VSB TECHNICAL UNIVERSITY OF OSTRAVA | ENERGY AND ENVIRONMENTAL TECHNOLOGY CENTRE | ENET CENTRE

The use of polymer compounds in the deposits from the combustion of briquettes in domestic heating as an identifier of fuel quality

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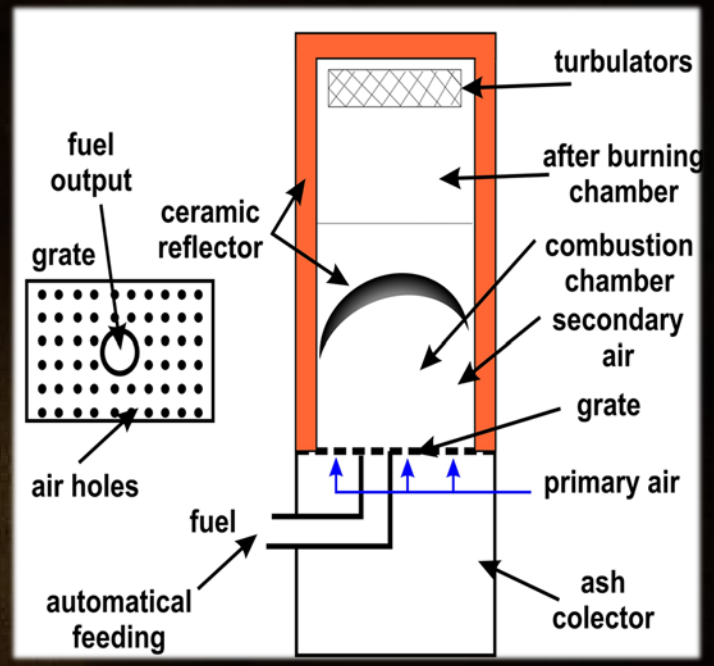
Aim of the work

- Verify the possibility of identifying the quality of briquettes burned in domestic boilers based on the chemical composition of deposits
- Influence of the polymer and additive admixture (in briquettes), specific organic compounds have been selected and monitored in deposits during combustion at domestic boilers



EC3

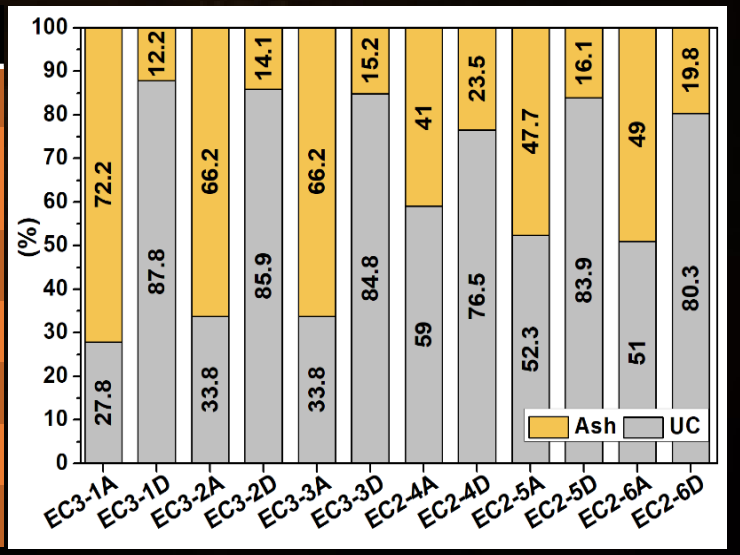
- The briquettes were burned in continuous burning boilers of emission class EC2 and EC3, defined according to EN 303-5 with manual stoking
- The combustion was conducted for eight hours

	WM - EC2	WW - EC2	WM - EC3	WW - EC3
Deposits in boiler (g/kg fuel)	2.38 ± 0.29	0.38 ± 0.08	0.8 ± 0.12	0.44 ± 0.13
Ash (g/kg fuel)	41.9 ± 6.48	6.18 ± 2.15	23.5 ± 4.33	6.52 ± 1.44
Fuel consumption (kg/h)	4.48 ± 0.39	4.06 ± 0.72	4.03 ± 0.37	5.22 ± 1.27

