PROFILES OF POLYCYCLIC AROMATIC HYDROCARBONS IN SMOKE FROM COMBUSTION AND THERMAL DECOMPOSITION OF POPLAR WOOD PELLETS AND SAWDUST

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The threat of climate change and the need to reduce green-house gas emissions have led to an *increase* in the **demand and use of biomass in energy generation**. Wood biomass is:

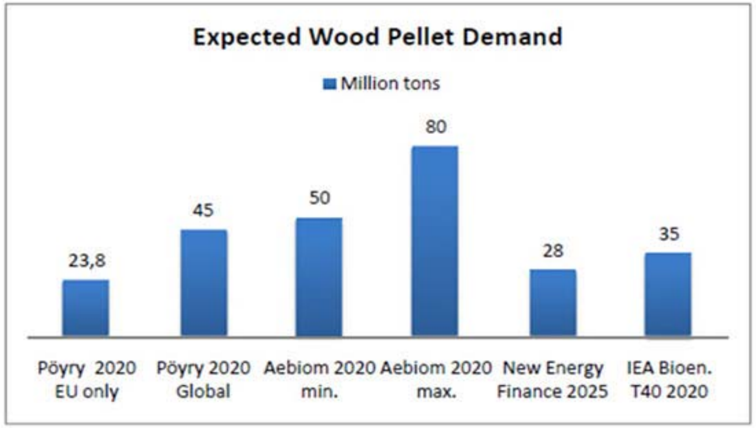
- ***low in cost and***
- ***renewable carbon dioxide-free fuel that contains a low amount of sulfur.***

Mechanical wood processing

Sawdust

Pellets

The use of wood pellet as biomass fuel is steadily increasing due to its high energy density, easy transportability and the lower amount of indirect green house gas emissions from its production and transportation comparing to oil, coal and natural gas.



Expected wood pellet demand in 2020 to 2025 according to different sources

The emission of PAHs is of great interest.

THE AIM OF THIS STUDY WAS TO:

Investigate the level and profile of PAHs in the smoke of wood pellets and sawdust of poplar clone I-214 during combustion and thermal decomposition.

To evaluate the carcinogenic potency of simultaneous occurrence of total 16 PAHs detected in smoke from the combustion and thermal decomposition of the poplar wood pellets and sawdust using BaPeq values, due to check if wood pellets and sawdust could be used as an eco friendly fuel.

Samples:

- **poplar wood pellets** of Canadian poplar clone I-214 (*P. x euramericana cl. I-214*), and
- **sawdust**.

Physical and chemical properties of the investigated pellets are presented in Table 1.

Table 1. Physical and chemical properties of pellets

Serial number	Parameter	Unit	Method	Result
1.	Diameter	mm	SRPS EN 14961-1	6
2.	Length	mm	SRPS EN 14961-1	5-40
3.	Bulk density	kgm^{-3}	SRPS EN 15103	647
4.	Individual particle density	kgm^{-3}	SRPS CEN/TS 15150 Annex	1179
5.	Particle content (<3.15 mm)	%	SRPS EN 15149-2	0.92
6.	Total moisture content	%	SRPS EN 14774-2	5.17
7.	Ash content	%	SRPS EN 14775	1.16
8.	Volatile matter content	%	SRPS EN 15148	79.22
9.	Higher calorific value	$kJkg^{-1}$	SRPS EN 14918	18688
10.	Lower calorific value	$kJkg^{-1}$	SRPS EN 14918	17380
11.	Additives	Additives were not used in the technology process, nor the biomass was chemically processed		

Combustion process

The gas burner was put out at the moment of sample ignition.

Thermal decomposition process under atmospheric conditions

The gas burner remained turned on until the sample turned to ash.

