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Reclaiming creosote by thermal desorption in used wood ties

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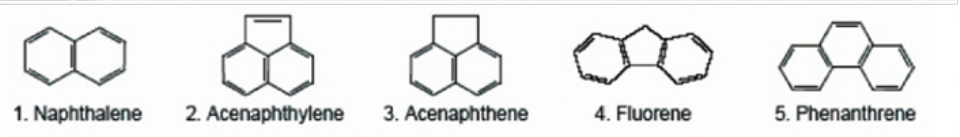
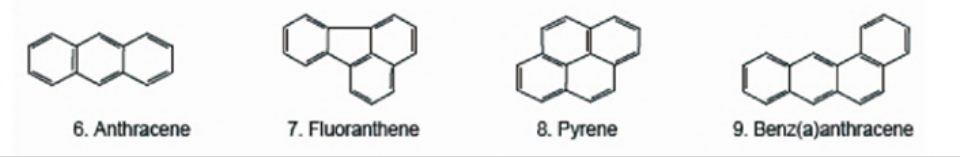
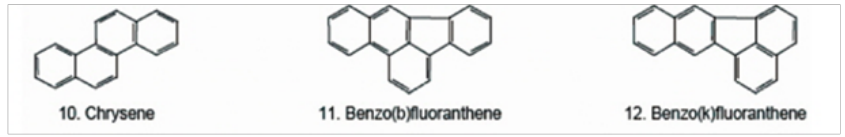
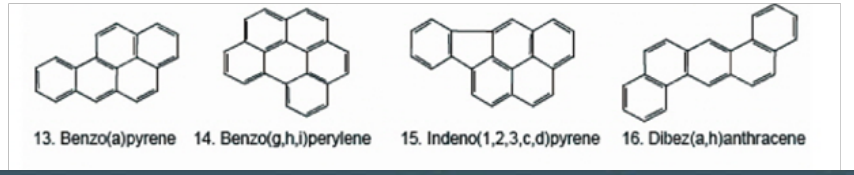
Wood preservatives

- Treating wood (railroad ties, utility poles, piling and bridge timbers)
  - **Creosote (95% of treated wood)**
    - Distillation products of coal tar
    - Polycyclic aromatic hydrocarbons (PAHs, 85% of creosote compounds)
    - 16 PAH compounds (20-40 % of creosote, Priority pollutants by EPA)
    - 9 kg of creosote in 0.1 m^3 of wood tie
    - **65 % of total creosote is found in typical 35 year spent wood ties**
  - Copper Naphthenate, pentachlorophenol, copper chrome arsenate









Railroad ties -Production

❑ Railroad ties (crossties, sleepers)

- Total railroad ties in service track (approx. 700 – 800 million ties) in the U.S.
- Wood ties (over 93%), concrete (6.5 %), plastic/composite (0.5%)

❑ Used railroad wood ties (16 – 19 million ties a year in the U.S.)

- Commercial and residential landscape timbers (18%)
- Fuels in co-generation & gasification (80 % of wood ties)
- Landfill (0.3%) or re-use in track (0.9%)

RTA. 2012. Basic Statistics, (Ed.) http://www.rta.org/faqs-main, Railroad Ties Association.

Used railroad wood ties - Problems

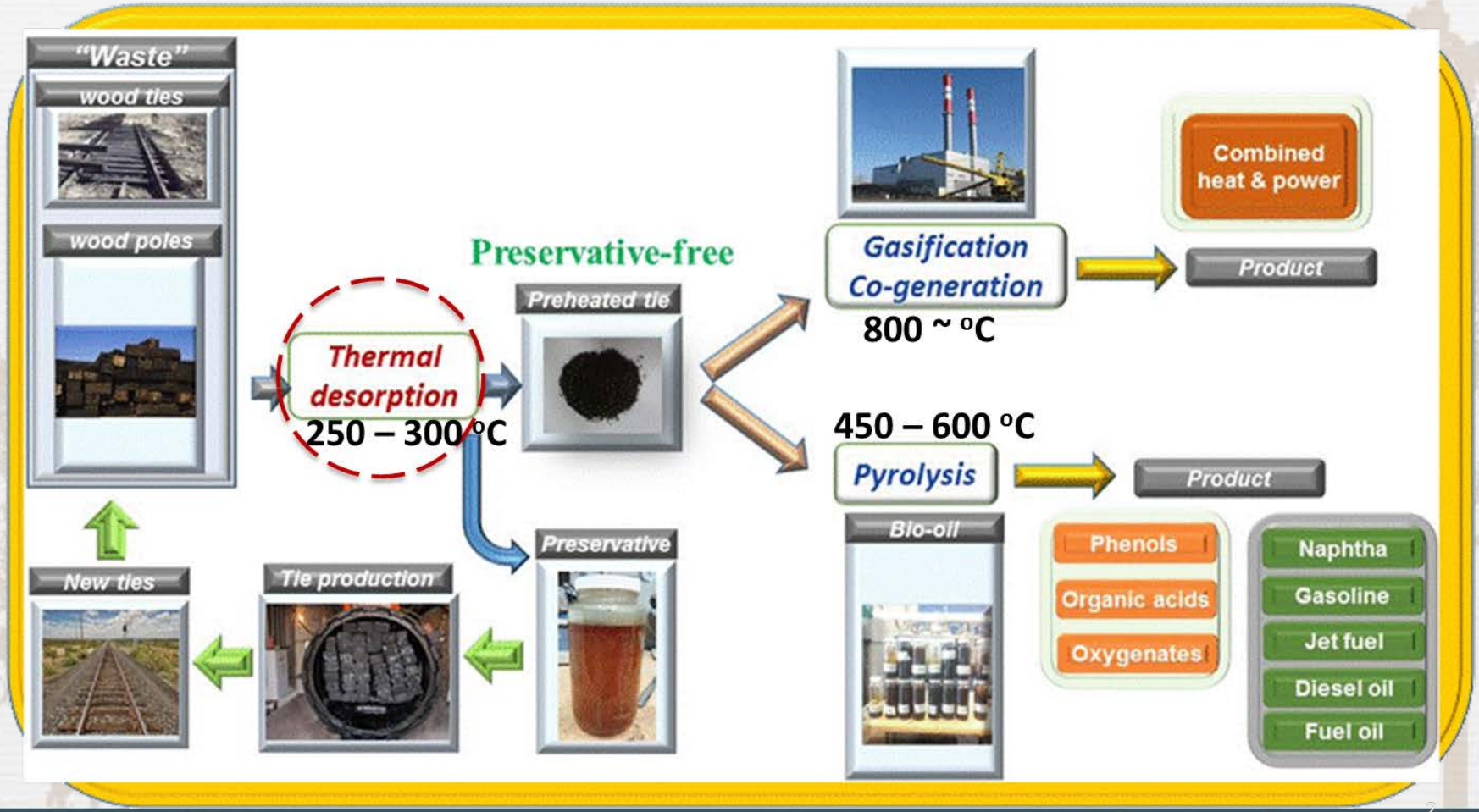
- The US E.P.A regulations (2014)
  - Classified as ‘waste’ to limit the use of ties to boilers equipped with a fuel oil delivery system (expensive, rare).
  - No longer be easily used for boiler fuel
  - Costly waste for incineration, environmentally impact to landfill.