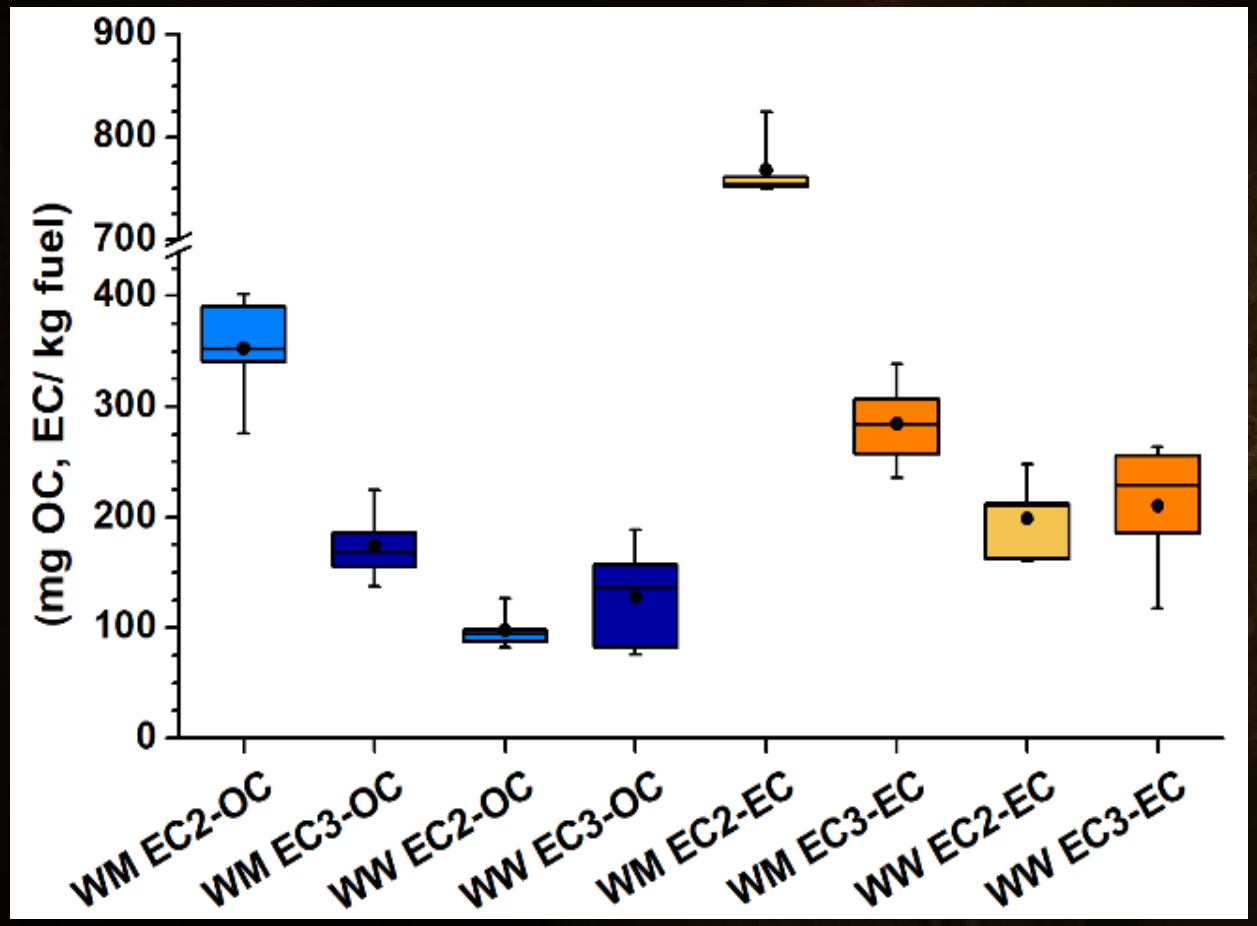
Basic properties of deposits

- The production of by-products when WWB and WMB are burned in the EC2 boiler shows that burning WM produces up to **6 times** more **deposits** and about **2.5 times** more **ash** per kg of fuel
- Burning WMB in an EC3 boiler produces **2.5 times** more **deposits** and **1.5** more **ash** than burning WWB
- Significant relationship between the **UC concentrations in deposits** and the **amounts of captured UC** was found (**r = 0.97**)
- Significant relationship between UC and OC has been demonstrated, indicating that the amount of **OC increases** with **decreasing UC levels** (**r = 0.84**)

Product	UC	Ash	C	H	N	S	O	O/C	EC	OC	OC/EC
	%								%		
Briquettes WW		0.33	48.5	5.91	0.14	0.41	44.74	0.81			
Briquetes WM		1.95	46.3	5.42	1.64	0.71	44.01	0.83			
EC3-AVG	86.2	13.8	66.6	3.27	3.60	0.17	12.75	2.93	37.5	22.7	0.60
EC3-STD	1.48	1.48	2.36	0.21	0.61	0.03	1.19	0.21	1.78	1.23	0.06
EC2-AVG	80.2	19.8	63.3	2.97	2.08	0.39	11.88	3.23	43.3	17.8	0.41
EC2-STD	3.70	3.70	6.91	0.55	0.36	0.05	4.12	1.84	4.28	2.50	0.08



