Thermal and catalytic pyrolysis of polymer blends having composition similar to that originating in WEEE

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Aim of the work

- Catalytic pyrolysis & identification of pyrolysis products of four polymeric blends: ABS/HIPS/PC, ABS/HIPS/PC/TBBPA, ABS/HIPS/PC/PP and ABS/HIPS/PC/PP/TBBPA
- Evaluation of catalysts' effect on products distribution (formation of valuable products and reduction of brominated compounds)

Contents

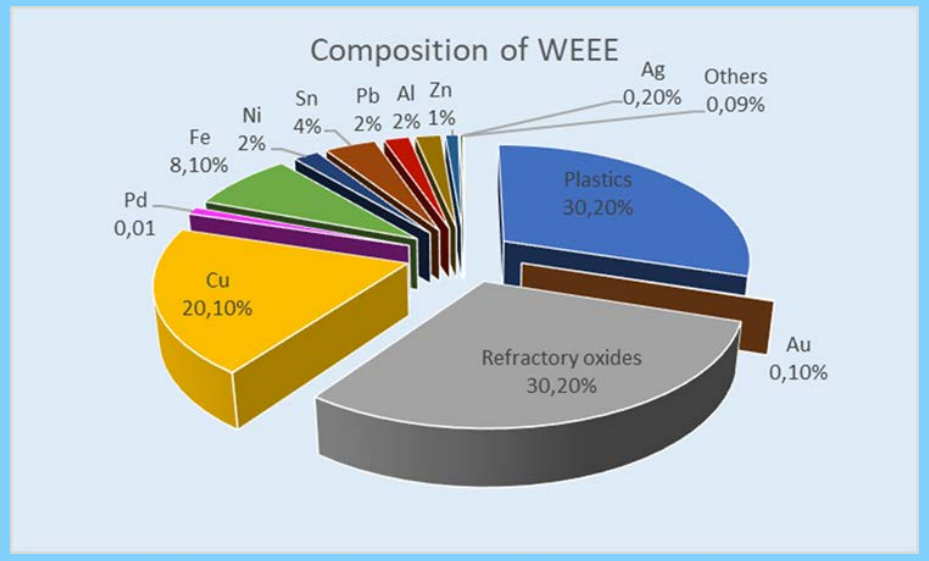
- Introduction
- Materials and methods
- Results
- Conclusions

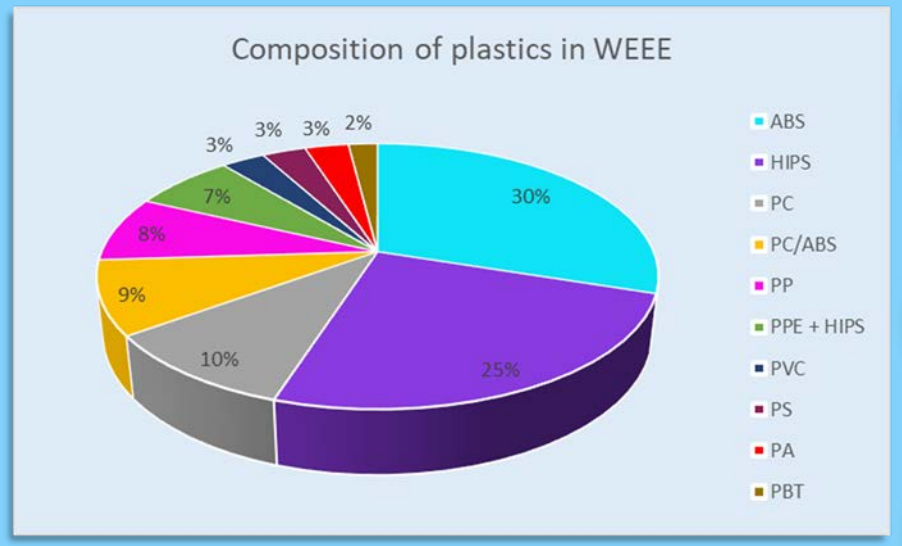
Introduction

- Waste electric and electronic equipment (WEEE) has increased enormously → due to rapid expansion and consumption of electronic devices and their short lifespan
- Due to their non-biodegradability → need for environmentally friendly solutions for their disposal

