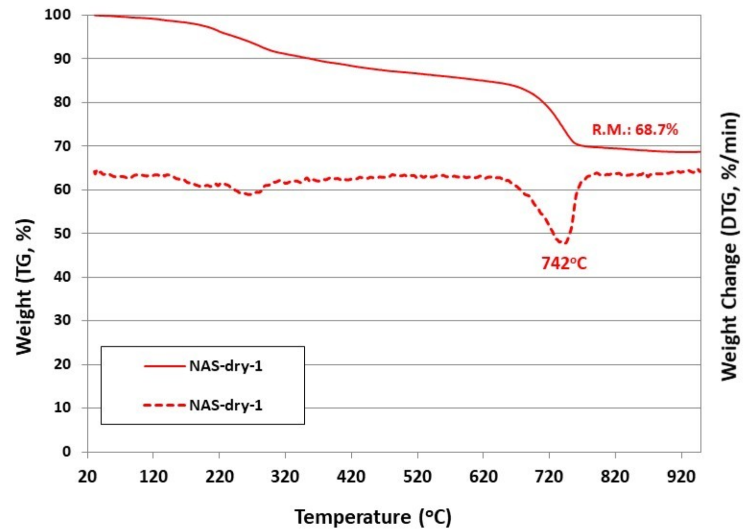
- 700 - 1000° C, utilizing air/O_2.
- Energy recovery through heat exchange (steam generation).
- Solid Residue storage in landfills (ash + heavy metals).
- Metal Recycling (only for the scrap metal wastes).

Characteristics and properties of wastes

Petroleum Sludge & Sediments

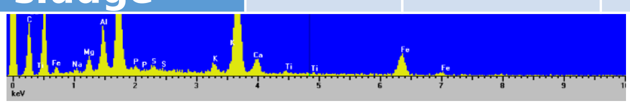


- **The petroleum sludge collected from ship tanks contain high amount of volatiles**
- **Analysis of vapors suggested being mainly water vapor**



- **High temperature weight loss refer to decomposition of stable (poly)aromatics**

Waste type	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	HHV (MJ/kg) (calculated)	HHV (MJ/kg) (measured)
Petroleum sludge	15.04	1.32	0.35	1.10	4.19	5	5.90



Petroleum sludge	77.8

	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
% atom ratio (EDS)	1.4	4.9	10.1	28.7	1.2	1.3	2.2	31.9	0.9	17.6

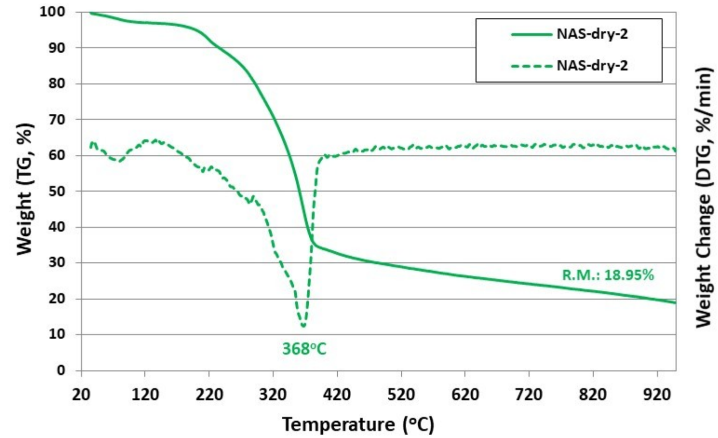
Characteristics and properties of wastes

Wood containing creosote

Representative composition of beech-tar creosote

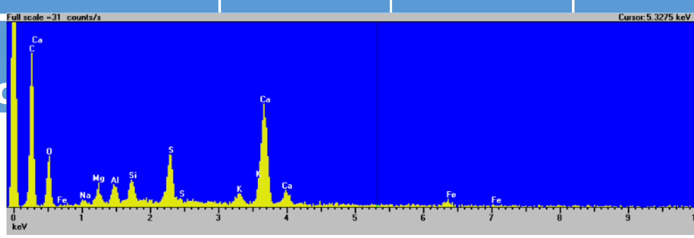
Phenol	C_6H_5OH	5.2%
o-cresol	$(CH_3)C_6H_4(OH)$	10.4%
m- and p-cresols	$(CH_3)C_6H_4(OH)$	11.6%
o-ethylphenol	$C_6H_4(C_2H_5)OH$	3.6%
Guaiacol	$C_6H_4(OH)(OCH_3)$	25.0%
3,4-xylenol	$C_6H_3(CH_3)_2OH$	2.0%
3,5-xylenol	$C_6H_3(CH_3)_2OH$	1.0%
Various phenols	C_6H_5OH—	6.2%
Creosol and homologs	$C_6H_3(CH_3)(OH)(OCH_3)$—	35.0%