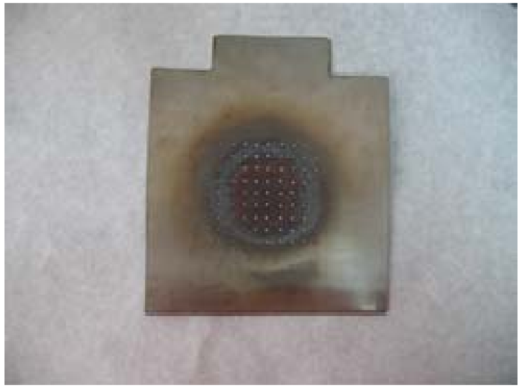


Fig. 1.1 Inox plate for combustion process

~5 g of pellets or sawdust

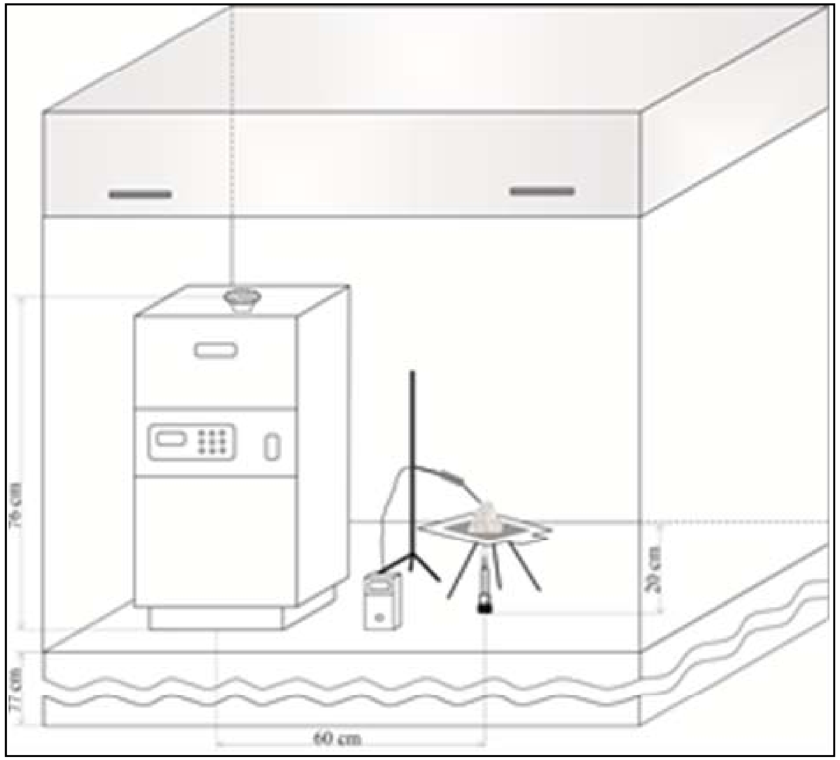
Fig.1.1 Inox plate for thermal decomposition process

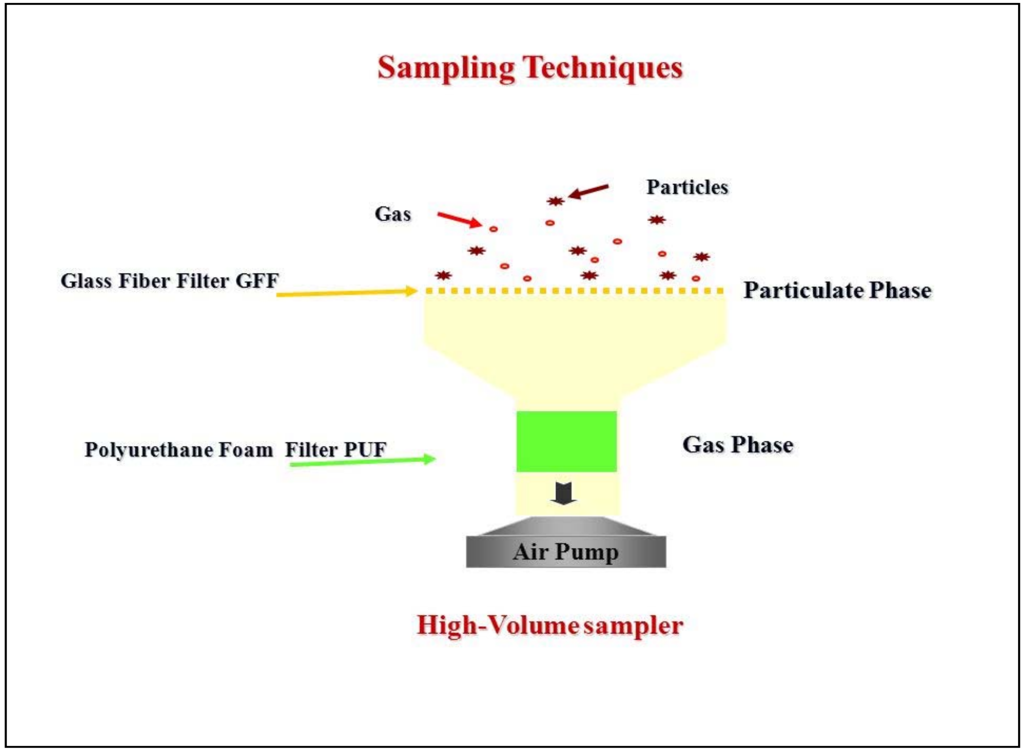
21 °C, 102.5 kPa

Fig. 1. The panels of inox (20×20×0.1 cm)