Composition of WEEE

- WEEE comprise various materials: glass, metals and plastics
- Plastics account for ~20-30 % of WEEE fraction
- Abundant polymers in WEEE: ABS, HIPS, PC
- WEEE usually contain additives: UV and thermal stabilizers, (brominated) flame retardants - BFRs, colorants, plasticizers, etc





Recycling of WEEE

- WEEE's handling via: landfilling, energy recovery, mechanical recycling and chemical recycling
- Among them chemical recycling (pyrolysis) → more advantageous and often selected as environmentally friendly method → monomers and secondary valuable materials can be produced and the liquid fraction can be used as fuel
- Pyrolysis takes place in an inert atmosphere, high temperatures (300–900°C) and in the absence/presence of catalysts
- The quality and distribution of pyrolysis products → affected by various parameters, such as: temperature, residence time, heating rate, presence of catalysts, etc.

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Materials

Materials (from Sigma-Aldrich):

- ABS poly(acrylonitrile-butadiene-styrene)
- HIPS (high impact polystyrene)
- PC (polycarbonate)
- PP (polypropylene)
- TBBPA (3, 3′, 5, 5′-Tetrabromobisphenol A)

Catalysts (from CERTH):

- Acidic: Al_2O_3 and ZSM-5
- Basic: MgO
- Fe/Al_2O_3 and Fe/MgO

Blends preparation

- Blends prepared via a twin-screw extruder (at 210°C)
- Extrudates → processed into films (hot pressing at 200°C)
- Four Blends:
  sample 4: 46% ABS, 39% HIPS and 15% PC
  sample 6: 41% ABS, 34% HIPS, 14% PC and 11% PP
  sample 8: 46% ABS, 39% HIPS, 15% PC and 9% TBBPA
  sample 9: 41% ABS, 34% HIPS, 14% PC, 11% PP and 9% TBBPA

Methods

- Evolved Gas Analysis (EGA)
- Single Shot Analysis

Pyrolyser (EGA/PY-3030D): He (purge gas) sample mass < 2 mg (ratio of blend's mass: catalyst's mass was 2: 1)

Methods

Evolved Gas Analysis (EGA):

- Information about decomposition temperature range
- Samples heated: 100 – 700°C, with 20°C/min

Single Shot Analysis:

- Pyrolyser coupled with GC/MS (Py-GC/MS)
- Determination of pyrolysis products at Tmax (0.5 min)
- Chromatographs → subjected to interpretation via Shimadzu post-run software (NIST 17 Library)
- SCAN mode in the settings before pyrolysis → scan whole spectrum
- Selected ion monitoring (SIM) mode → targeting specific ions (250, 252 and 254) → determination of dibromophenol

