Valorization of organic hazardous wastes via pyrolysis

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Introduction

- The management of municipal and industrial organic solid wastes is one of the most crucial environmental problems in modern societies. According to the European Commission Directive 2008/98/EC, "the following waste hierarchy shall apply as a priority order in waste prevention and management legislation and policy: prevention; preparing for reuse; recycling; other recovery, e.g. energy recovery; and finally, disposal". Thus, it is clear that when the "re-use" is not possible, the production of energy via combustion/incineration or gasification and/or the recycling of the organic wastes via conversion to their primary building blocks or high added value chemicals and fuels, should be applied.
- To this end, one of the most important thermochemical processes in biomass valorization, that of pyrolysis, may offer a solution to the sustainable management of hazardous organic solid wastes.
- In this work, we studied the valorization of three representative types of solid organic hazardous wastes, i.e. wood containing creosote preservatives, residual paints & topcoats, and petroleum sludge and sediments, via fast and slow pyrolysis.
- In situ upgrading of the pyrolysis vapors was performed by the use of acidic zeolitic catalysts, towards a deoxygenated pyrolysis oil, enriched in aromatics, aliphatic hydrocarbons and phenols.

Experimental

Hazardous organic solid wastes

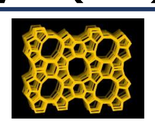
Wood containing creosote preservatives

Paint Residues on Scrap Metal

Petroleum Sludges and Sediments

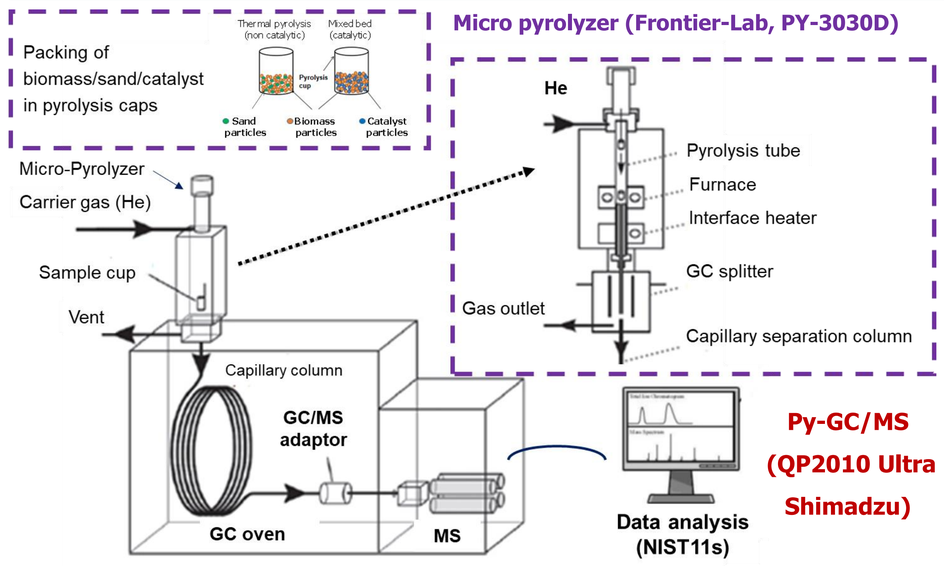
Catalysts for fast pyrolysis (CFP)

- **H-ZSM-5** (Si/Al = 11.5, 25, 40)
- **Mesoporous ZSM-5 zeolites**

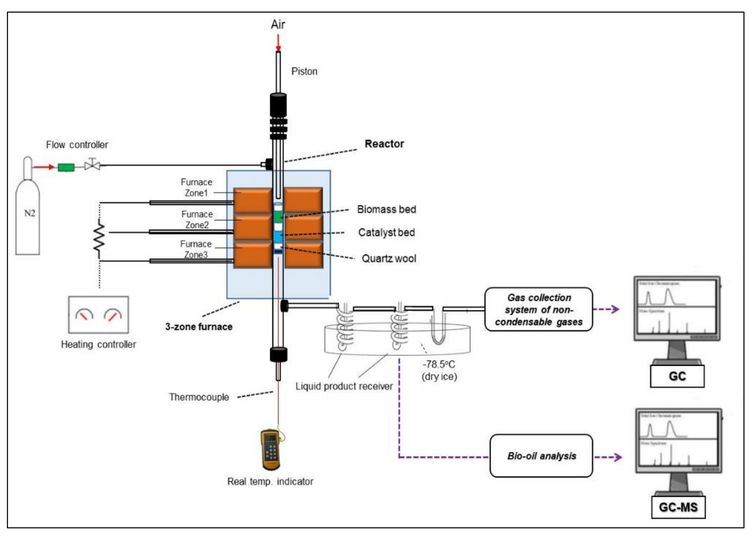


ZSM-5 (MFI)