- **Wood based tar creosote: phenolic nature**
- **Coal based tar creosote: petroleum/aromatic nature**

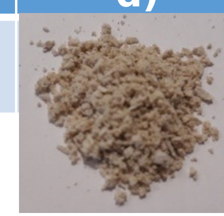


- **Typical TGA profile for wood (lignocellulosic biomass) decomposition**

Waste type	C (wt. %)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	HHV (MJ/kg) (calculated)	HHV (MJ/kg) (measured)
			5	5.60	35.94	19.51	



Wood creosote	1.49



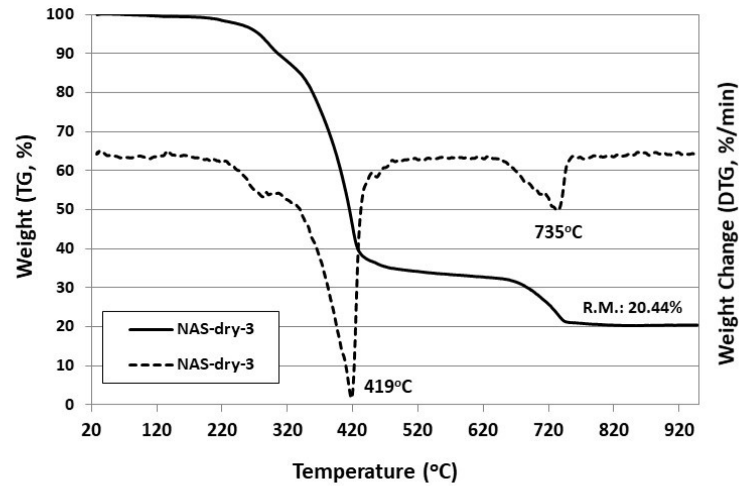
	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
% atom ratio (EDS)	3.2	6.0	7.6	9.6	-	16.4	5.7	46.3	-	5.2

Characteristics and properties of wastes

Residual paints

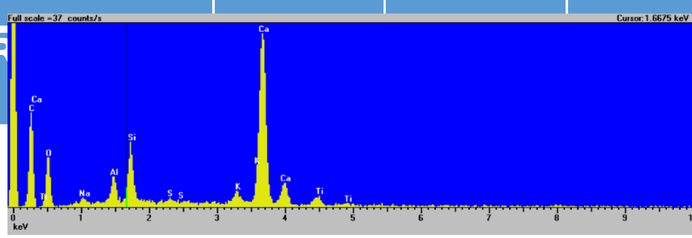
Representative composition of acrylate topcoats

Components	(%)
Hydrocarbons, C9, Aromatics (< 0.1% benzene)	25-50
xylene	10-25
2-methoxy-1-methylethyl acetate	≤ 5
ethylbenzene	≤ 5
2-methyl- 2-Propenoic acid, 2-(dimethylamino) ethyl ester, polymer with butyl 2-propenoate, compounds. with polyethylene glycol hydrogen maleate C9-11-alkyl ethers, 2-Propenoicacid, 2-ethylhexylester, etc.	≤ 0,3

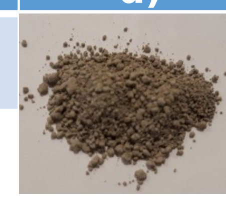


- **Typical TGA profile of acrylates plus high T peak due to aromatics**

Waste type	C (wt. %)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	HHV (MJ/kg) (calculated)	HHV (MJ/kg) (measured)
R[illegible]	[illegible]	[illegible]	[illegible]	0.45	14.70	19.42	