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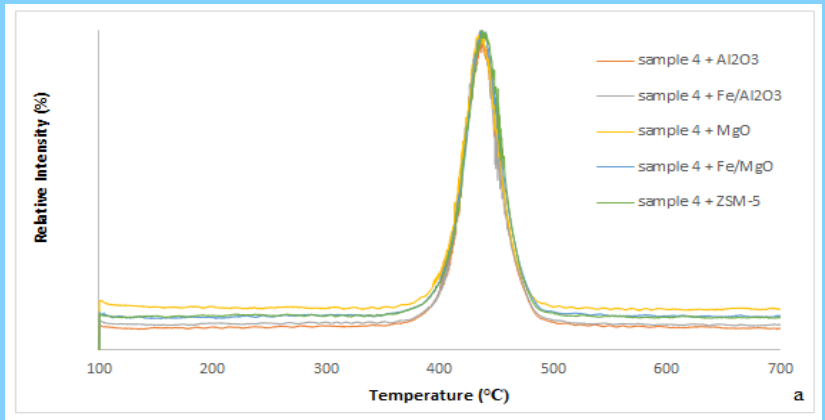
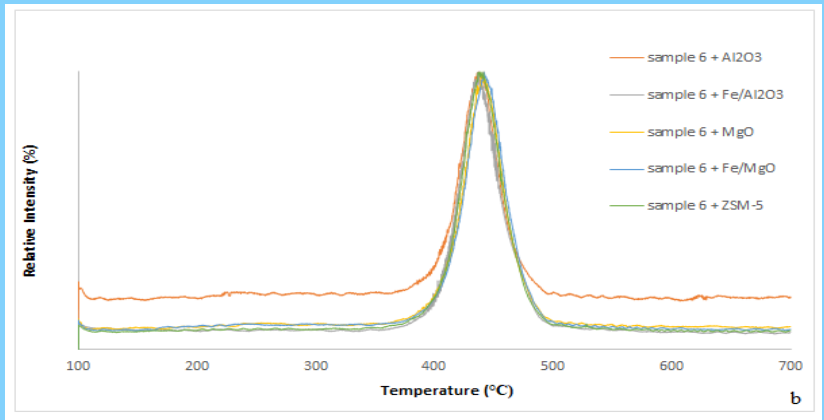
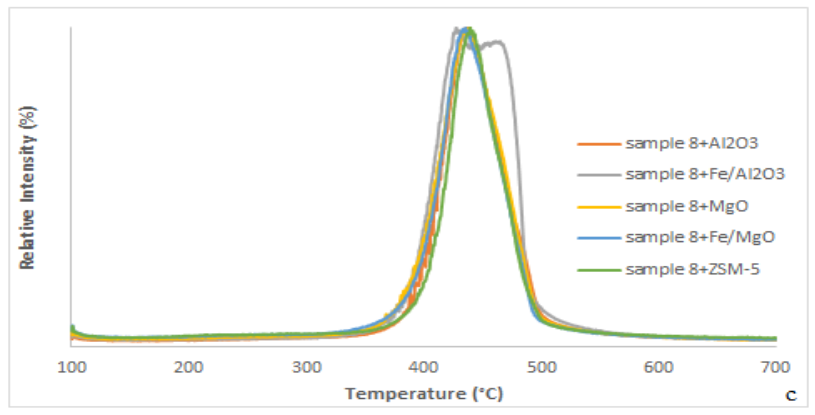
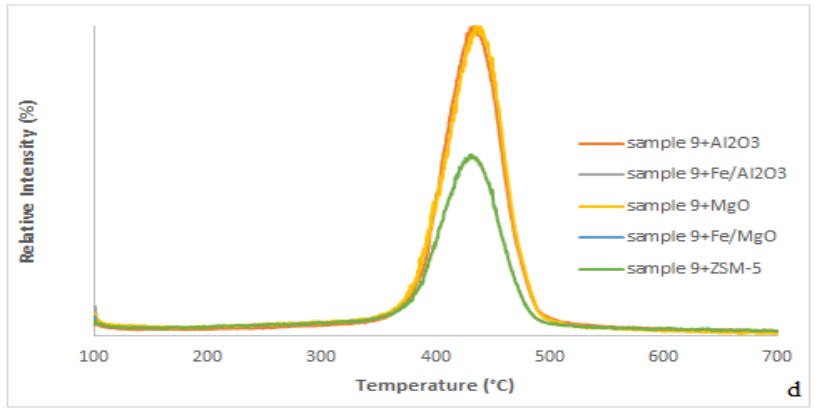
Degradation Results from EGA