Py/GC-MS system



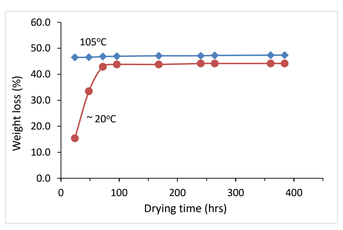
Fixed-bed down-flow unit



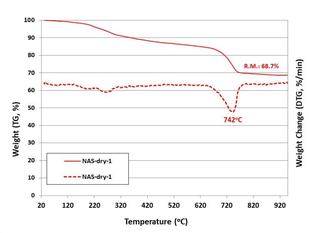
Results

Characteristics of petroleum sludge

Petroleum Sludge & Sediments

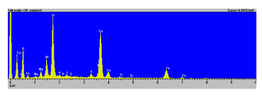


- The petroleum sludge collected from ship tanks contain high amount of volatiles
- Analysis of vapors suggested being mainly water vapor



- 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	5.52	5.90



Waste type	Ash (wt.%)
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

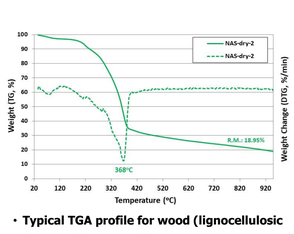
Characteristics of wood containing creosote

Wood containing creosote

Representative composition of beech-tar creosote

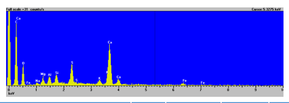
Phenol	C6H5OH	5.2%
o-cresol	(CH3)C6H4(OH)	10.4%
m- and p-cresols	(CH3)C6H4(OH)	11.6%
o-ethylphenol	C6H4(C2H5)OH	3.6%
Guaiacol	C6H4(OH)(OCH3)	25.0%
3,4-xylenol	C6H3(CH3)2OH	2.0%
3,5-xylenol	C6H3(CH3)2OH	1.0%
Various phenols	C6H5OH—	6.2%
Creosol and homologs	C6H3(CH3)(OH)(OCH3)—	35.0%

- 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)
Wood creosote	50.37	5.64	0.95	5.60	35.94	19.51	20.95



Waste type	Ash (wt.%)
Wood creosote	1.49

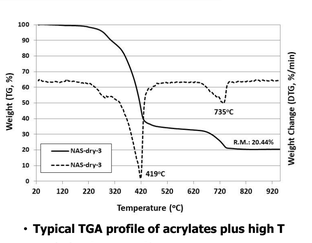
	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
% atom ratio (EDS)	3.2	6.0	7.6	9.6	-	16.4	5.7	46.3	-	5.2

Characteristics of residual paints

Residual paints

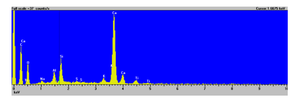
Representative composition of acrylate topcoats

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

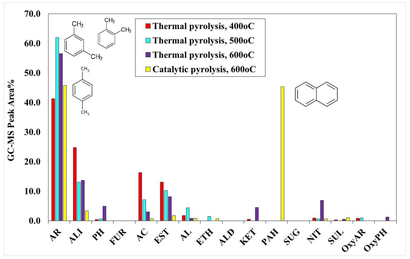
Waste type	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	HHV (MJ/kg) (calculated)	HHV (MJ/kg) (measured)
Residual paints	48.58	6.17	0.10	0.45	14.70	19.42	21.97



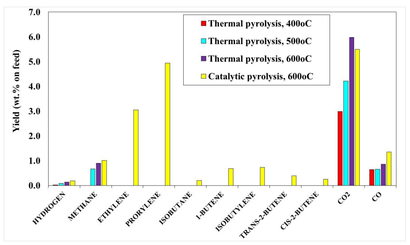
Waste type	Ash (wt.%)
Residual paints	30.5