PAHs sampling was performed at:

- Flow rate of 250 ml/min with sampler TCR TECORA Echo HiVol .
- Sample temperatures were measured using a digital thermometer DTI, by thermocouple NiCr-Ni.





EXTRACTION OF PAHs

ANALYSES OF PAHs

Soxhlet extractor

Vacuum rotary evaporator

Stream of nitrogen

Gas chromatography

10% diethyl ether/ n-hexane/ 14 h

~ 5 ml

~ 1 ml

GC/MS Working Conditions

Column	DB-5, 30m×0.25mm×0.25µm
Gas carrier	Helium
Gas carrier flow velocity	1.45 ml/min
Injector temperature	280°C
Ion Source temperature	240°C
Interface temperature	330°C
Injection mode	split
Volume injection	3µl
Detector voltage	1.2kV

Temperature Programme of GC Column

Rate (°C/min)	Temperature (°C)	Hold Time (min)
-	60	0.8
20	200	0
2.5	225	0
3	266	10
5	300	0
10	320	4.5

Parameters that are usually taken into account throughout method validation are limit of detection (LOD), limit of quantification (LOQ), recovery (%) and repeatability, RSD%.

Table 3. Validation parameters: Limit of detection (LOD), limit of quantification (LOQ) and recovery (%)

Compound	LOD (ng m^{-3})	LOQ (ng m^{-3})	Recovery (%)	Measurement uncertainty (%)
Naphthalene	0.018	0.055	93	26.71
Acenaphthylene	0.014	0.042	80	46.93
Acenaphthene	0.015	0.044	92	28.41
Fluorene	0.012	0.036	93	25.00
Phenanthrene	0.011	0.032	98	13.94
Anthracene	0.009	0.028	88	35.14
Fluoranthene	0.014	0.042	101	19.67
Pyrene	0.015	0.046	99	17.86
Benz[a]anthracene	0.012	0.037	106	21.88
Chrysene	0.012	0.037	98	21.41
Benzo[b]fluoranthene	0.017	0.052	99	13.47
Benzo[k]fluoranthene	0.013	0.038	95	18.00
Benzo[a]pyrene	0.016	0.047	88	40.27
Indeno[1,2,3-cd]pyrene	0.019	0.056	97	25.50
Dibenzo[a,h]anthracene	0.016	0.052	81	45.25
Benzo[g,h,i]perylene	0.018	0.054	80	44.86

Pre-combustion Flaming combustion Smoldering combustion Glowing or embering combustion