Producing greenhouse gases such as carbon dioxide and methane

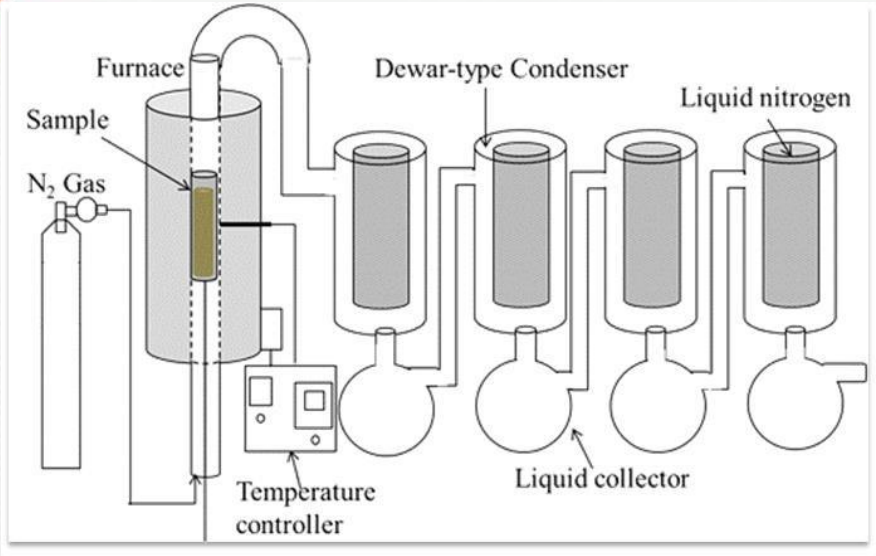
U.S. EPA, 2014. Non-hazardous secondary materials rulemakings.

Goal & Objective - Alternative processes

- Develop an economically and environmentally viable **two-step thermochemical process** for recycling of used wood ties



Research approach

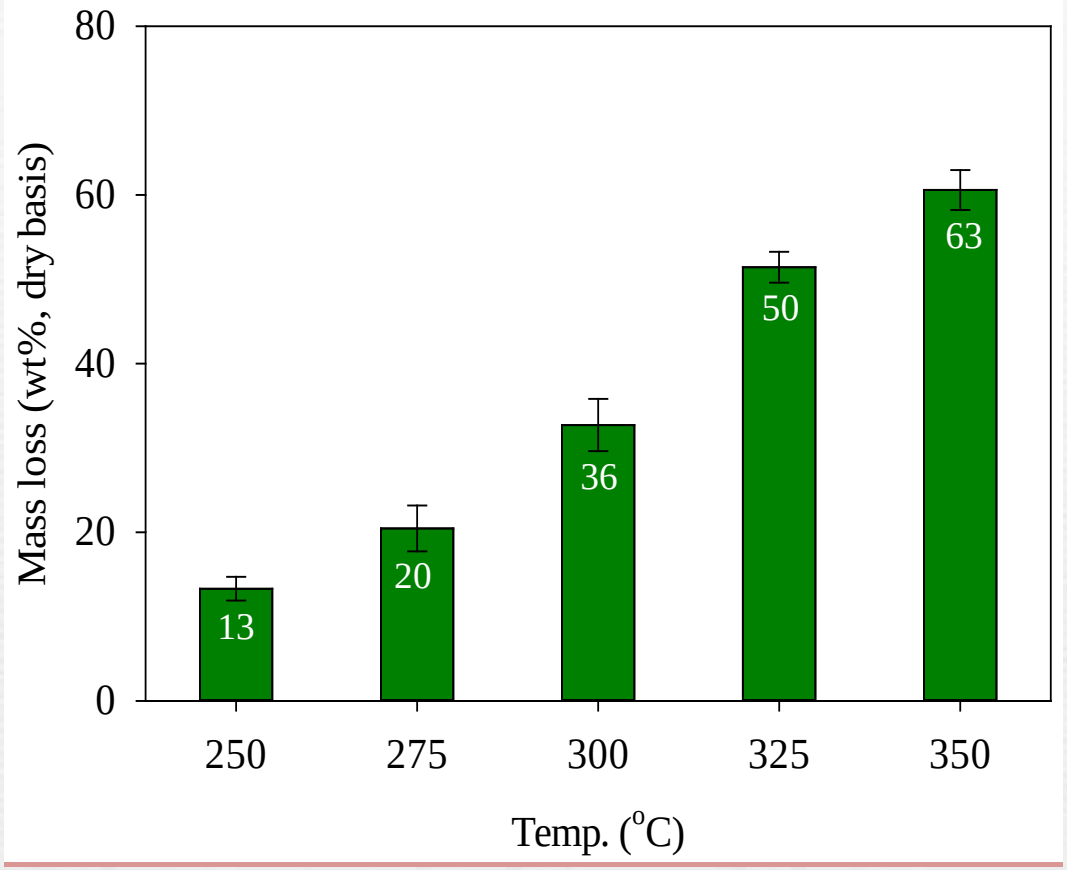


- Material
  - Used creosote-treated railroad tie obtained from National Salvage& Services Corp.
  - Particle sizes between 0.45 - 2 mm
- Experimental conditions
  - Thermal desorption temperature: 250, 275, 300, 325 and 350 ºC
  - Residence time: 30 min

Liquid fraction recovered with
1) Methanol
   (for identification)
2) Dicholoromethane
   (for quantification)

Solid fraction

Results – Mass loss of wood tie



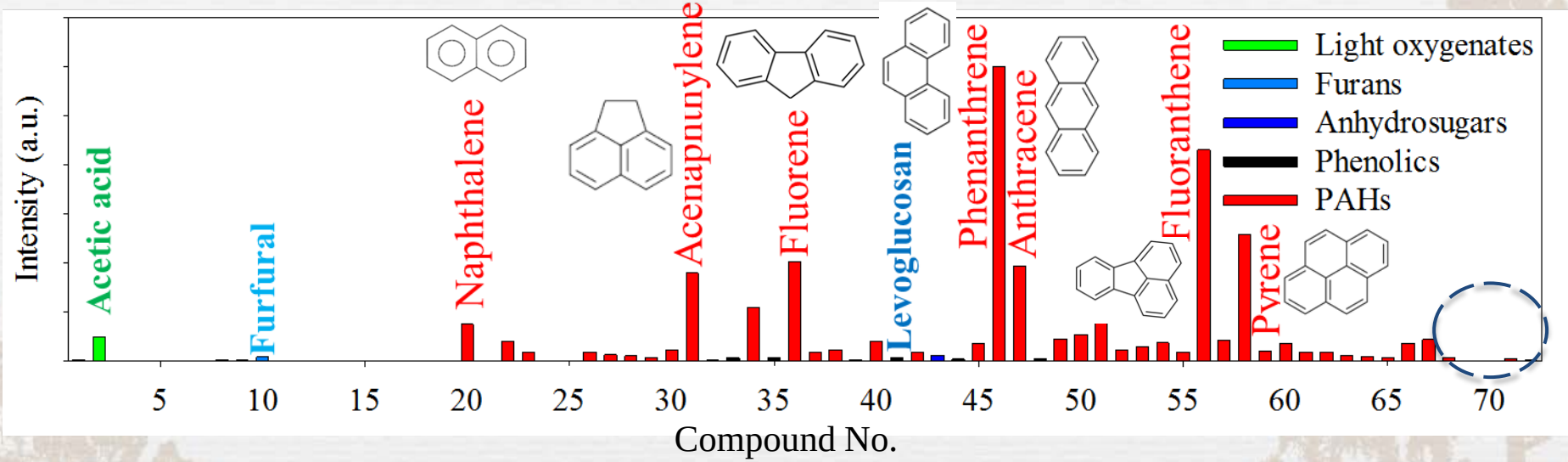
Untreated | 250 °C | 275 °C | 300 °C | 325 °C | 350 °C

Creosote content in untreated wood tie : 11.4 wt% (dry basis)