Organic and elemental carbon in deposit

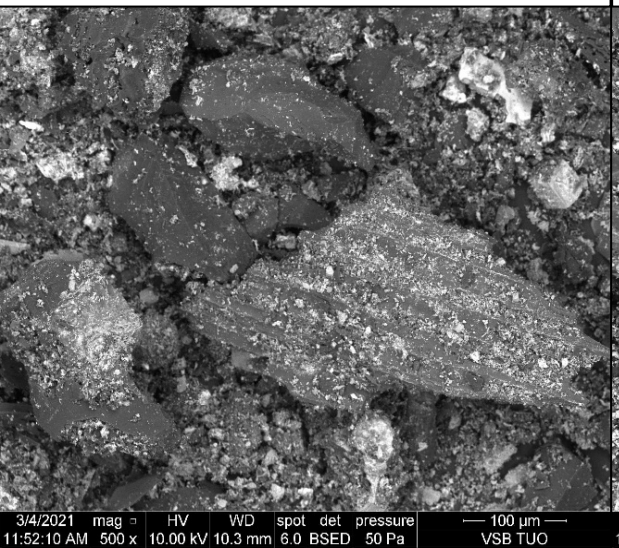


- The amount of OC produced in the combustion of **WW** is about **3 times higher** than for **WMB** in the **EC2** boiler, for **EC** about **4 times higher**
- In the **EC3 boiler**, the difference between the amount of EC and OC produced from the combustion of **WW** and **WMB** is less pronounced **(1.4×)**
- When burning **WMB**, the production of **EC** and **OC** in the **EC2 boilers** is up to **3 times** higher than in the **EC3 boilers**

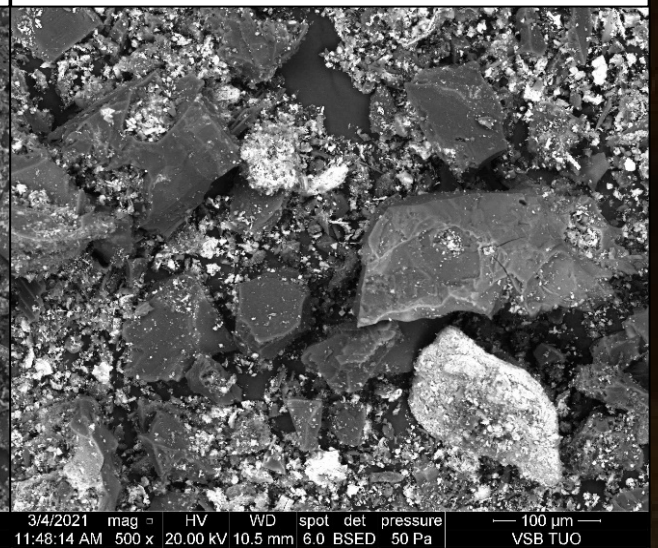
The inorganic particles

- Different conditions during the combustion process in the two boilers (temperature) could also be confirmed by mineralogical phase analysis of the deposit by a calcite difference or by the transition of calcium to the amorphous phase
- Deposits from EC2 contain **10.6 ± 2.0%** of calcite, while deposits from EC3 contain **3.6 ± 0.6%**
- Inorganic particles (white) are made up of a mixture of **KCl**, **K-Mg-Cl-PO_4**, **Fe oxides** and **$CaCO_3$**
- In the deposit sample from the EC2 boiler, the amount of inorganic particles is higher
- The inorganic particles mostly crystallize on the surface of carbon particles, in some cases filling the cavities in the melt or dissolving in the melt

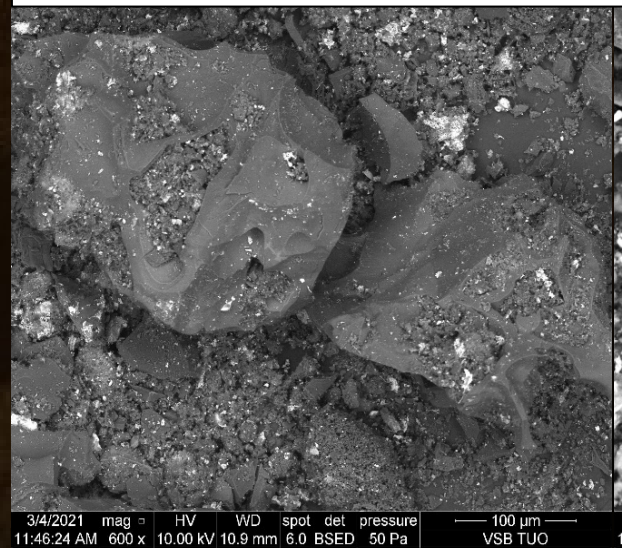
The structure of the original ligno-cellulose matrix