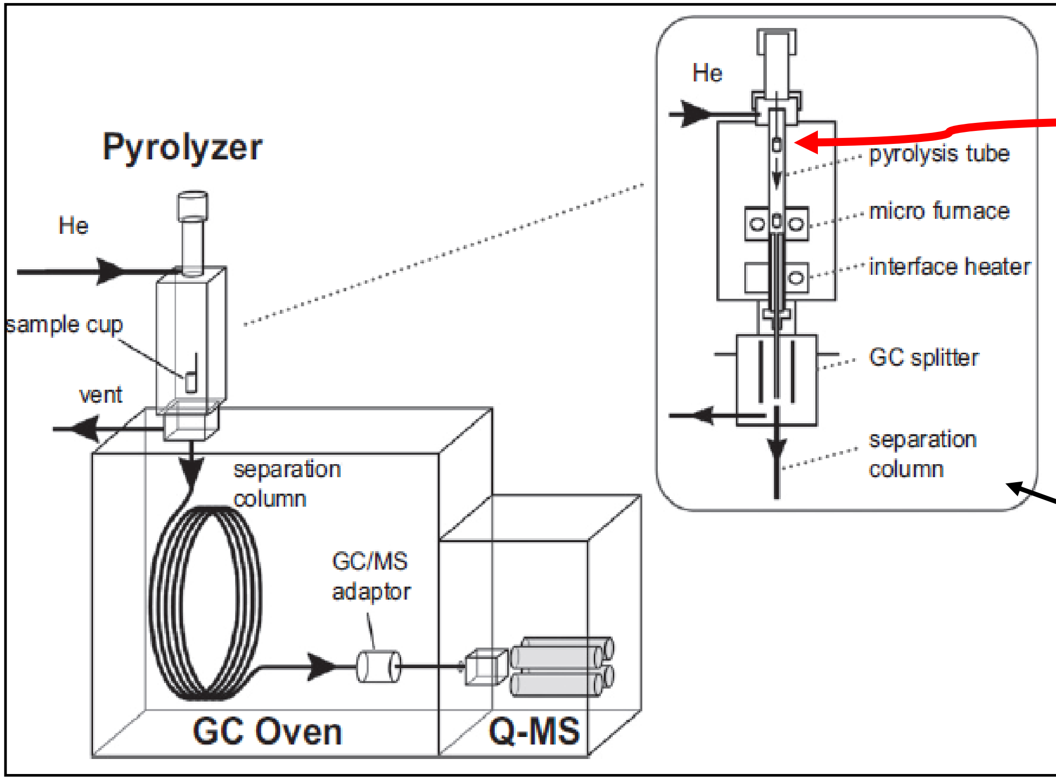


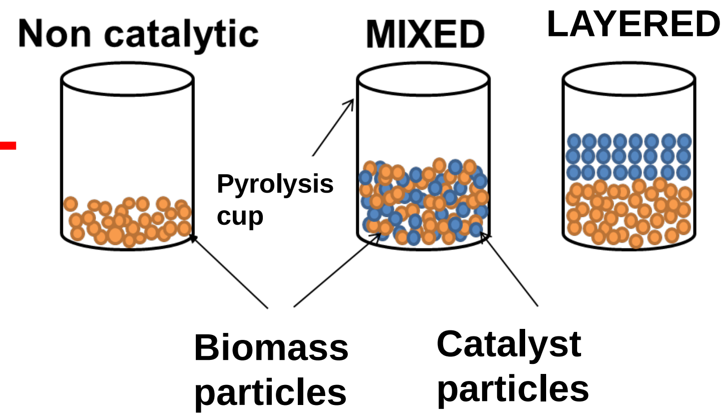
Residual paints	30.5

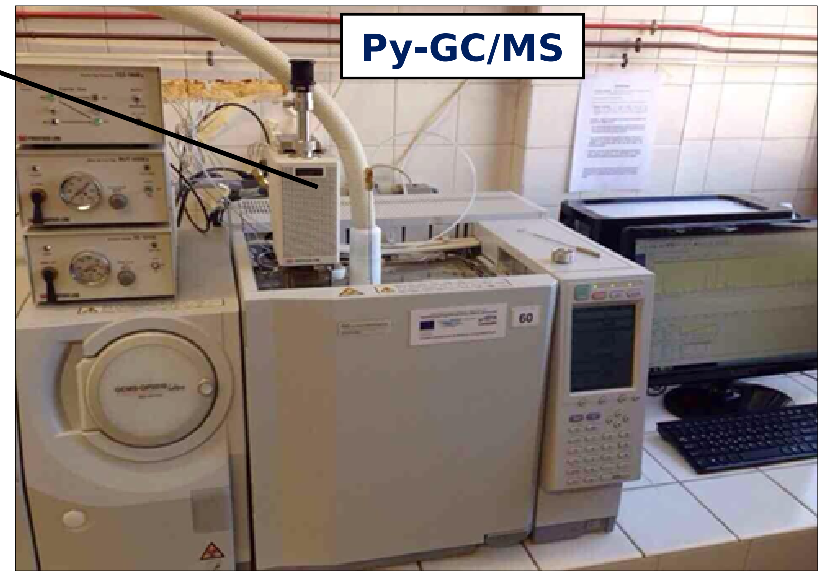


	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
% atom ratio (EDS)	2.3	-	6.3	13.6	-	0.6	3.3	67.6	6.3	-

Pyrolyzer-GC/MS (Py-GC/MS)