Results – Liquid fraction – GC/MS

Liquid fraction
Rinsed with methanol

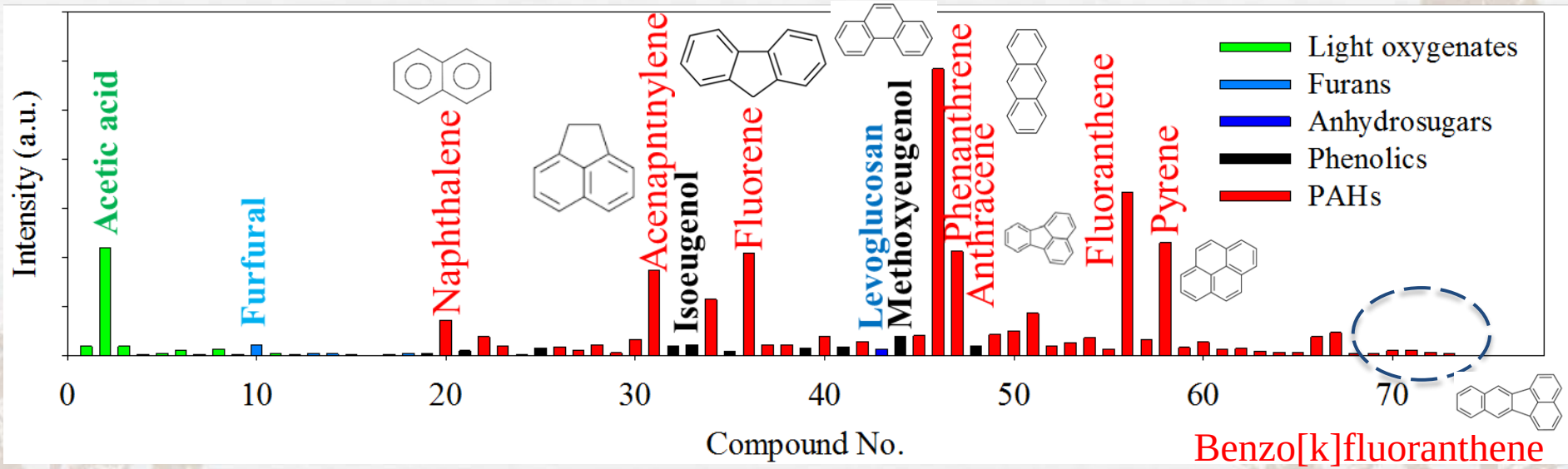
Thermal treatment at 250 °C



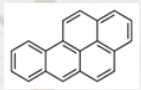
Results – Liquid phase – GC/MS

Liquid fraction
Rinsed with methanol

Thermal treatment at 300 °C



Benzo[k]fluoranthene
Benzo[a]pyrene



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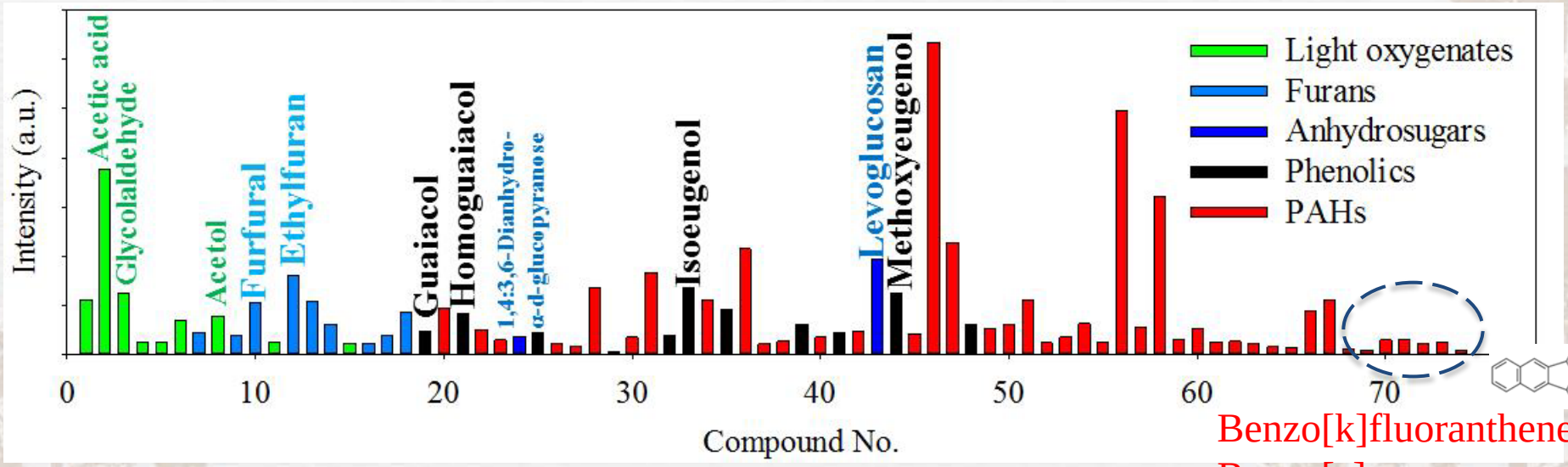
Results – Liquid phase – GC/MS

Liquid fraction

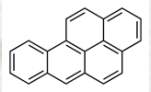
Rinsed with methanol

Thermal treatment at 350 °C



Benzo[k]fluoranthene

Benzo[a]pyrene



Results – Liquid fraction - Fractionation

Liquid fraction

Rinsed with dichloromethane

Extracted liquid fraction with Dichloromethane (DCM, 250 mL)

← *Add water (200 mL, pH 14, NaOH)*

Separation

Organic phase → **PAHs**

Aqueous phase

← *Adjust pH 2 (HCl)*

Add DCM (200 mL) →

Organic phase → **Phenolics**

Aqueous phase

← *Add diethyl ether (1:1)*

Organic phase → **Light organics**

Aqueous phase → **Anhydrosugars**

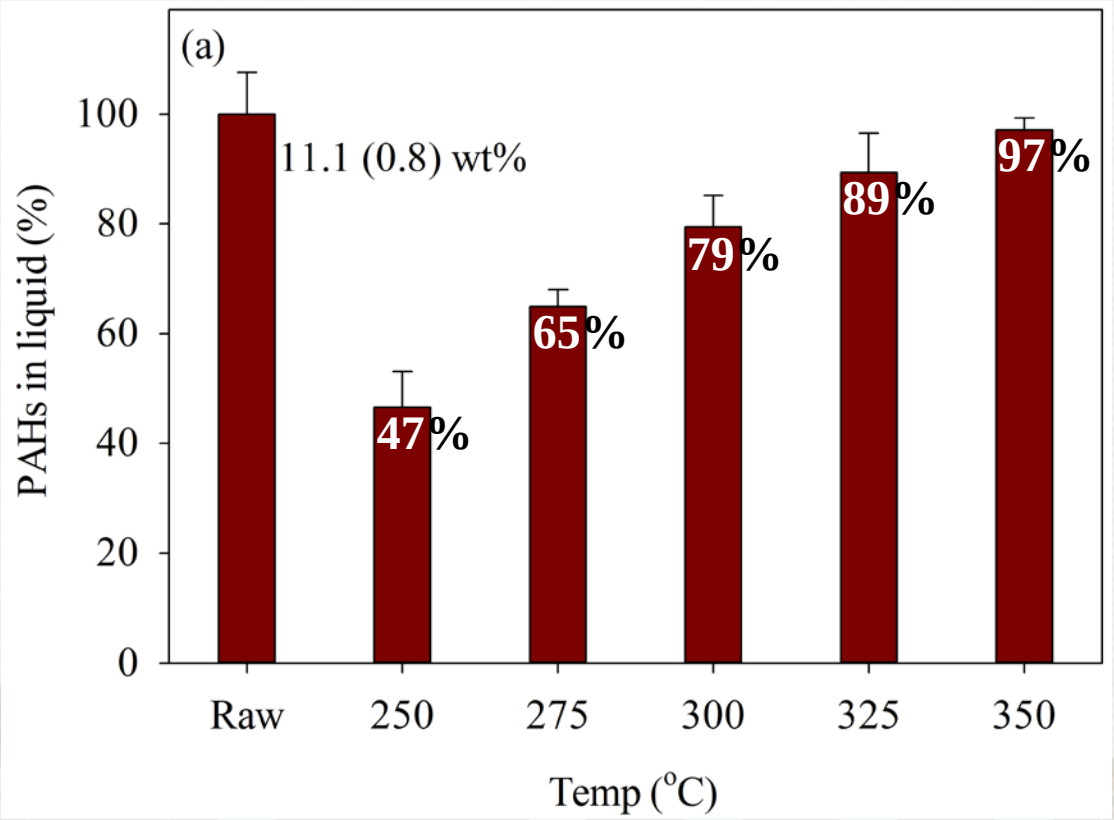
Middaugh DP et al. Field scale testing of a hyperfiltration unit for removal of creosote and pentachlorophenol from ground water: Chemical and biological assessment. Archives of Environmental Contamination and Toxicology. 1994;26:309-19.