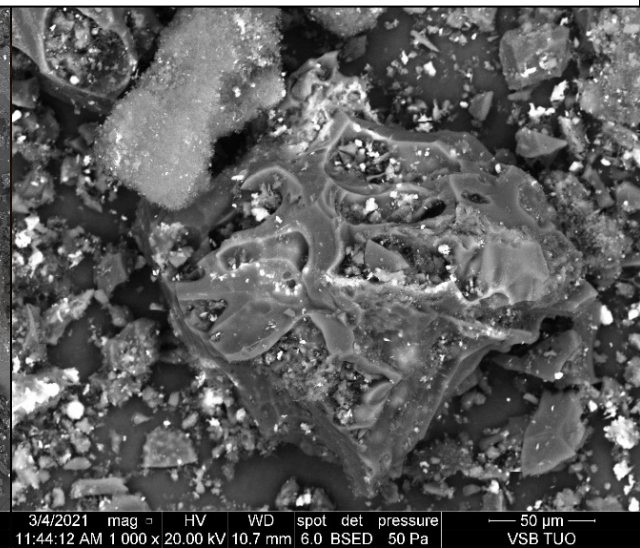


Particles in the deposits from EC2 boiler after the combustion of WM briquettes



Particles in the deposits from EC3 boiler after the combustion of WM briquettes



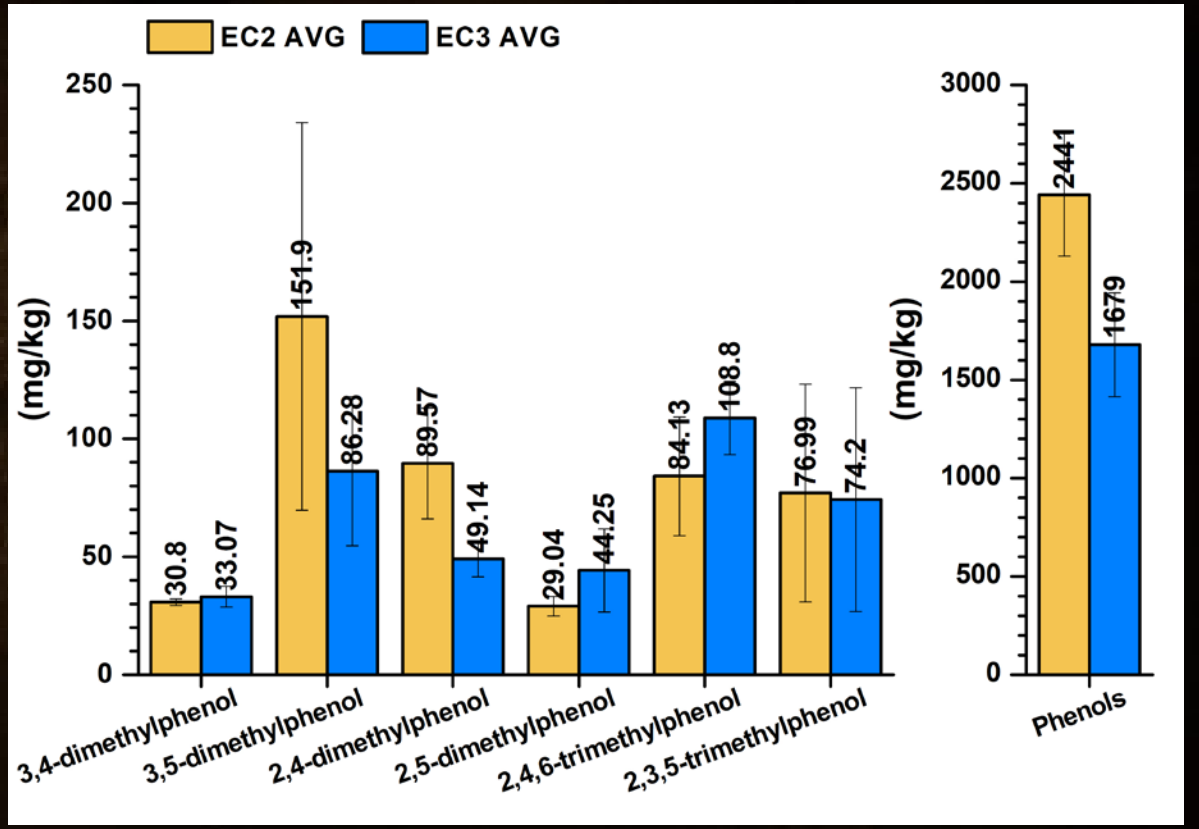


Chemical compounds identifying resins and adhesives in the deposits

Phenol-formaldehyde resins (PF-R)

- PF-Rs are thermosetting resins with a vast application potential, especially in furniture manufacturing
- **Dimethylphenols**, **trimethylphenols**, are present in deposits from burning WMB
- Formaldehyde and phenol are the main product of thermal degradation (TD) of PF-R, but it cannot be used as an indicator for burning PF-R (phenol is also produced TD of lignin)
- The difference in the concentrations of dimethylphenols and trimethylphenols in deposits from the combustion of WM briquettes in boilers EC2 and EC3 is not significant