Fig. 2 Phases of pellets combustion

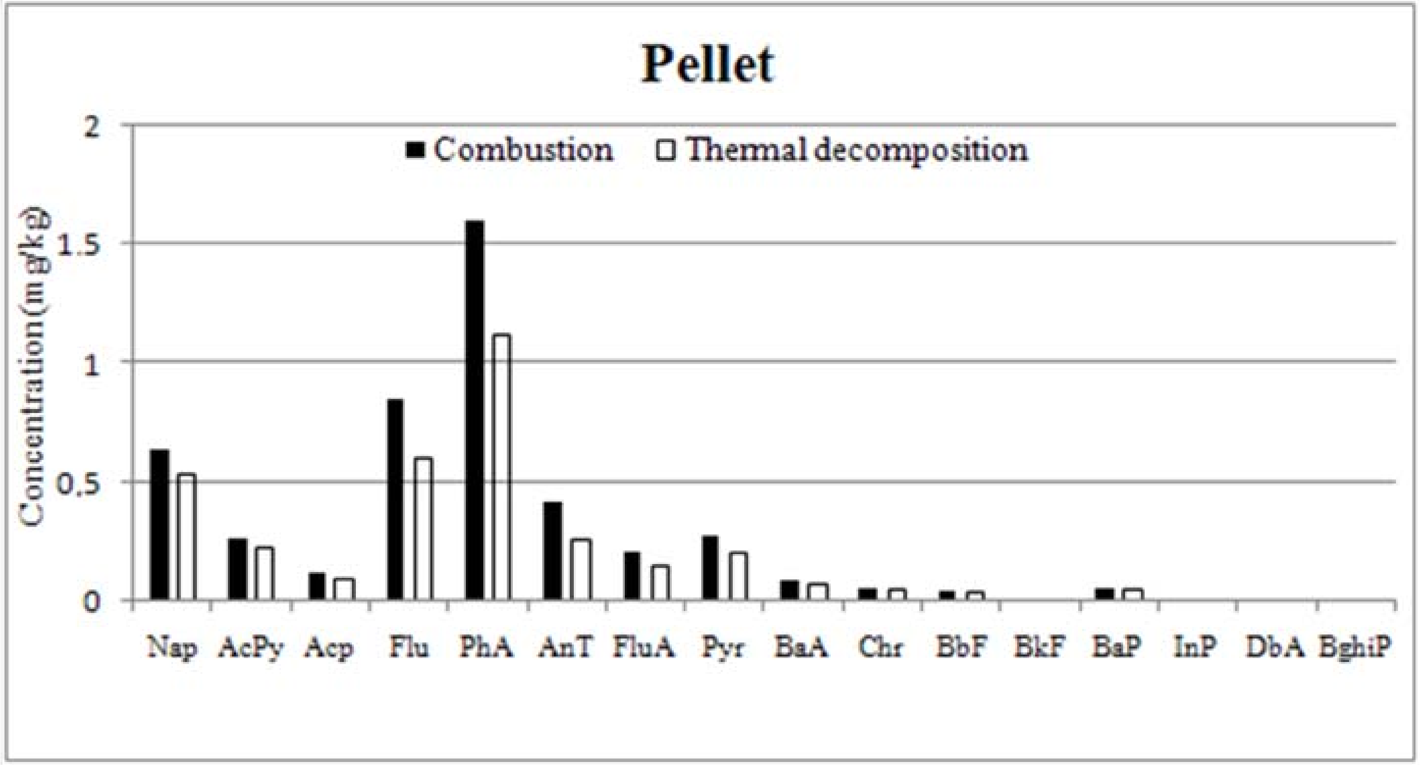


Fig. 3. Released PAHs masses per mass unit of the sample – Combustion and thermal decomposition of pellets