Py-GC/MS (QP2010, Shimadzu), Pyrolysis reactor (Frontier-Lab, Multi–Shot Pyrolyzer, EGA/PY-3030D),

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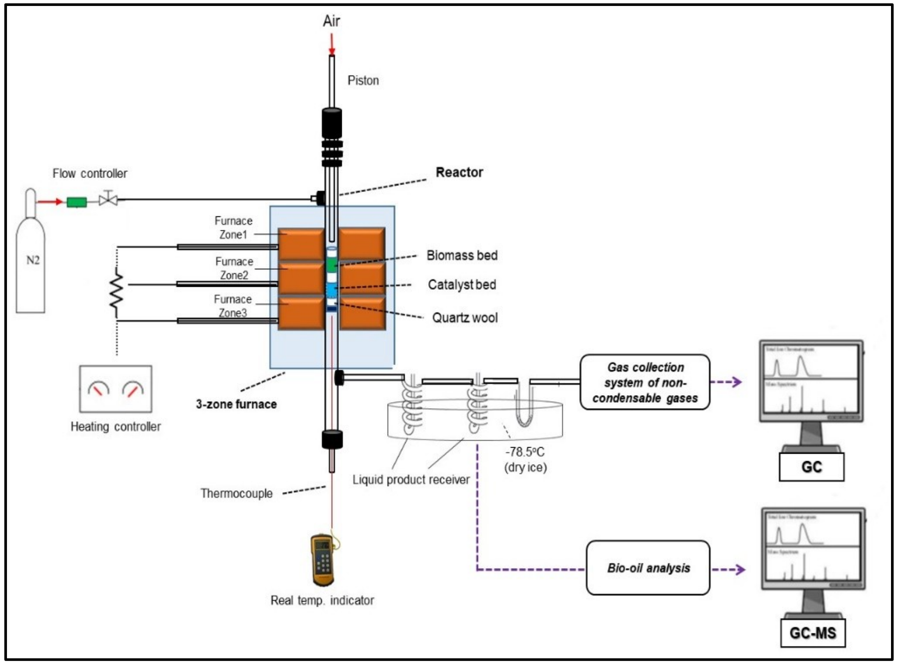
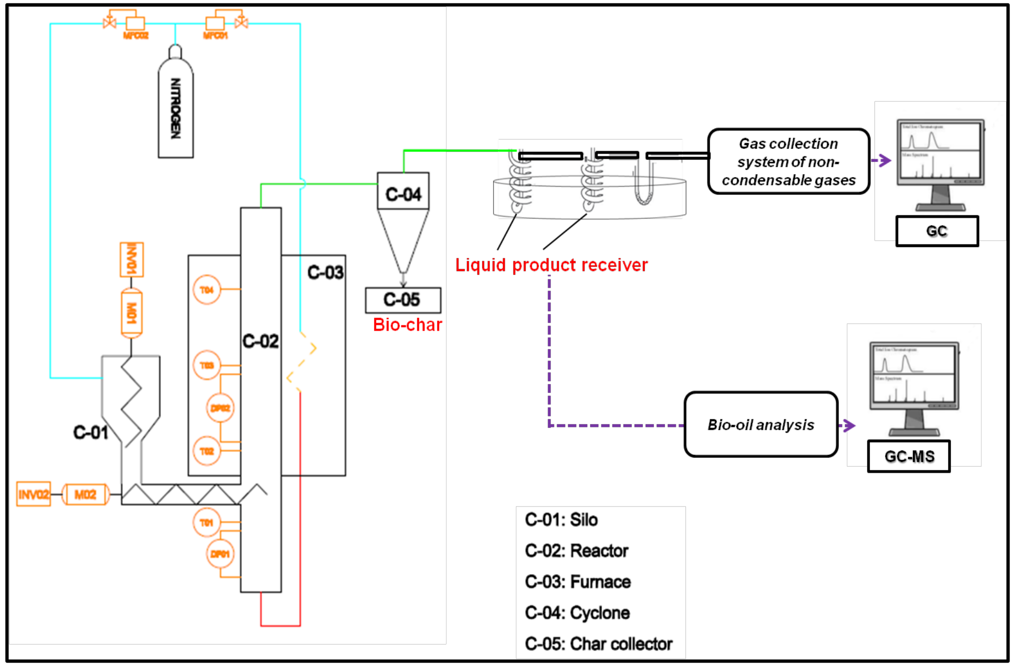
Pyrolysis – analysis conditions