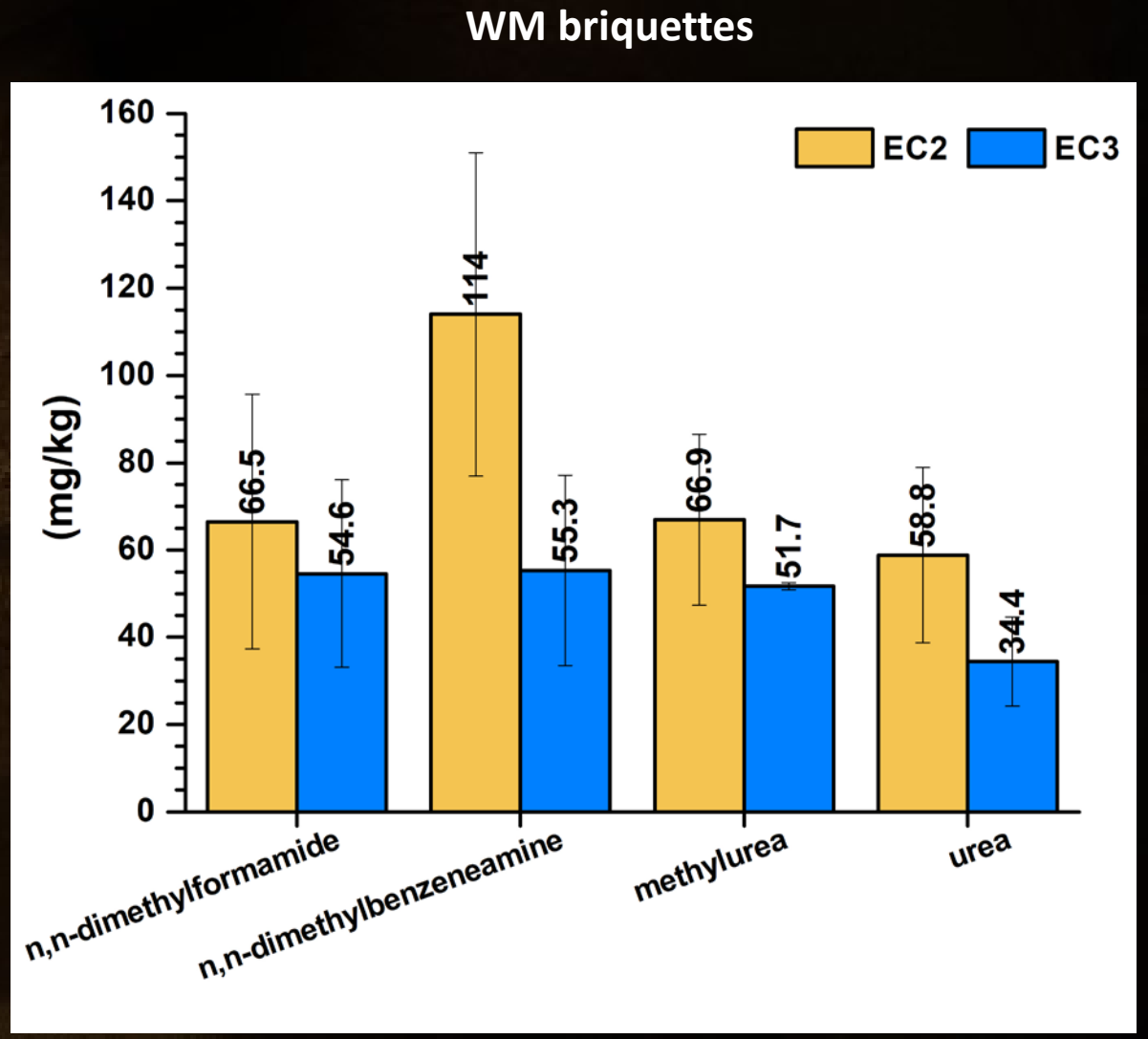
WM briquettes



Chemical compounds identifying resins and adhesives in the deposits

Urea-formaldehyde resins (UF-R)

- UF-R is one of the most important amino-resins; the most frequently used adhesives for sticking wood, veneering,, particleboard, plywood, ect.
- PF-R, the deposit from boiler EC3 shows lower concentrations of compounds, demonstrating the presence of UF-R in the fuel used than the deposit from EC2
- n,n-dimethylbenzene amine in deposits from EC2 at **2 higher** concentrations than in deposits from EC3