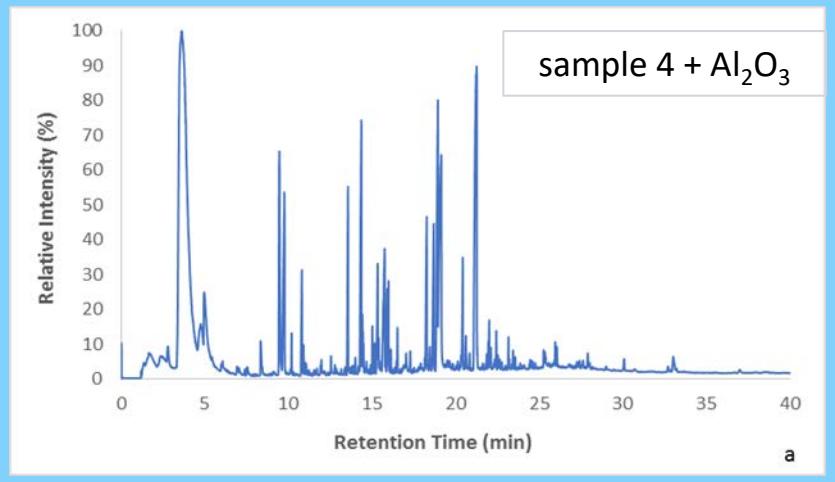


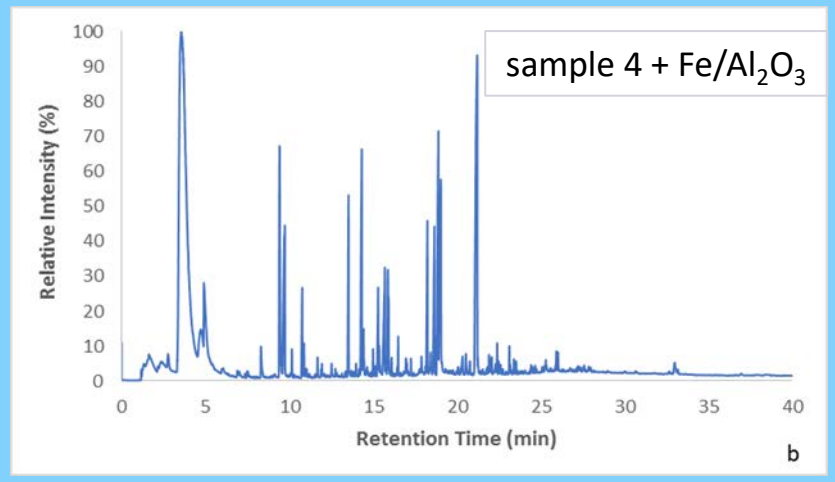


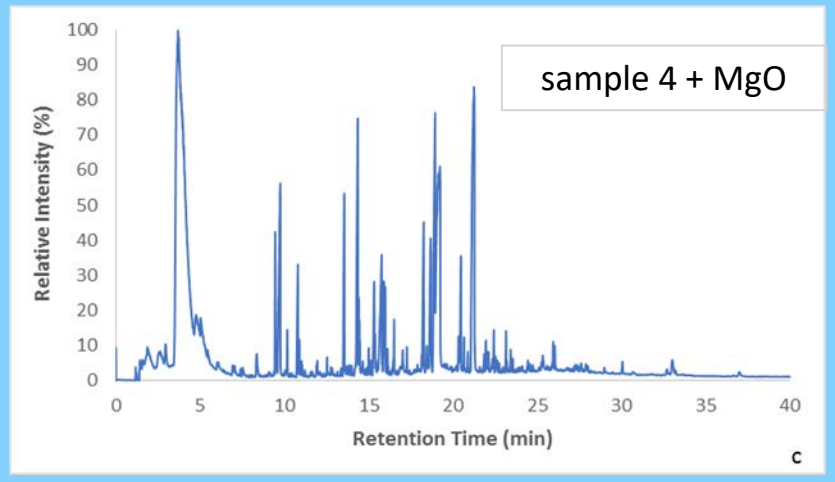


- The degradation of all blends in the presence of all catalysts → similar → begins and ends at very close temperatures (regardless of the type of the catalyst)
- The different catalysts had almost no effect on Tmax → ~ 430 - 440°C