Sipilä K et al. Characterization of biomass-based flash pyrolysis oils. Biomass and Bioenergy. 1998;14:103-13.

Results – **PAHs Recovery**

Liquid fraction

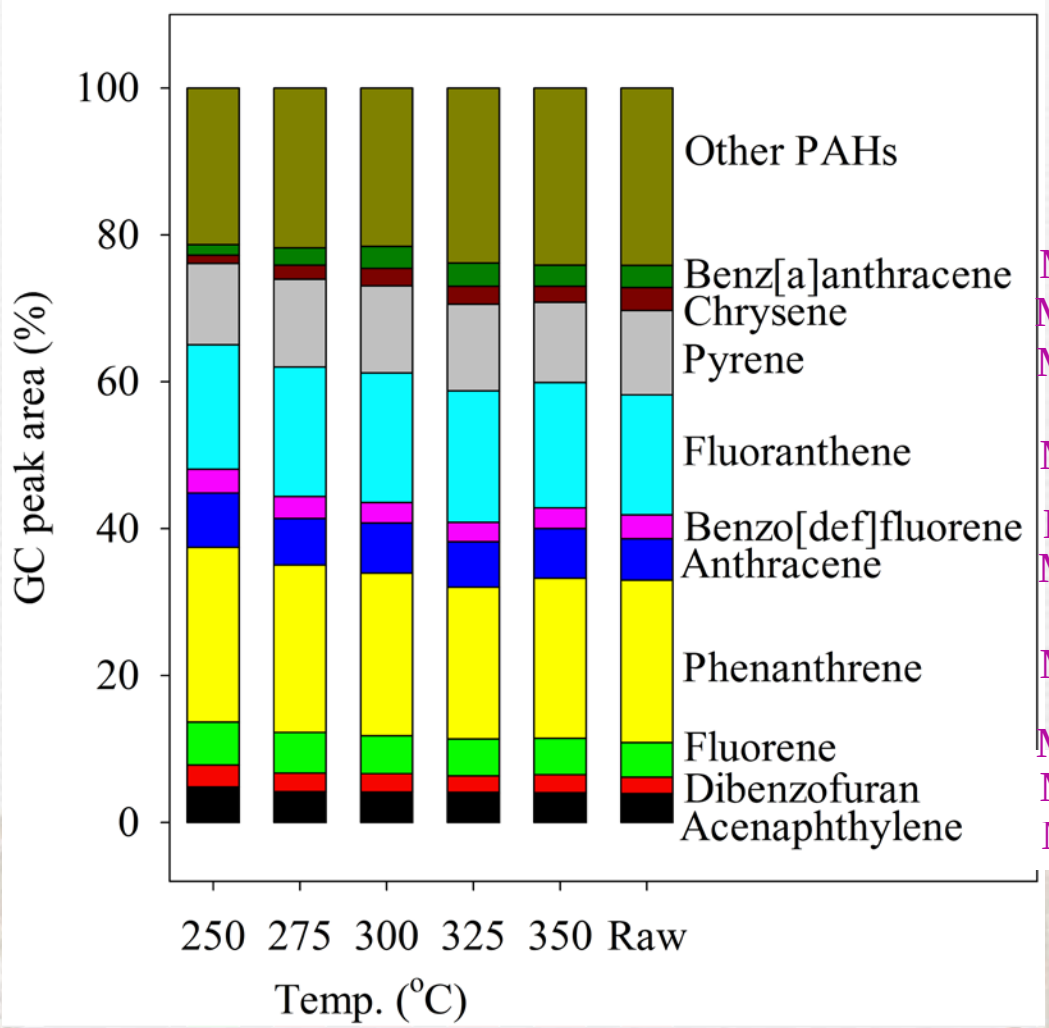
Rinsed with dichloromethane



Results – **PAHs Distribution**

Liquid fraction

Rinsed with dichloromethane



MW:228 Bp: 438 °C

MW:228 Bp: 393 °C

MW:202 Bp: 393 °C

MW:202 Bp: 375 °C

MW:190 Bp: 353 °C

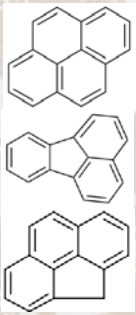
MW:178 Bp: 342 °C