- Pyrolysis experiments: 470-600°C
- GC Oven: 40 ◦C (hold 5 min), ramp at 10 ◦C/min to 300 ◦C (hold 7 min)
- GC injector temp.: 300 ◦C
- Split ratio: 1:150
- Column: Ultra Alloy-5 (15m length & 0.75mm diameter)
- Helium as inert gas
- m/z=45-500
- Peak classification: Nist11s library

Bench-scale fixed bed reactor

Micro-pilot continuous fluidized/riser bed reactor





Lazaridis et al. Catalytic fast pyrolysis of kraft lignin with conventional, mesoporous and nanosized ZSM-5 zeolite for the production of alkyl-phenols and aromatics , Frontiers in Chemistry, 6:295. 2018. doi: 10.3389/fchem.2018.00295

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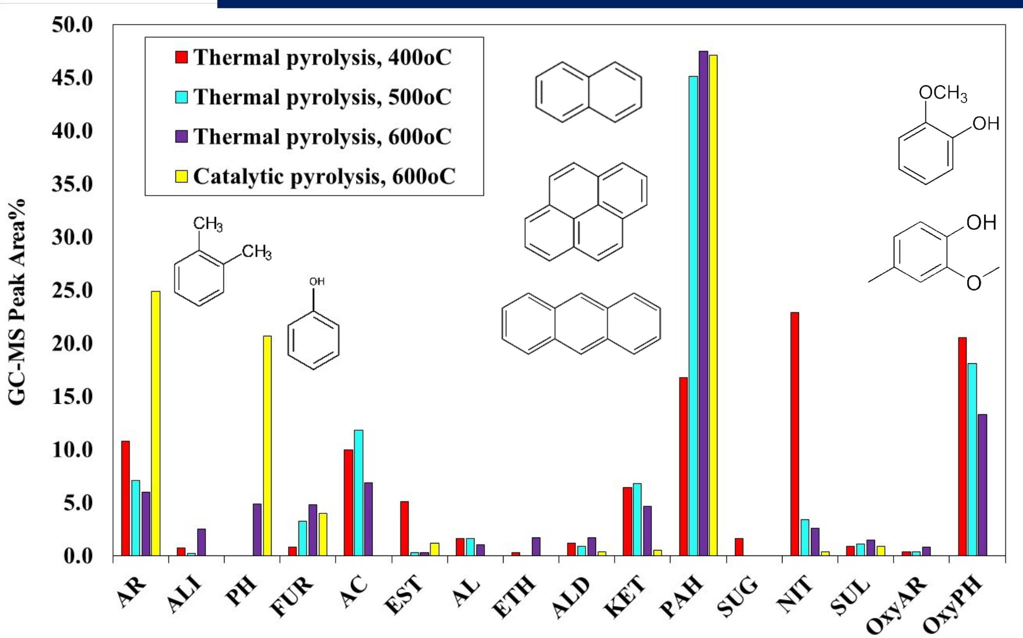
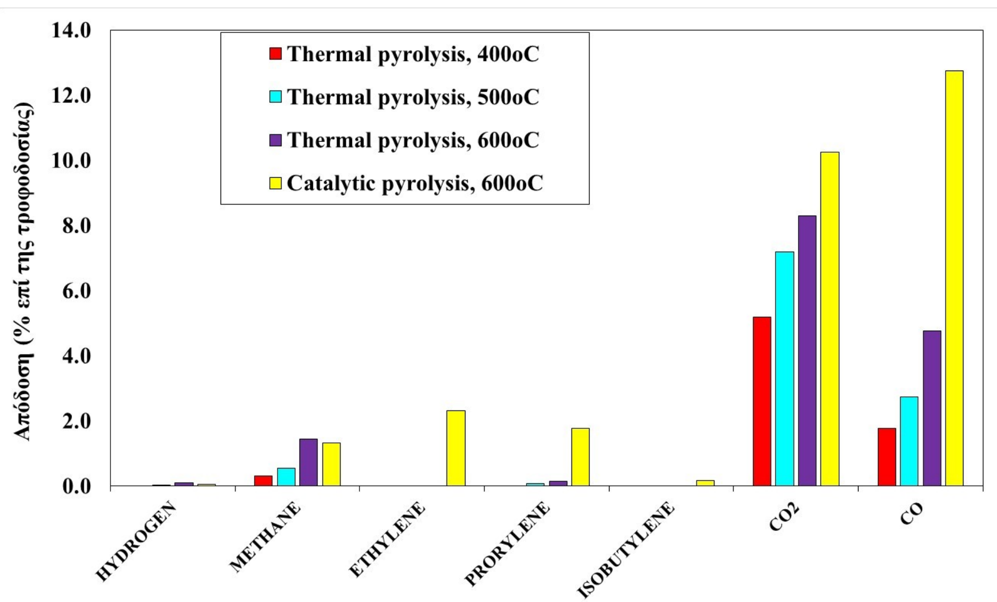
Fast pyrolysis of creosote-impregnated wood