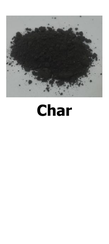
	Na	Mg	Al	Si	P	S	K	Ca	Ti	Fe
% atom ratio (EDS)	2.3	-	6.3	13.6	-	0.6	3.3	67.6	6.3	-

Fast pyrolysis of petroleum sludge

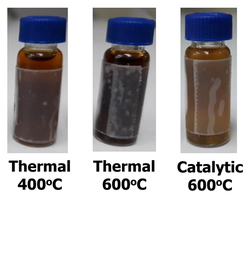


Petroleum sludges	Thermal pyrolysis			ZSM-5
	400ºC	500ºC	600ºC	600º C
Total liquids (oil) (wt. %)	8.8	15.2	15.8	12.6
Gases (wt. %)	3.7	5.6	7.9	10.0
Total solids (ash + char / ash+char+coke on catalyst) (wt. %)	82.0	77.8	75.1	76.2
Mass balance (wt.%)	94.5	98.6	98.8	98.8



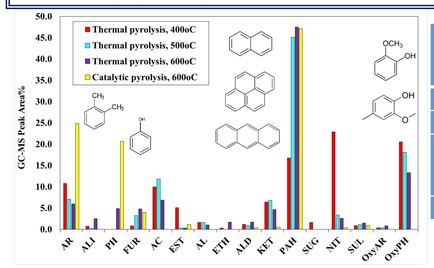


Char

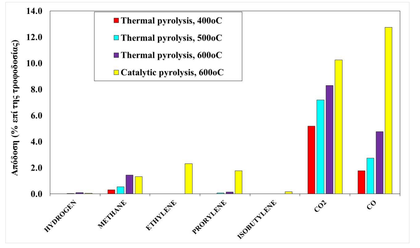


Thermal 400ºC | Thermal 600ºC | Catalytic 600ºC

Fast pyrolysis of creosote-impregnated wood



Creosote impregnated Wood	Thermal pyrolysis			ZSM-5
	400ºC	500ºC	600ºC	600º 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 (wt.%)	98.4	98.2	97.6	97.6



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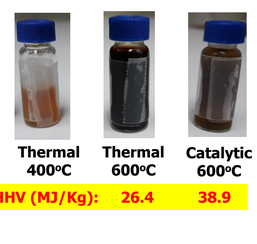
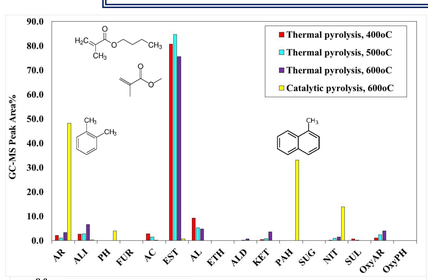


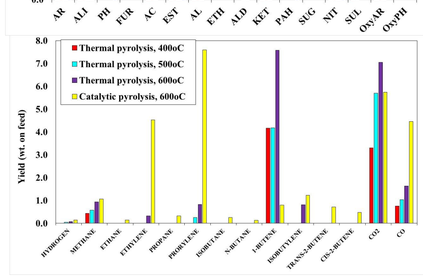
Thermal 400ºC | Thermal 600ºC | Catalytic 600ºC

HHV (MJ/Kg): 26.4 | 38.9

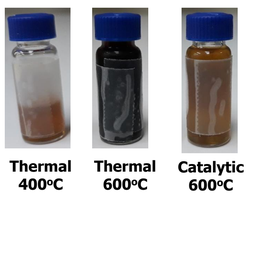
Fast pyrolysis of residual paints



Residual (acrylic) paints	Thermal pyrolysis			ZSM-5
	400ºC	500ºC	600ºC	600º 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 (wt.%)	94.3	98.7	91.1	97.1



Char



Thermal 400ºC | Thermal 600ºC | Catalytic 600ºC

Concluding Remarks

- Tailored production of oil, char and gases by tuning of pyrolysis parameters (heating rate, temperature, vapor residence time)
- Higher T (ca. 400 - 600ºC) 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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