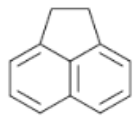
MW:178 Bp: 340 °C

MW:166 Bp: 295 °C

MW:168 Bp: 285 °C

MW:152 Bp:280 °C

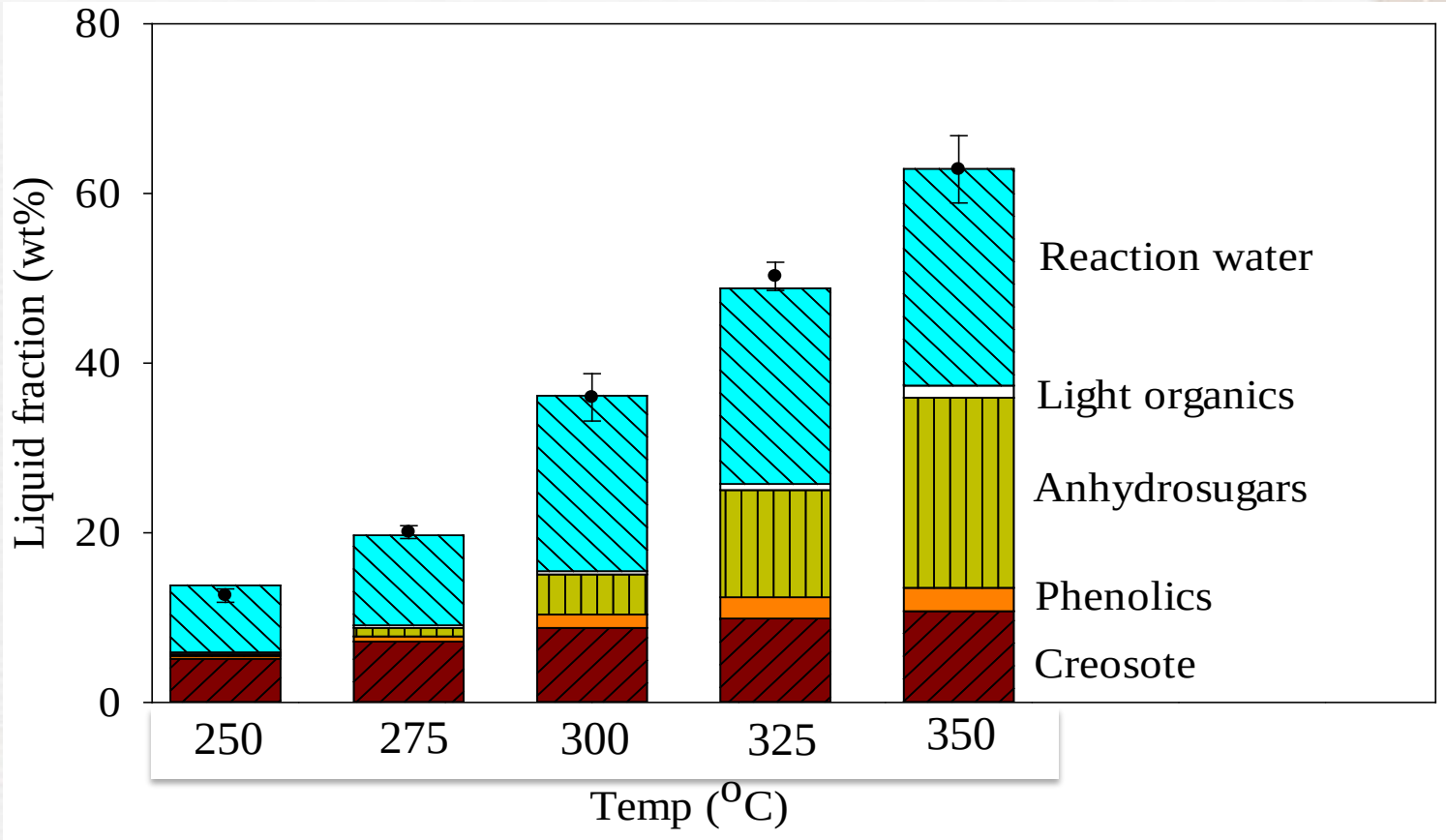




Results – **Wood-decomposed products**

Liquid fraction

Rinsed with dichloromethane



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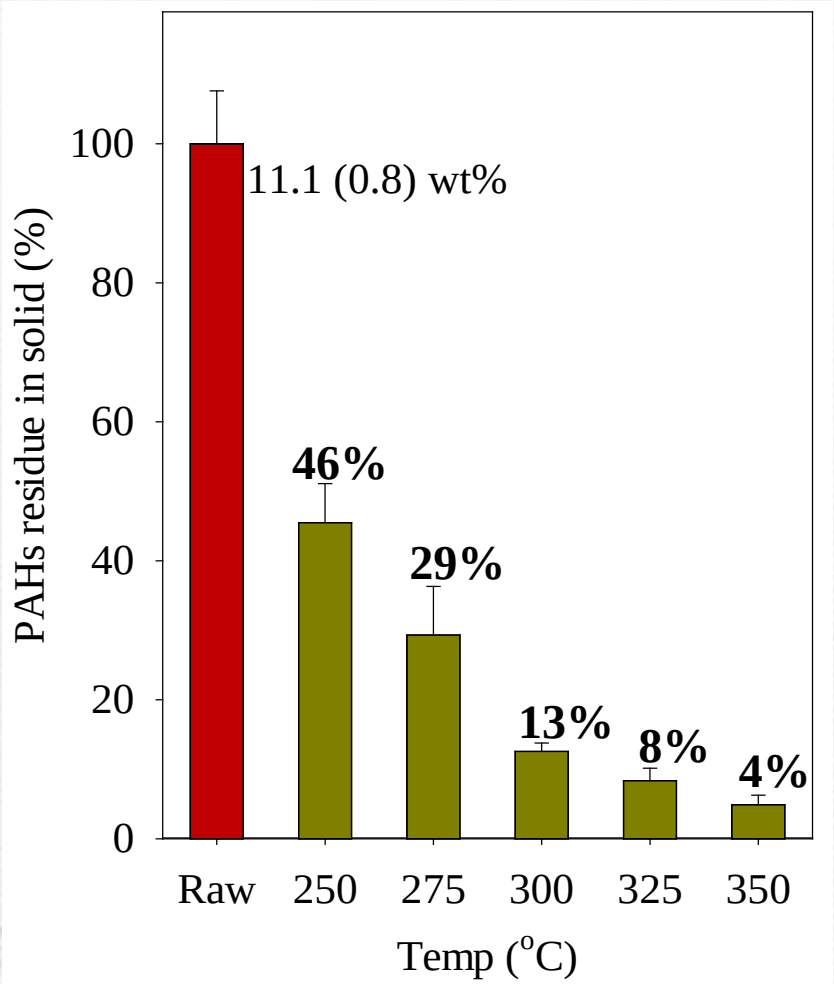
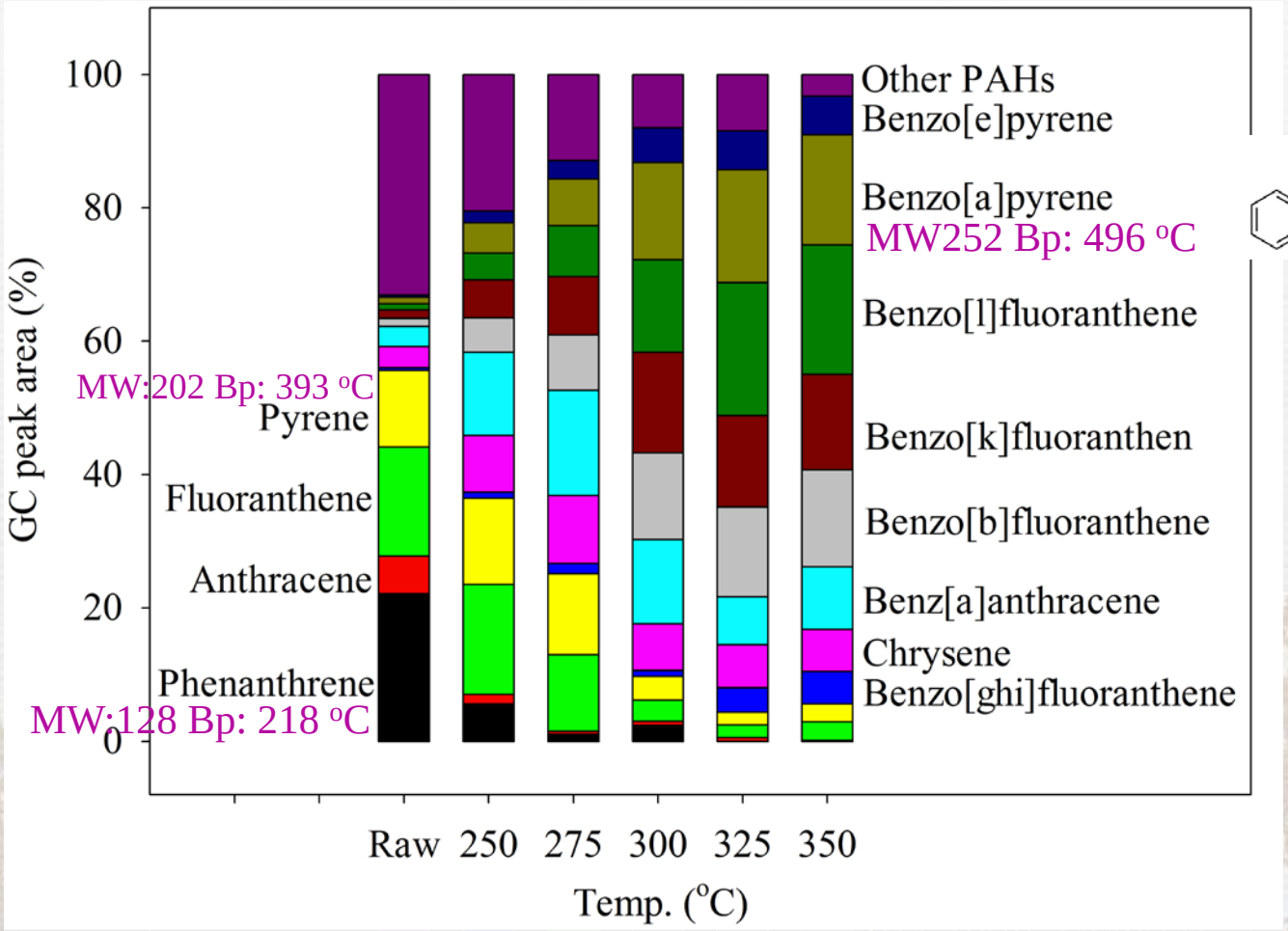
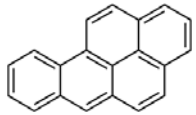
Results – Solid fraction- PAH residues



