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KINETIC STUDY OF TIRE CARBON BLACK AND BIOMASS SOOT STEAM ACTIVATION USED FOR THE REMOVAL OF PHENOL AND CHLORINE FROM DRINKING WATER

Anna Trubetskaya, Elisabeth Schröder, Manuel Garcia-Perez

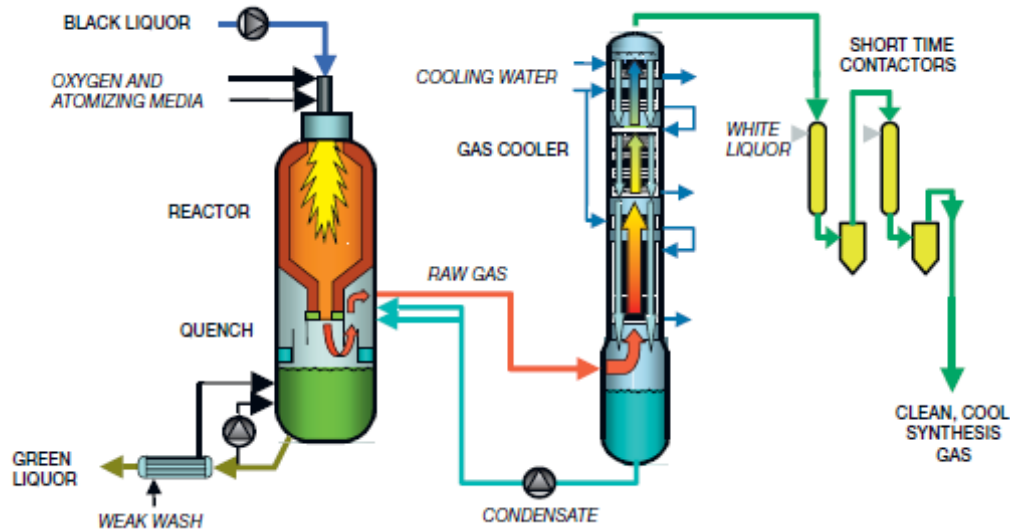
June 17th, 2019



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Biomass Gasification: Entrained flow gasification

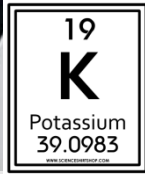
ChemRes catalytic gasification plant in Piteå, Sweden



- ✓ 100% conversion of feedstock at 1050°C when alkali are added generate to biomethanol
- ✓ Low soot and tar formation
- ✓ Low quality feedstocks (solid & liquid)
- ✓ Thermal power: 300MWth (20 ton BL/day)