Creosote impregnated Wood	Thermal pyrolysis			ZSM-5
	400°C	500° C	600° C	600° C
Total liquids (oil) (wt. %)	35.9	42.0	46.9	41.9
Gases (wt. %)	7.3	10.6	14.7	17.3
Total solids (ash + char / ash+char+coke on catalyst) (wt. %)	55.2	45.6	36.0	38.4
Mass balance (w	.4	98.2		6

Char

Thermal 400°C

Thermal 600°C

Catalyti c

HHV (MJ/Kg): 26.4 38.9

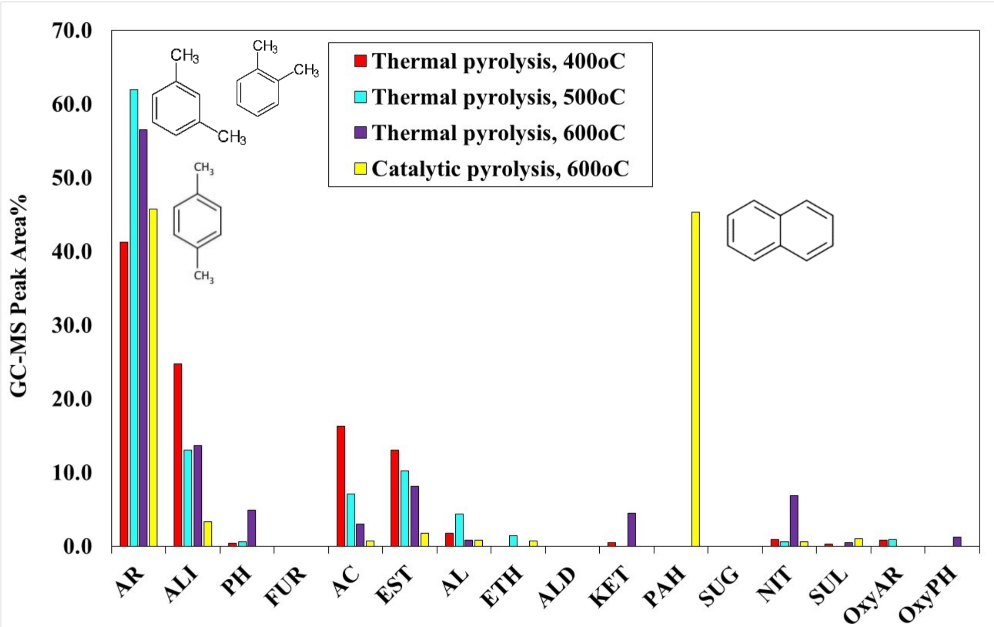
Slow pyrolysis of creosote-impregnated wood