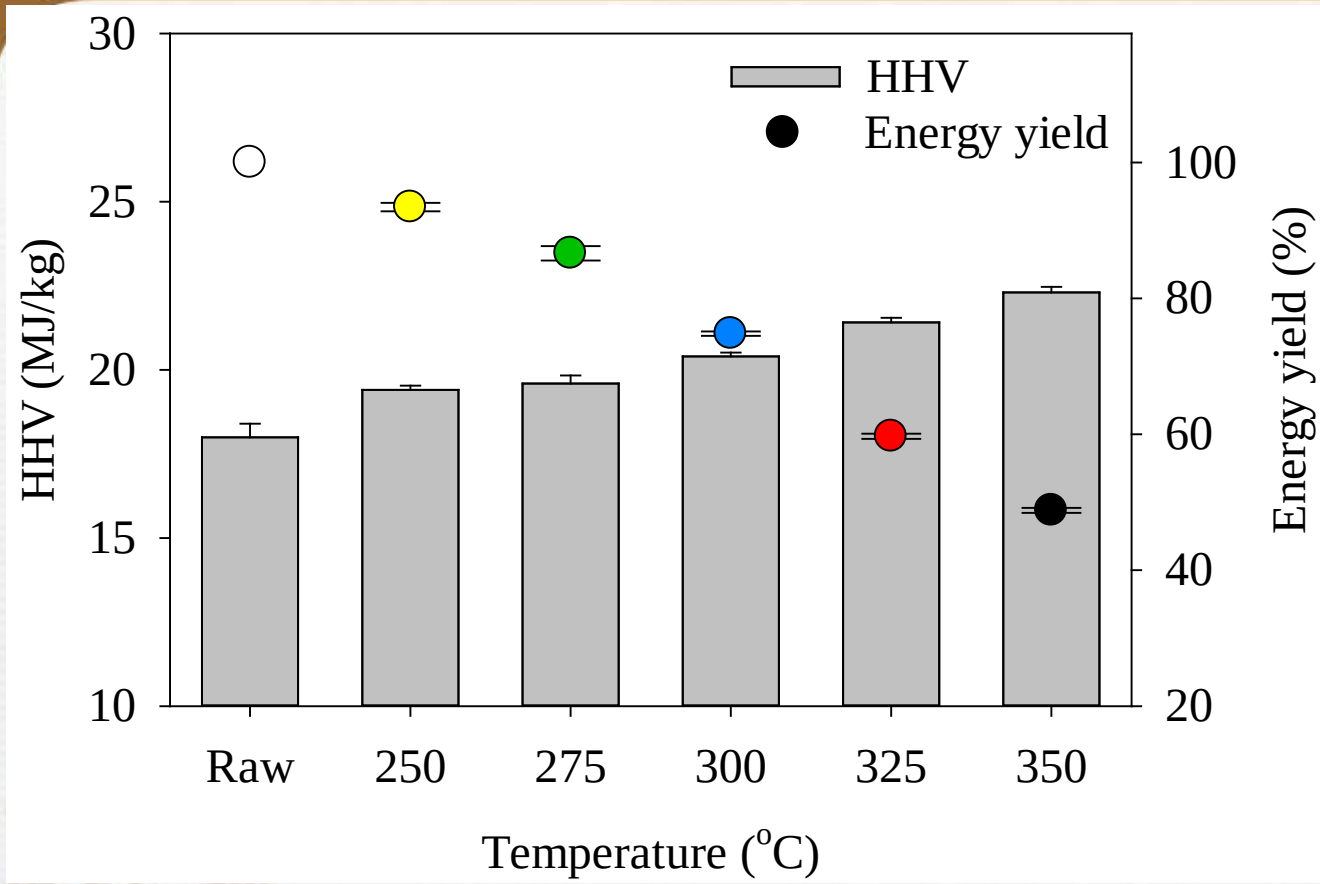
Accelated solvent extractor
at 100 °C
Dichloromethane

Results – Solid fraction- PAH residues





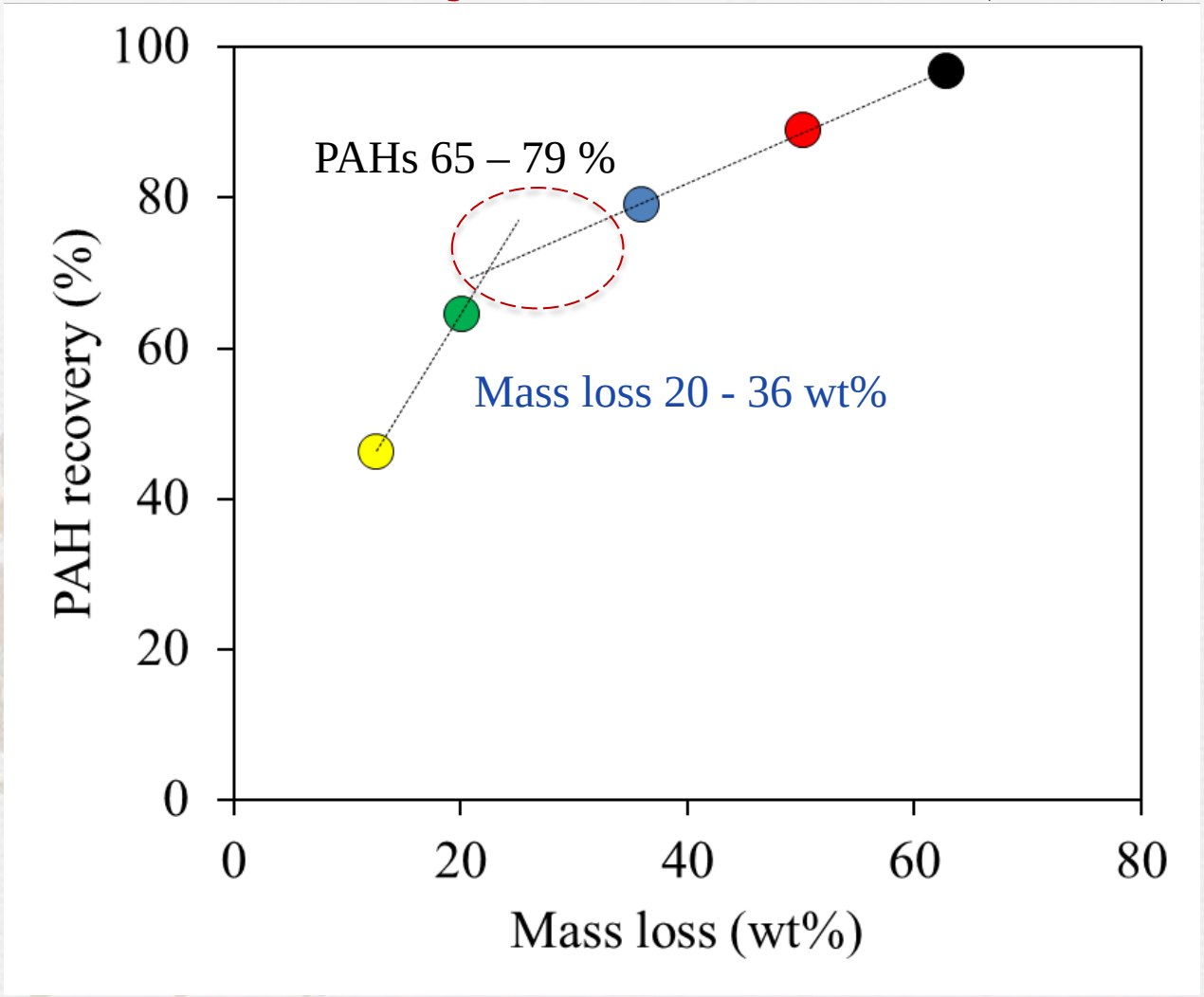
Results – Solid fraction- Characteristics