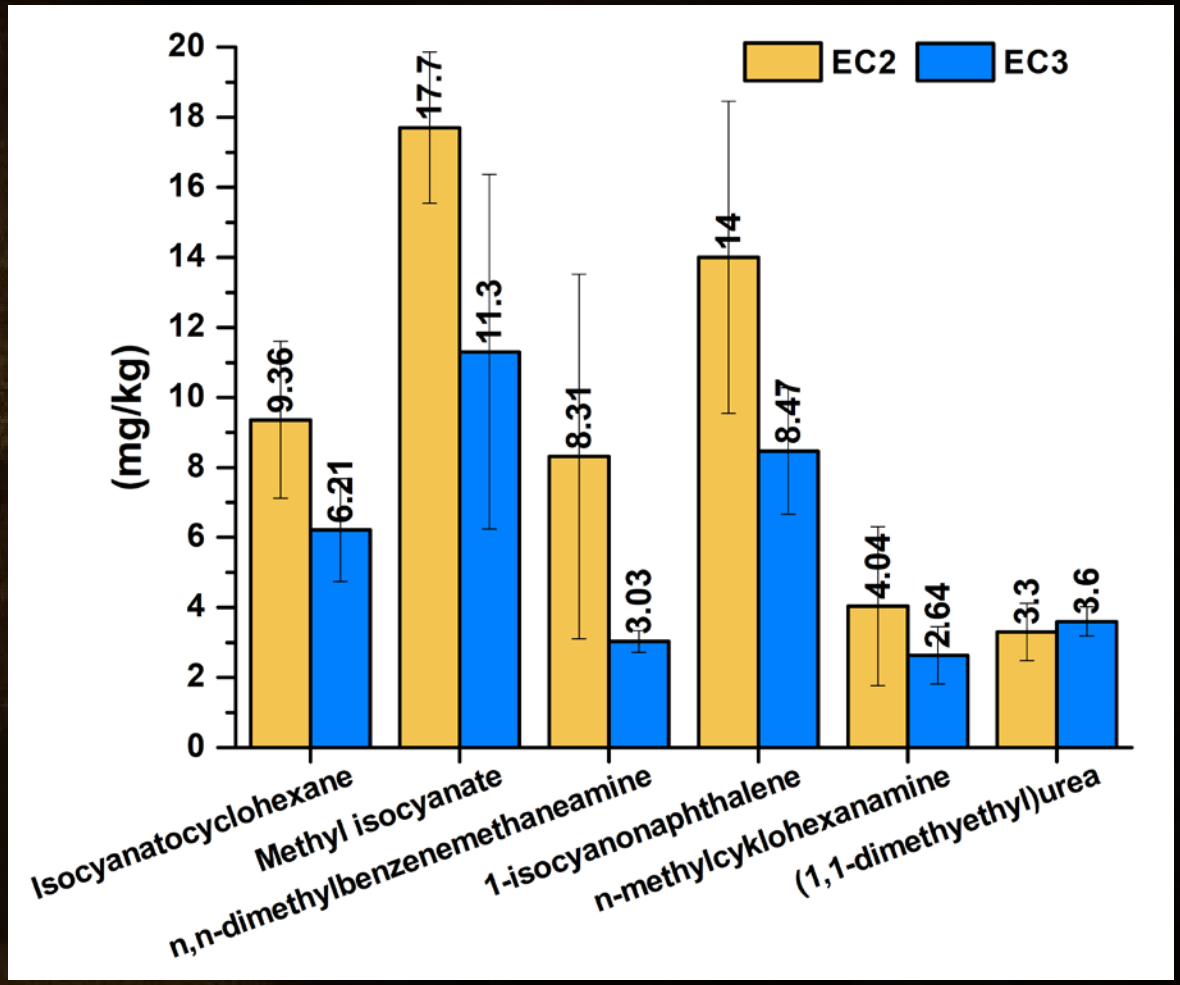


Chemical compounds identifying resins and adhesives in the deposits

Polyurethanes in glues, lacks and adhesives

- Polyurethanes (PU) are classified as condensation polymers which consist of different segments connected by various chemical bonds
- In the deposits from WMB combustion, compounds with isocyanates have been identified as coming from thermal degradation of PU