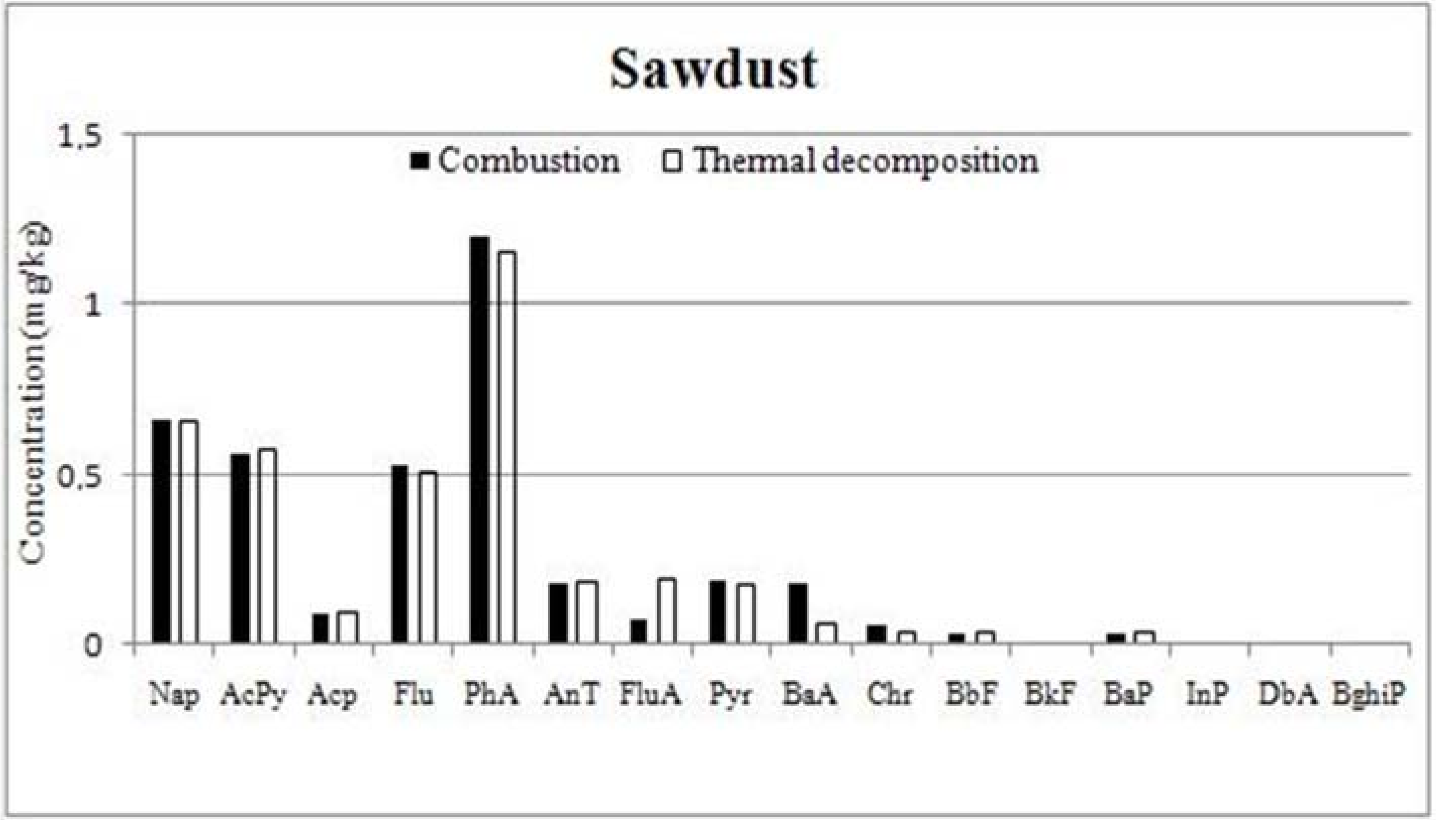


Fig. 4. Released PAHs masses per mass unit of the sample – Combustion and thermal decomposition of sawdust

Phenanthrene is more common because it is thermodynamically more stable than the anthracene for 6 kcal/mol.

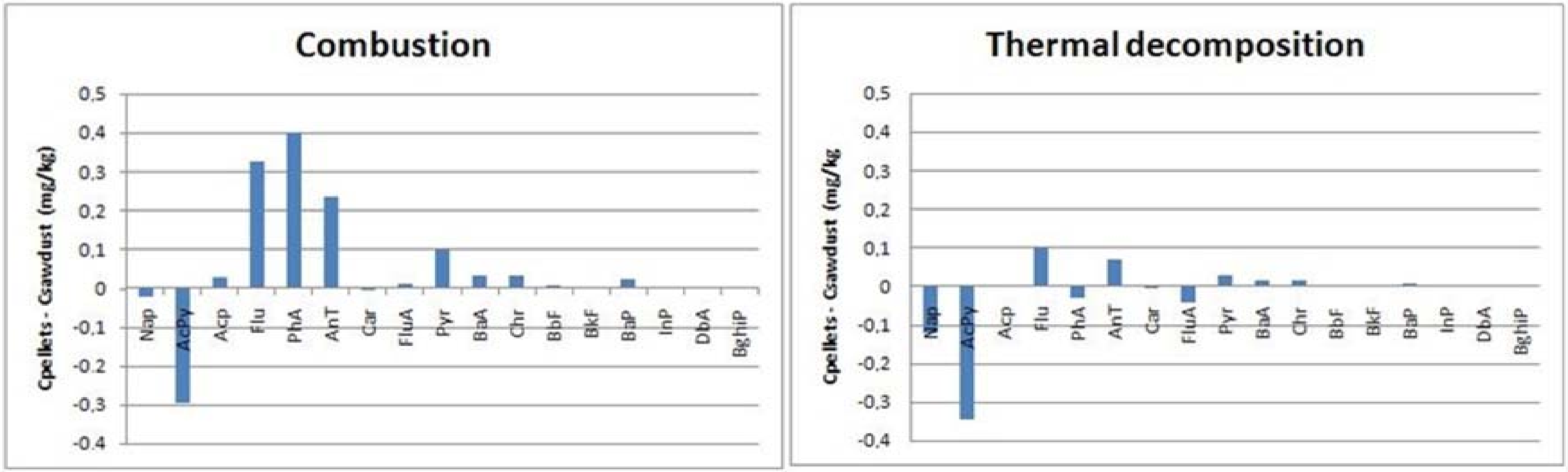


Fig. 5 Differences in PAH concentration obtained during the process of combustion and thermal decomposition under atmospheric conditions

- The levels of phenanthrene and fluorene were enhanced in smoke from pellets during the combustion.