Untreated
250 °C-treated
275 °C-treated
300 °C-treated
325 °C-treated
350 °C-treated

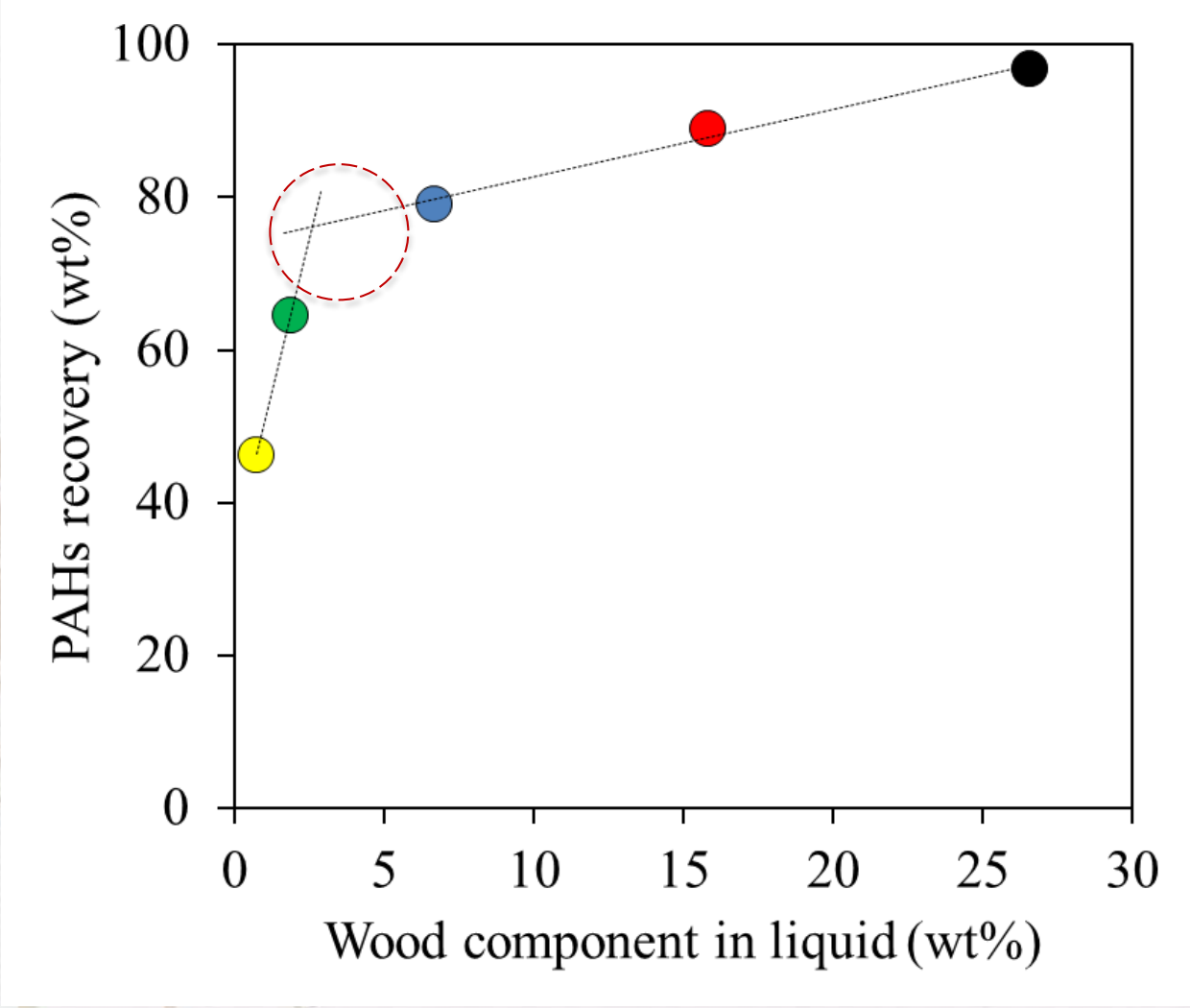
Untreated 250 °C 275 °C 300 °C 325 °C 350 °C

PAHs recovery vs. Mass loss (wt%)

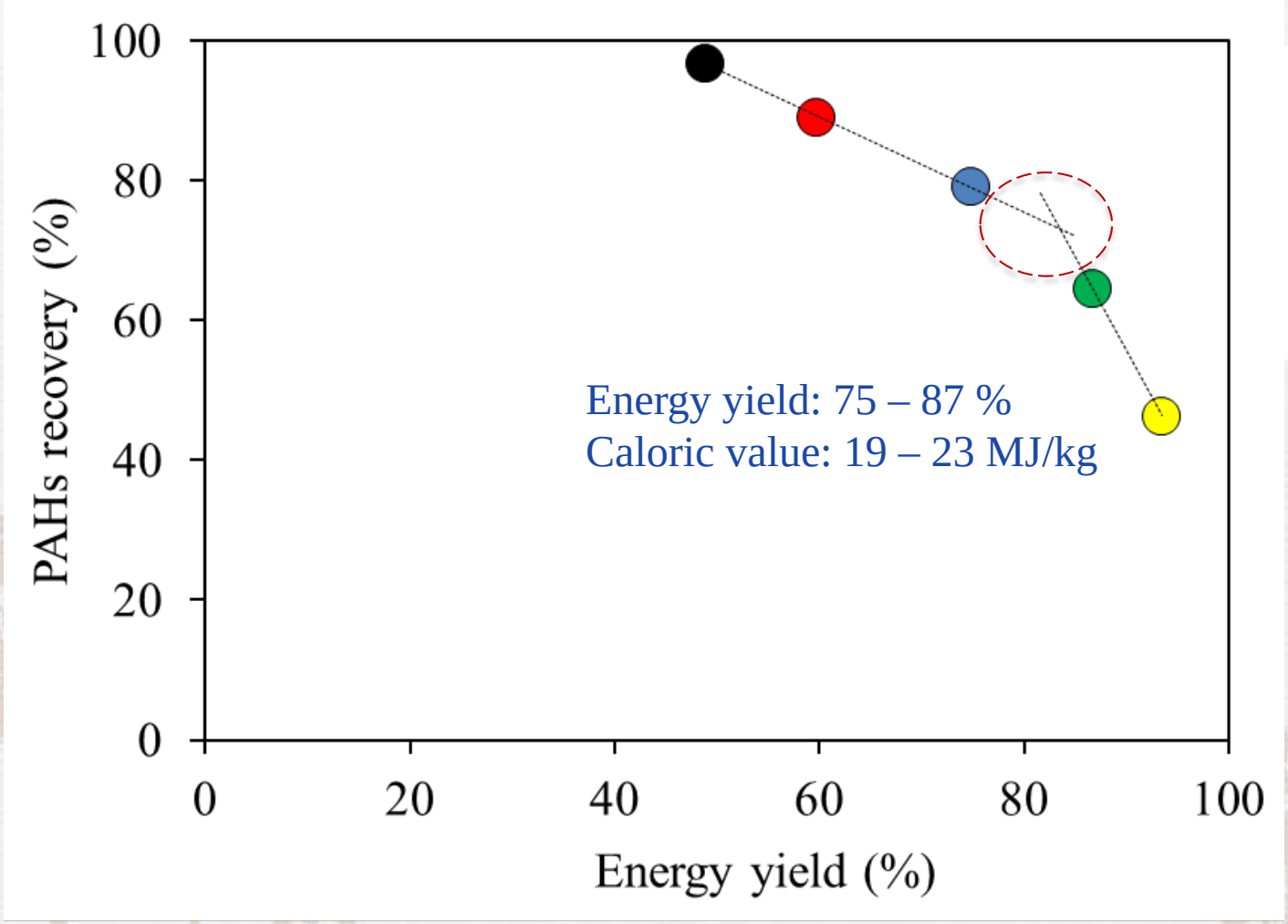


- Untreated
- 250 °C-treated
- 275 °C-treated
- 300 °C-treated
- 325 °C-treated
- 350 °C-treated