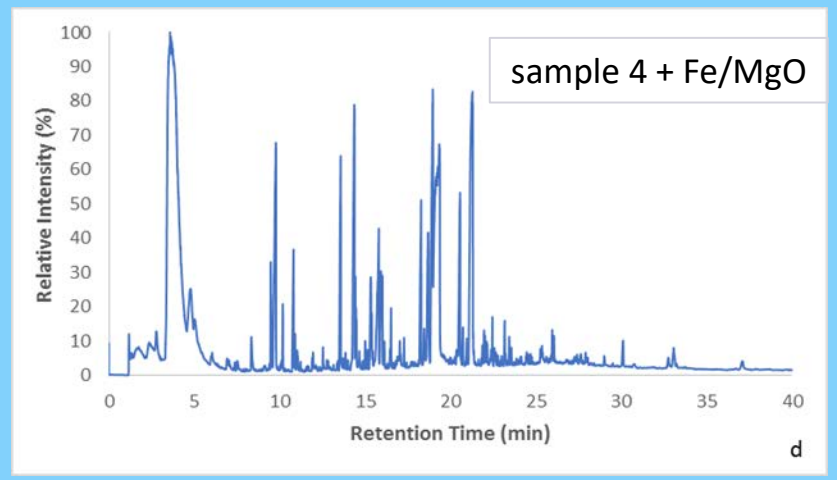
Chromatographs after catalytic pyrolysis at Tmax, for sample 4

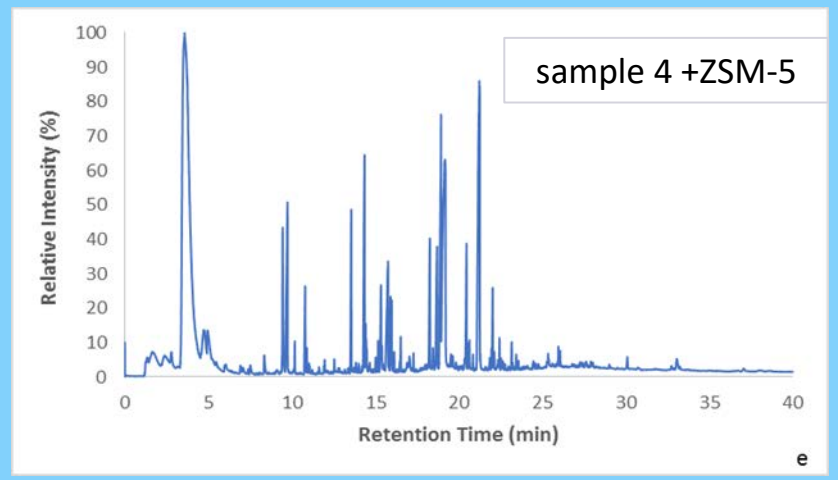






Chromatographs after catalytic pyrolysis at Tmax, for sample 4





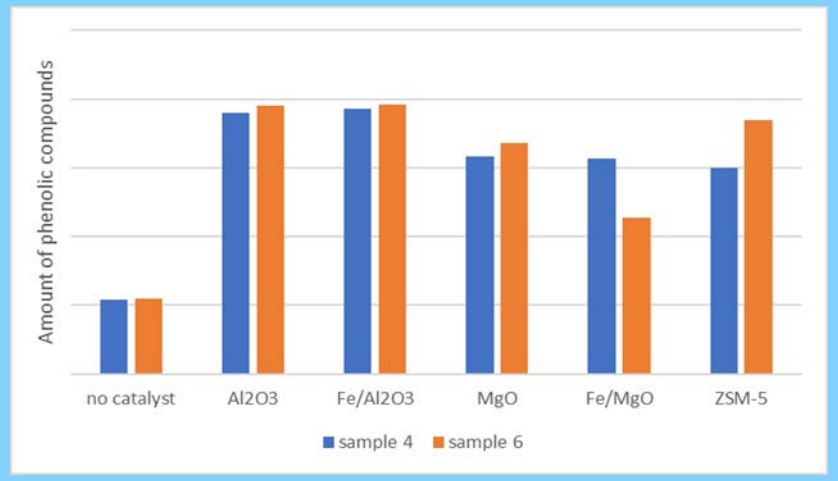
- Dominant peaks → received within 25 min
- During the last 5-10 min → no peaks obtained
- Chromatographs: similar → differences: peaks' intensity and number
- Same observations in cases of sample 8, 6 and 9