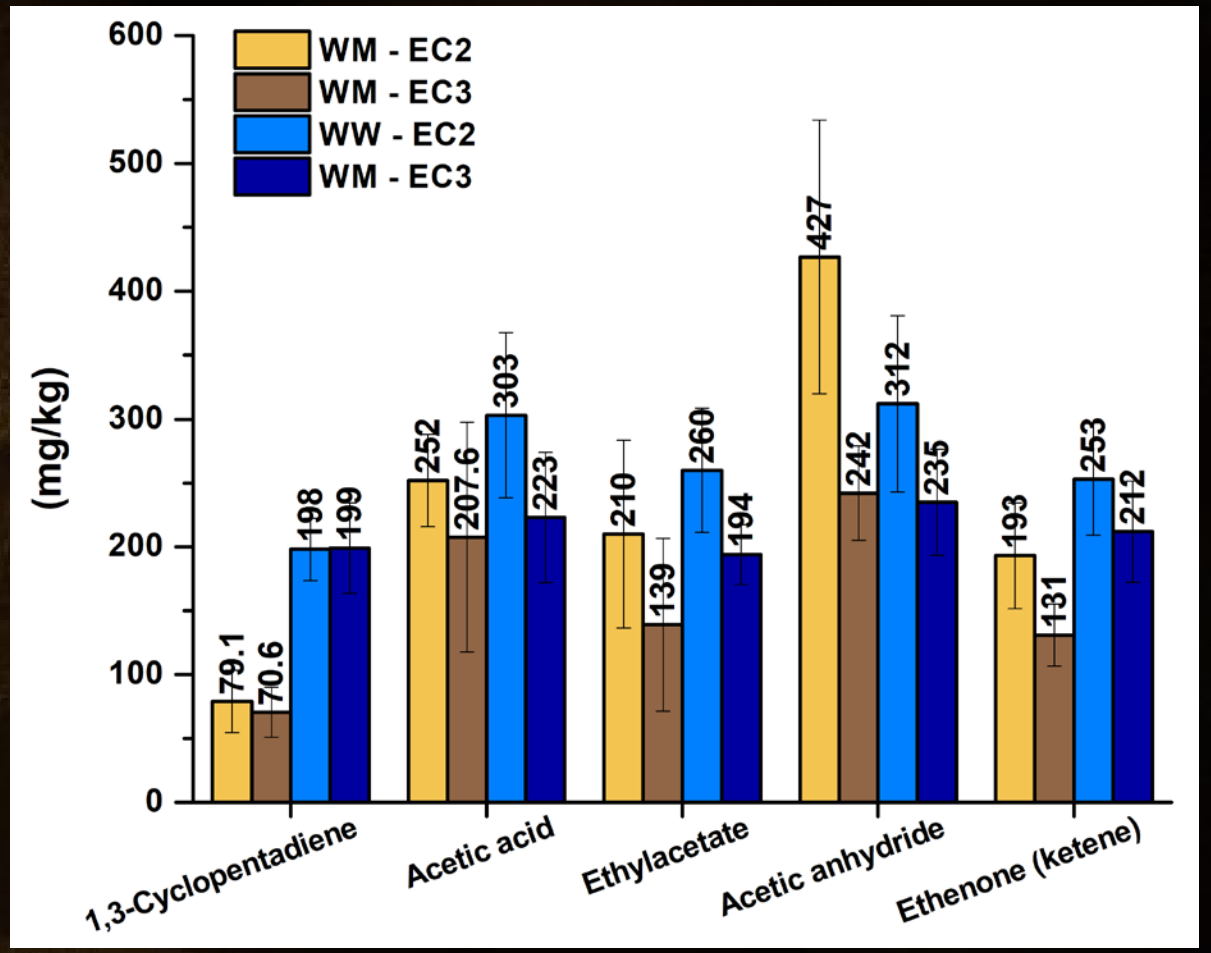
WM briquettes



Chemical compounds identifying resins and adhesives in the deposits

Polyvinyl acetate (PVAc)

- PVAc is one of the thermoplastics; widely used glue in wood processing
- In the deposits from the combustion of **WMB**, acetic anhydride is found in the highest concentration for EC2 (37 wt.%) and 31 wt.% for EC3 and from **WWB** has lower concentrations both for EC2 (24 wt.%) and EC3 (22 wt.%)
- Higher levels of organic compounds from TD of PVAc in the deposits from WW briquettes are affected by higher amounts of used waste wood (decks, fries, claws) containing PVAc adhesives