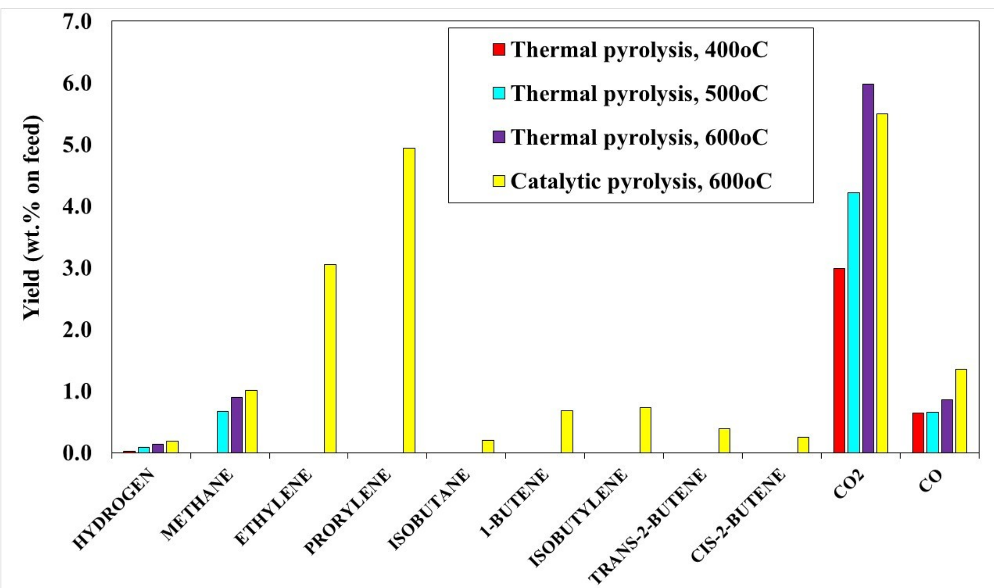
(Heating rate 30-50°C/min)

Creosote impregnated Wood	Thermal pyrolysis		
	400° C	**500° C**	**600° C**
Total liquids (wt. %)	45.7	47.9	52.5
Gases (wt. %)	11.5	12.9	15.0
Total solids (ash + char) (wt. %)	36.0	31.5	25.2
Mass balance (wt.%)	93.2	92.0	92.8

Creosote impregnated Wood	Thermal pyrolysis, 600°C		
	25 cm^3/min	**50 cm^3/min**	**100 cm^3/min**
Total liquids (wt. %)	46.9	51.2	52.5
Gases (wt. %)	23.5	19.6	15.0
Total solids (ash + char) (wt. %)	25.9	25.6	25.2
Mass balance (wt.%)	96.3	96.5	92.8

Fast pyrolysis of (dry) petroleum sludge

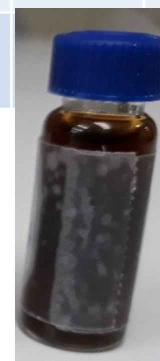




Petroleum sludges	Thermal pyrolysis			ZSM-5
	400°C	500°C	600°C	600°C
Total liquids (oil) (wt. %)	8.8	15.2	15.8	12.6
Gases (wt. %)	3.7	5.6	7.9	10.0
Total solids (ash + char / ash+char+coke on catalyst) (wt. %)	82.0	77.8	75.1	76.2
Mass balance (w %)	5		98.	3