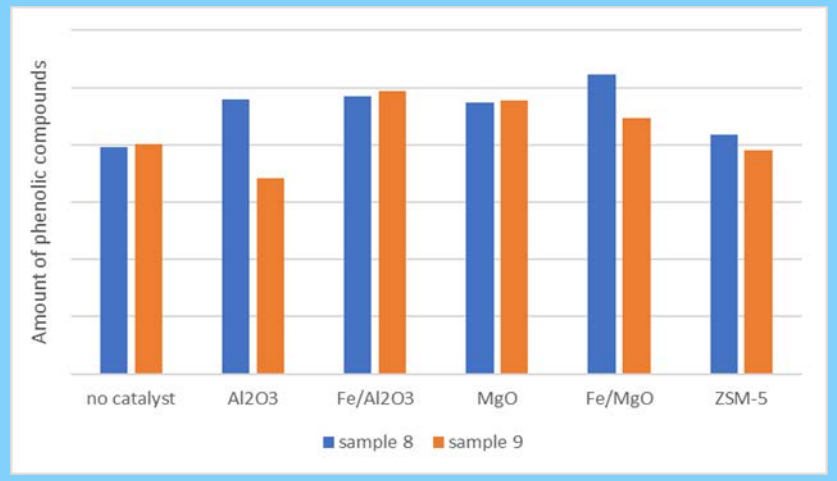
Main products obtained after catalytic pyrolysis of blends

- Many products in the presence of each catalyst → same: such as styrene, alpha-methylstyrene, benzenebutanenitrile, etc. → appearing at the same retention times → due to the degradation of the polymers; catalysts enhance their production
- Benzene derivatives (range of C_8 – C_{10}) (e.g. styrene), various aromatic nitrogenated compounds (e.g. benzenebutanenitrile), aromatic HC and phenols → high added value products → used as chemical feedstock for the production of new products
- Catalysts enhance the formation of phenolic compounds with one or two aromatic rings, including phenol, p-isopropylphenol, p-isopropenylphenol, 4-(1-methyl-1-phenylethyl)-phenol
- In cases of sample 4 & 6 (absence of TBBPA) → phenolic compounds (except for Biphenol A) were formed only when catalysts were used
- In cases of sample 4 & 6 (absence of TBBPA) → all catalysts favoured the production of phenolic compounds

Main products obtained after catalytic pyrolysis of blends

- In cases of sample 8 & 9 → catalysts increased the production of phenolic compounds → since they were also formed during their thermal pyrolysis because of TBBPA's presence in these blends