- It is explained by the larger surface of sawdust which can receive more heat, thus generates a larger amount of PAHs.

BaPeq value is calculated based on TEF:

BaPeq=Sum(PAHi * TEFi)

BaPeq value (mg/kg)	Pellets	Sawdust
Combustion	**0.081**	0.047
Thermal degradation under atmospheric conditions	0.057	0.049

The BaPeq values obtained in smoke during the combustion of sawdust, and thermal decomposition of pellets and sawdust were 40%, 29% and 39%, respectively, lower then the BaPeq value of smoke obtained during the combustion of pellets.

Mean BaPeq value (0.08 mg kg-1) in smoke from the combustion of pellets was:

Corn straw pellets (0.08 mg kg-1)

Crop residues (0.09 mg kg-1)

Brushwood (3.1 mg kg-1)

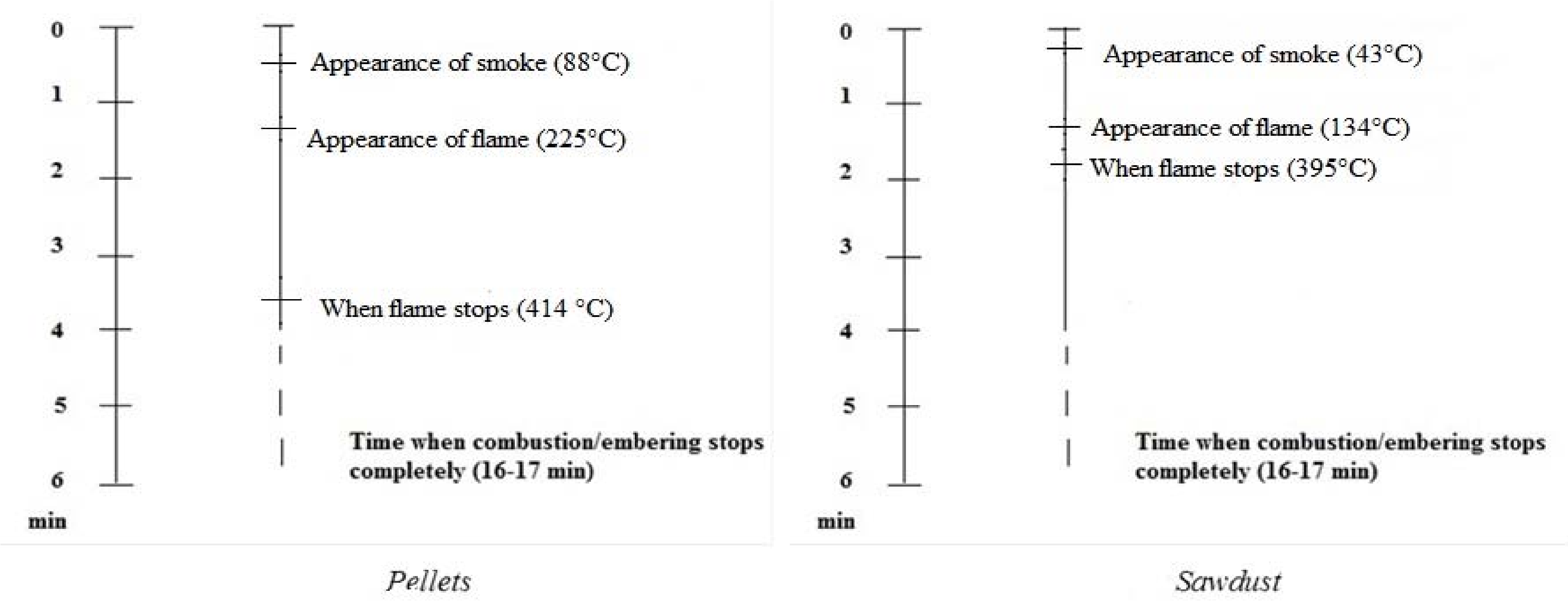
Bituminous briquettes (41 mg kg-1)