Char

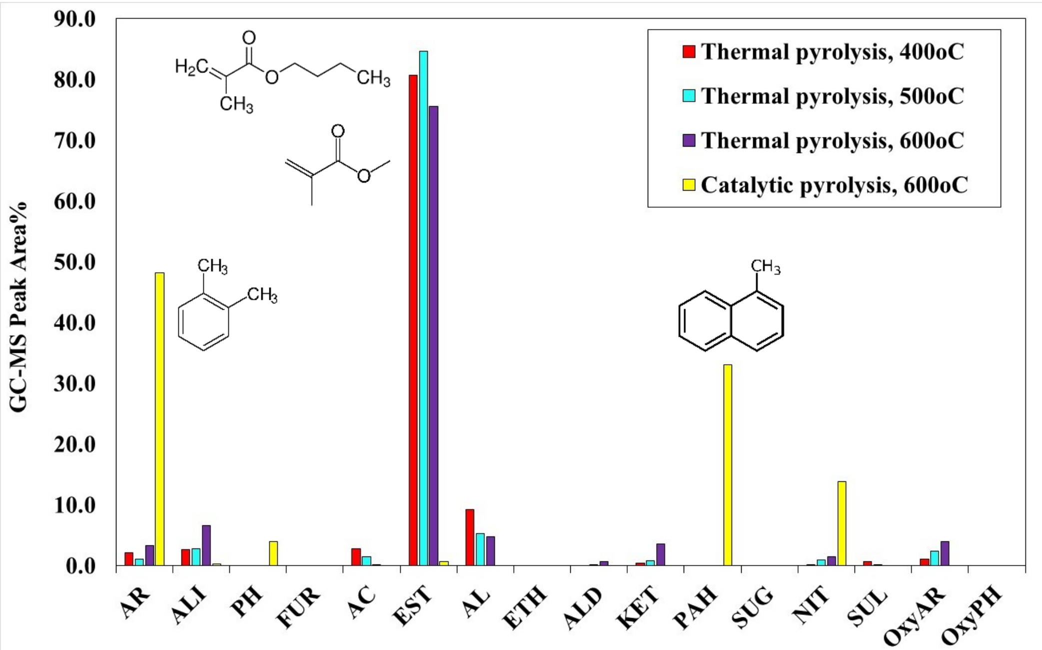
Thermal 400°C

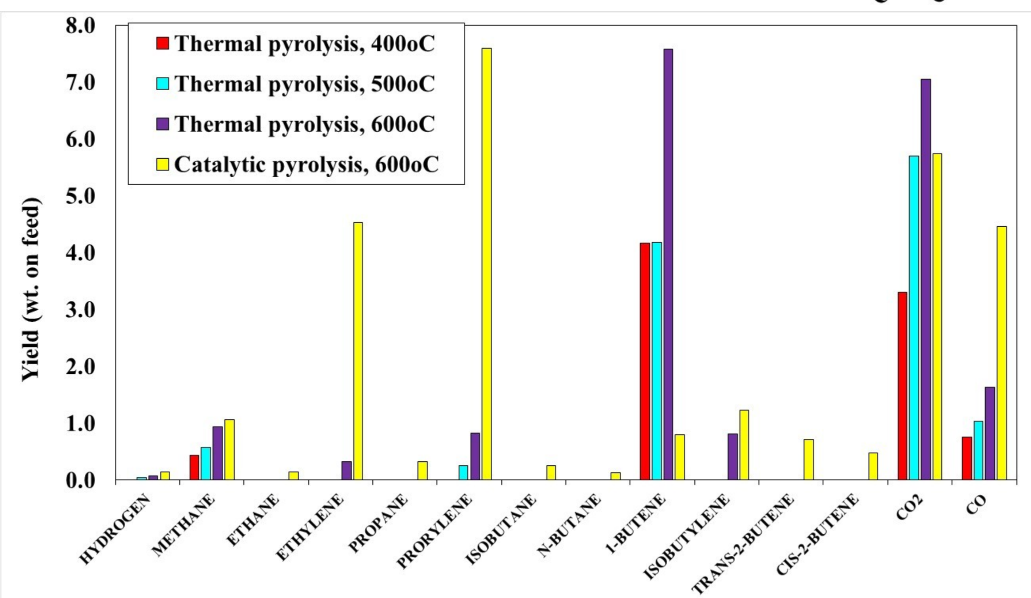


Thermal 600°C

Catalytic 600°C

Fast pyrolysis of residual paints





Residual (acrylic) paints	Thermal pyrolysis			ZSM-5
	400°C	500°C	600°C	600°C
Total liquids (oil) (wt. %)	40.3	46.3	36.0	32.4
Gases (wt. %)	8.7	11.8	19.2	26.3
Total solids (ash + char / ash+char+coke on catalyst) (wt. %)	45.3	40.6	36.9	38.3
Mass balance (w[illegible]	[illegible]3	[illegible]	91.[illegible]	[illegible]1

Char

Thermal 400°C

Thermal 600°C

Catalytic 600°C

Conclusions and outlook

- Tailored production of oil, char and gases by tuning of pyrolysis parameters (heating rate, temperature, vapor residence time)
- Higher T (ca. 400 □ 600°C) leads to higher oil & gases, and less char
- Composition/properties of products depend on process parameters
- Use of appropriate catalyst can effectively tune composition of oil & gases
- Oil can be used as bio-crude, drop-in fuels or source of chemicals
- Gases can be used as fuel or substrate (bio)chemical conversions
- Char/ash can be used as soil amendment, sorptive/catalytic material, filler, etc.

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Group

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