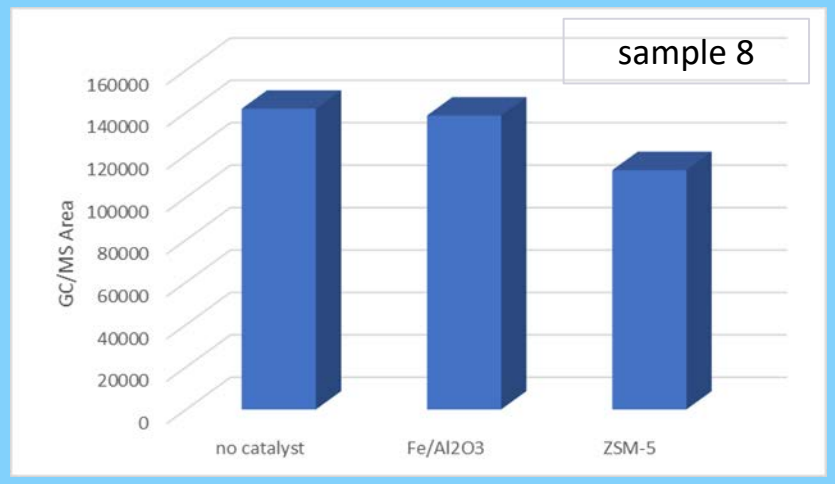


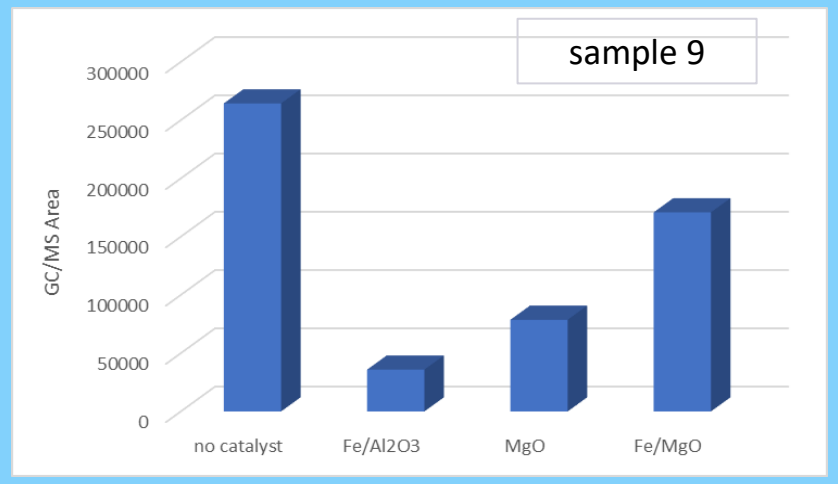


- Regardless of the blends' composition or the absence/presence of BFR → larger amounts of phenolic compounds → in case of Fe/Al_2O_3 (with the exception of sample 8, where it was the second one, after Fe/MgO)
- Catalyst's efficiency → its properties (for instance acidity) and Fe presence, → literature: Fe particles promote the formation of phenolic compounds

Catalysts' effect on debromination of sample 8 & 9

- In case of sample 8: SCAN and SIM mode → ZSM-5 the best catalyst (~20% debromination according to SIM mode) → Fe/Al_2O_3 reduced a little the bromine content
- In case of sample 9 → most effective catalysts: Fe/Al_2O_3 (best debromination ~89%) > MgO (~75% bromine reduction) >Fe/MgO (~40% debromination)





Catalysts' effect on debromination of sample 8 & 9

- The debromination efficiency → attributed to catalysts' textural properties, such as porosities and acidities
- Fe/Al_2O_3 → exhibited great debromination effect in both blends, despite the difference in their composition → Fe particles undeniably played a vital role in its debromination effect (literature: Fe particles achieve high debromination efficiencies)

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Conclusions and suggestions

- The degradation of all blends in the presence of all catalysts → quite similar (one-step mechanism)
- Catalysts → negligible effect on the degradation temperature of each blend (Tmax were very close; within the range of 430-440°C)
- Phenolic compounds → dominant products obtained (when catalysts were used) → can be used as feedstock in chemical industries
- In case of the non-brominated blends (sample 4 and 6) → phenolic compounds (with the exception of Bisphenol A) → only when catalysts were used
- In case of the brominated blends (sample 8 and 9) → phenolic compounds → already formed during thermal pyrolysis → catalysts enhanced their production

Conclusions and suggestions

- All catalysts for all blends tested (except for ZSM-5 and Al_2O_3 in sample 9) → increase in the phenolic products → the best in most cases: Fe/Al_2O_3
- Debromination in case of sample 8 → ZSM-5 and Fe/Al_2O_3
- Debromination in case of sample 9 → Fe/Al_2O_3 > MgO >Fe/MgO
- Fe/Al_2O_3 → efficient catalyst both for the reduction of bromine and the increase of the phenolic fraction (due to its properties and the presence of Fe particles)
- Fe particles → low cost → Fe/Al_2O_3 could be used as a catalyst in brominated plastics from real WEEE

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Thank you very much for your attention!