Chemical compounds identifying resins and adhesives in the deposits

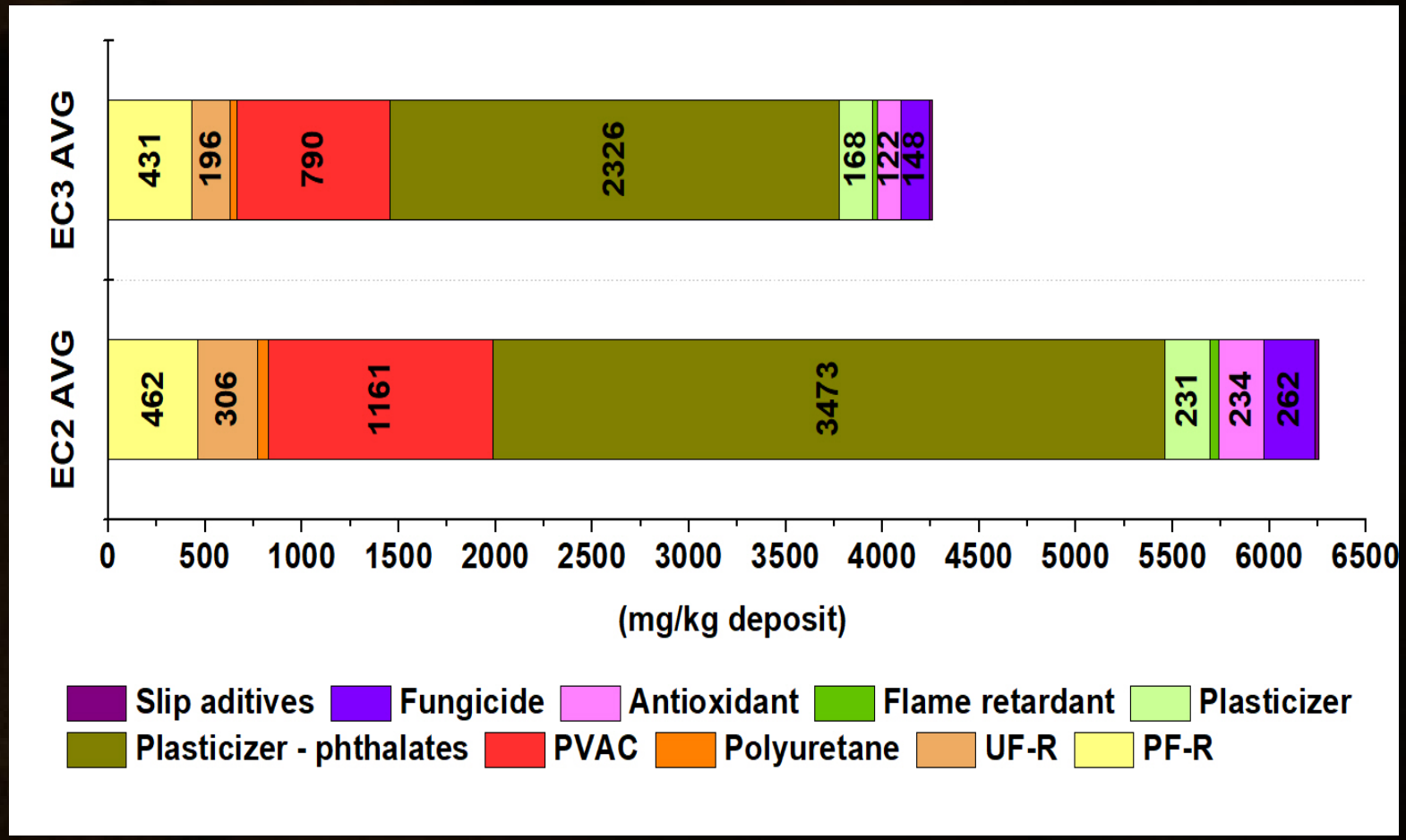
ADDITIVES

- Most wood products contain additives
- The identified **phthalates** were: **DEHP**, **dibutylphthalate**, and **diisobutylphthalte**
  - There was no statistically significant relationship between phthalates concentrations and EC, OC or UC to confirm the preferential carbon binding of phthalates
- **Non-phthalate plasticisers**: **Kodaflex TXIB** in WM deposits from **EC2** boilers occurs at about **1.5 times** higher concentrations than in the **EC3**
- **Flame retardants: 1-propanol:2-chloro phosphate** and **p-terphenyl** have been identified
  - The concentration of flame retardants in the deposits from the **EC2** boilers is about **45% higher** than in the deposits from the EC3 boilers
  - Concentration of flame retardant and the amounts of OC **(r = 0.90)** and for **EC (r = 0.95)**
- **Antioxidants:** deposit contains **butylated hydroxytoluene** (BHT) and **thiourea**
  - BHT has twice higher concentrations in EC2 than in deposits from the EC3 boilers
  - Thiourea concentrations are comparable in both types of deposits
  - A relationship between the ash content and BHT was found **(r = 0.92)**

Chemical compounds identifying resins and adhesives in the deposits

ADDITIVES

- **Slip aditives**: **erucamide (13-docosenamide),** erucamide concentrations in the EC2 are **1.8 times** higher than in EC3
- **Fungicide**: **phthalimide, t**he deposits from the WMB combustion contain about **1.8 times** more concentrations of phthalimide than EC3



Conclusion

- Higher concentrations of compounds characterizing synthetic polymers and additives were identified in the deposits from the domestic boiler EC2
- A lower combustion temperature in the EC2 boiler is characterised by the presence of ligno-cellulose particles (650 – 700 °C)
- A higher temperature in the EC3 boiler is characterised by the presence of a higher proportion of amorphous particles in the deposits and a lower amount of ash in the deposits
- The same compounds have been identified in the deposits from both boilers
- A statistically significant relationship between organic compound concentrations and ash content has been demonstrated → simultaneous origin of a glass phase containing charring products from the combustion of biomass and synthetic polymers with inorganic elements
- A chemical analysis of the deposits from domestic boilers can be used to identify the burned fuel, which can simplify the quality check of the fuel

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