Raw bituminous chunks (52 mg kg-1)

Wood pellets and sawdust of poplar clone I-214 (P. x euramericana cl. I-214) cultivated in the Republic of Serbia could be used as an **eco-friendly fuel.**

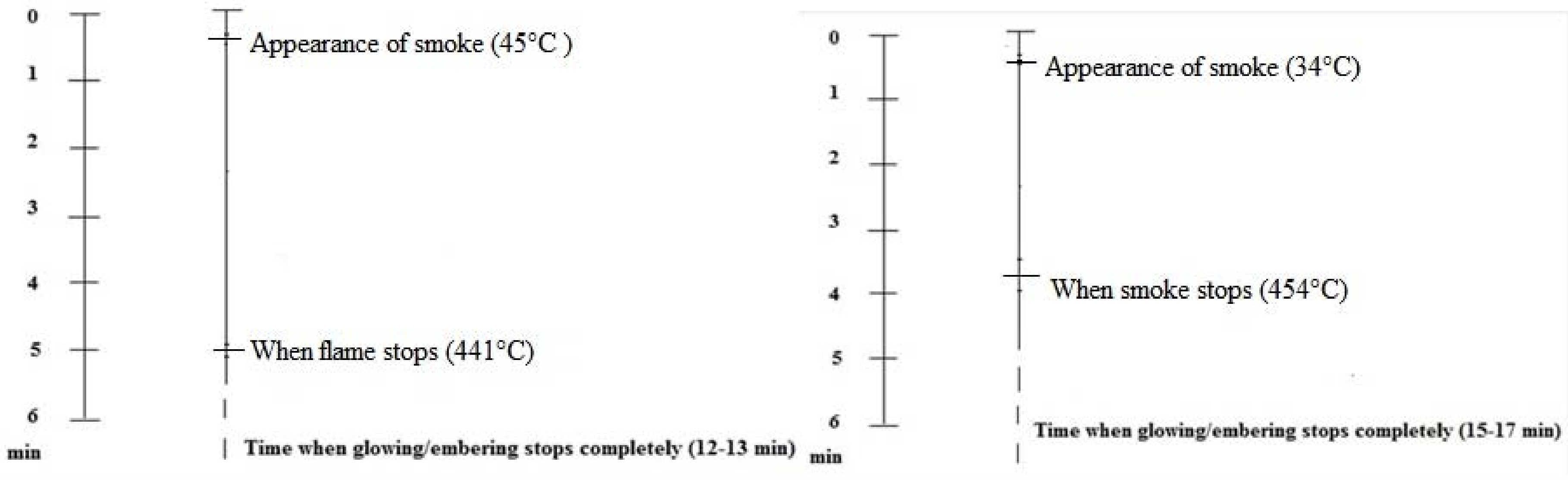
- The total level of PAHs was more pronounced in smoke from pellets than from sawdust during the **combustion**, **as a consequence of higher temperatures within the pellet itself**, that are sufficient for **pyrolitic** reactions. The sawdust is in a ***loose form***; it is easier to ***ignite at lower*** temperatures, while the **pellet** is **compact** in form and **ignited** at almost **100 °C higher** temperature, but when **the flaming combustion starts** the combustion **lasts longer**, providing higher temperatures **for pyrolytic reactions** within the pellet itself causing the *higher* production of *PAHs*.

The relative time scales for the different combustion stages of wood pellets and sawdust with approximate temperatures for the combustion stages.



- During the **thermal decomposition process**, the **level of PAHs** obtained is **approximately the same for pellet and sawdust** for most PAHs. There is ***no combustion*** process here, there is **no generation of own heat**. It is an **endothermic process**, both for pellet and sawdust. The smoldering stage of pellets lasted longer then with sawdust. For the same mass of pellets and sawdust, the time needed to turn them to ash was longer for sawdust.

Approximate time scale for the thermal decomposition process under atmospheric conditions processes



Pellets *Sawdust*

- The obtained data for **BaPeq values indicated** that wood pellets and sawdust of poplar clone I-214 (P. x euramericana cl. I-214) cultivated in the Republic of Serbia could be used as an **eco-friendly fuel** in comparison to bituminous chunks, bituminous briquettes and brushwood.

Thank you for your kind attention!