PAHs recovery vs. Wood component in liquid (wt%)



PAHs recovery vs. Energy yield (%)



Conclusions

- Determination of the operational thermal desorption temperature regarding the trade-off between creosote recovery and upgradability of thermally treated wood tie material

Thermal desorption temperature between 275 and 300 °C

1) Creosote recovery: 65 – 79 %
containing low wood-decomposed products

2) Upgradability of thermally treated wood tie for subsequent thermochemical processes
Mass loss: 20 – 36 wt%
Caloric value: 19 – 23 MJ/kg
Energy yield: 75 – 87 %

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Thank you for your attention

Therefore, a two-staged thermal treatment of used wood ties could be a good alternative technology for the re-use of wood ties that can produce value-added renewable energy and chemicals while reducing their environmental impacts including continued release of hazardous air pollutants if they were left to decompose or landfilled.

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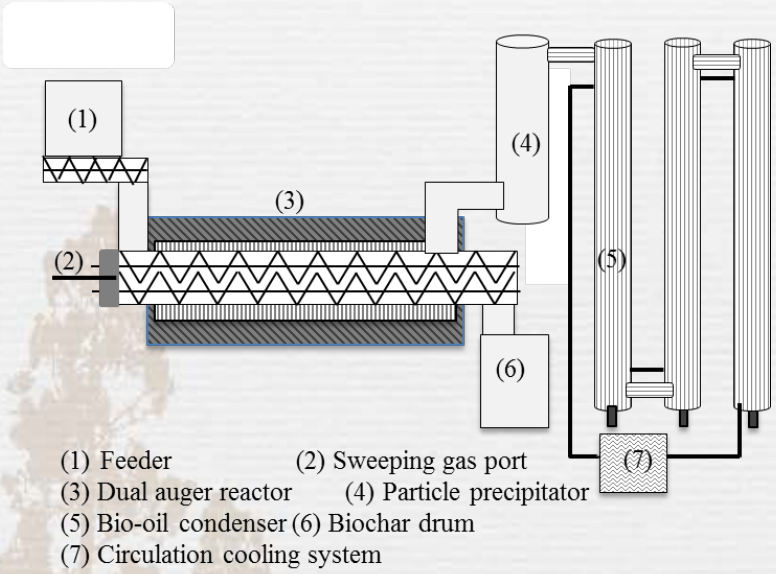
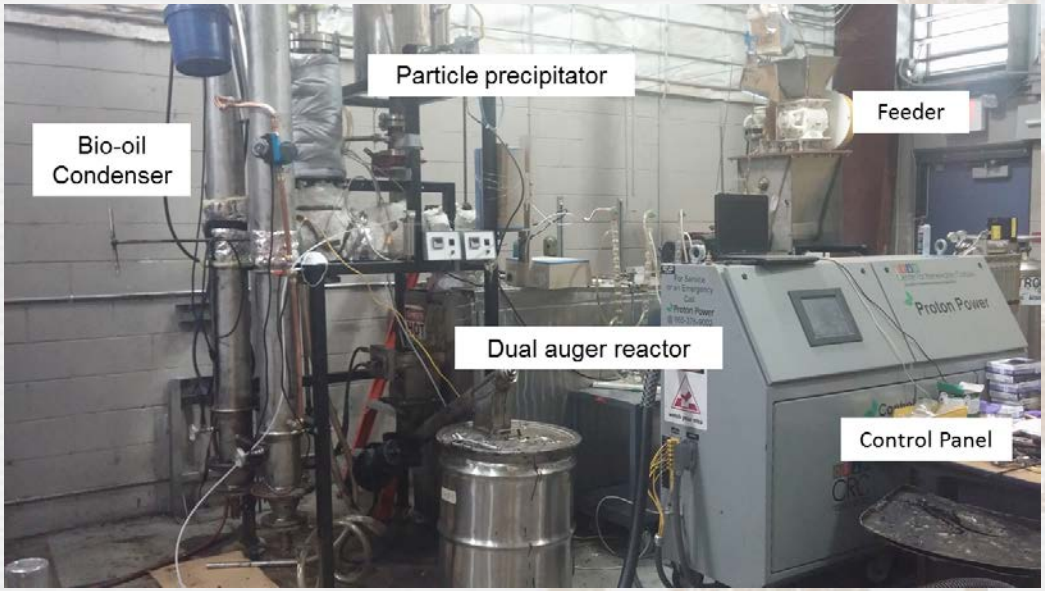
Semi-Pilot scale auger reactor

- Located at [Center for Renewable Carbon](#) in the University of Tennessee





Research approach – two stage pyrolysis

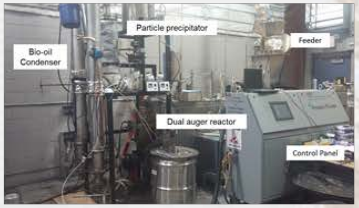
Fast pyrolysis

Feeding rate
3.5 kg/h

Thermal desorption

250 - 300 °C for 15 min

Feeding rate
8.0 kg/h



500 °C for 72s hold

Thermal desorption products

Untreated railroad ties
- Water content (20 %)
- Creosote content (7 %)

Temp (°C)	Product (wt%)				
	Liquid			Solid	NCG
	Total	Aqueous	Bio-oil		
250	27.6 (0.6)	25.7 (0.2)	1.9 (0.2)	64.5 (2.8)	7.8 (2.3)
280	35.1 (1.4)	32.0 (0.1)	3.1 (0.1)	56.5 (0.4)	8.5 (1.2)
300	38.7 (0.6)	34.1 (0.5)	4.6 (0.5)	53.7 (1.5)	7.6 (0.9)

Bio-oil property

Temp (oC)	pH	Water (%)	TAN (mgKOH/g)	Viscosity (mm²/s)	Molecules		
					M_n	M_w	M_w/M_n
250	4.2 (0.2)	13.8 (2.1)	12.5 (1.3)	8.8 (0.1)	100 (3)	299 (10)	3.0 (0.2)
280	3.7 (0.1)	7.9 (3.4)	24.7 (3.2)	12.3 (0.2)	90 (7)	275 (10)	3.1 (0.1)
300	3.5 (0.1)	6.7 (0.8)	28.1 (0.9)	14.5 (0.7)	74 (4)	240 (4)	3.2 (0.1)
P-2		4.8 (0.1)	ND		128 (3)	382 (11)	3.0 (0.1)

Bio-oil fractionation

Temp (°C)	Solvent fractionation (%)			
	Creosote	Wood-derived compound		
		Phenolics	Ether-soluble	Water-soluble
250	77 (2)	8 (0)	1 (0)	14 (2)
280	77 (3)	12 (0)	1 (0)	9 (3)
300	82 (1)	13 (1)	1 (1)	4 (1)