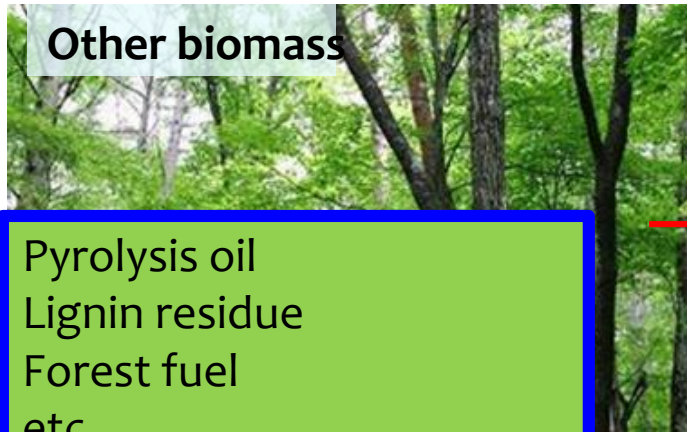


Introduction



Low heating value
High reactivity

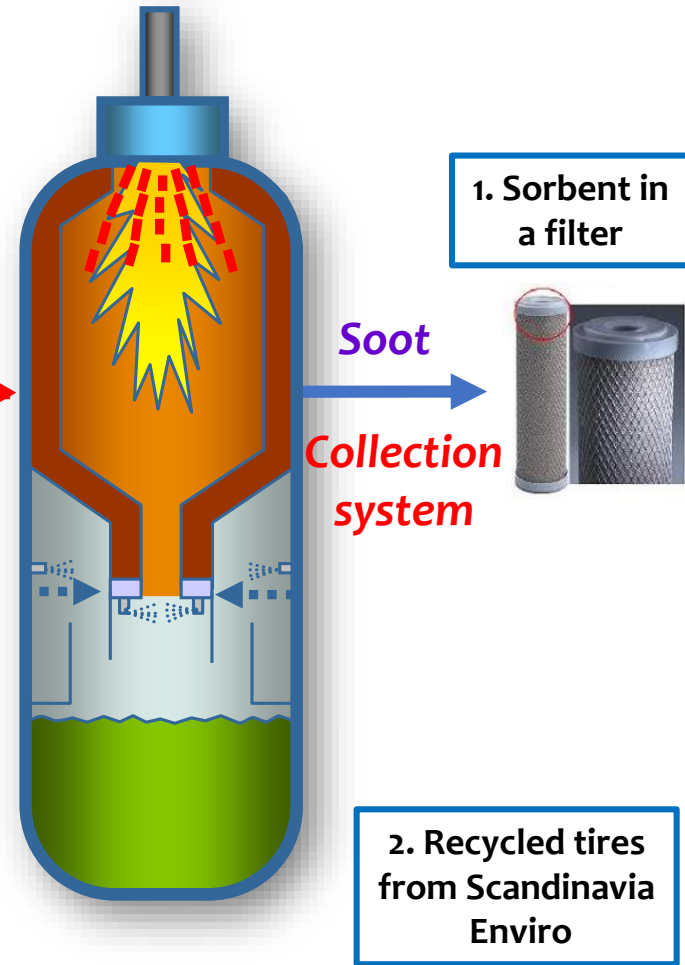
Mixing



Other biomass

Pyrolysis oil
Lignin residue
Forest fuel
etc.

High heating value
Low reactivity



1. Sorbent in a filter

Soot

Collection system

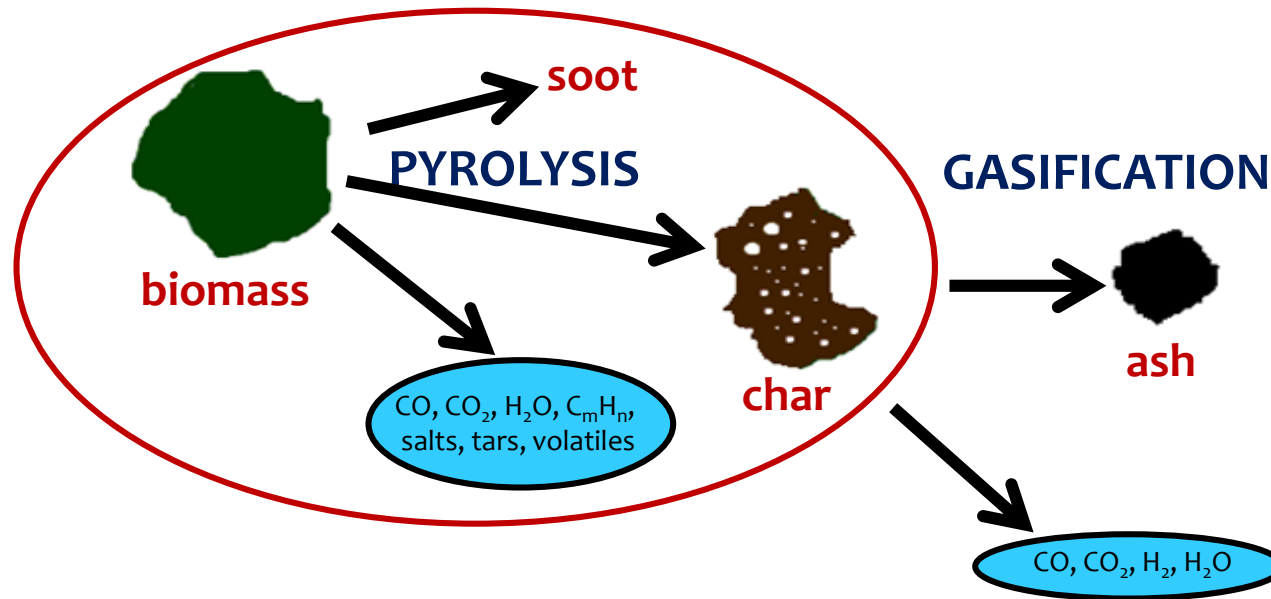
2. Recycled tires from Scandinavia Enviro



Introduction

Objectives

- to investigate the filtration performance of activated biomass soot and pyrolytic tire carbon black
- to correlate the material properties to the filtration performance
- to calculate the intrinsic kinetic parameters of the activation reaction order, activation energy and pre-exponential factor



Applied samples

	Pine-wood soot	Beech-wood soot	Wheat straw soot	Tire carbon black
Elemental composition (wt. %, db)				
Carbon	38.3	35	35.9	70
Hydrogen	17.8	19.2	18	0.6
Oxygen	31.4	33.5	25.7	5.3
Nitrogen	8.8	7.5	10.1	0.3
Chlorine	< 0.01	< 0.01	0.5	0.08
Sulfur	< 0.01	< 0.01	0.6	2.8
Ash (550°C, %, db)	0.3	3	6	21
Ash elemental analysis (mg kg⁻¹, db)				
K	200	3600	11000	2500
Si	50	200	8500	51000
Ca	600	2000	2500	9500
Na	30	100	150	2300

Experimental setup

Pinewood or Beechwood



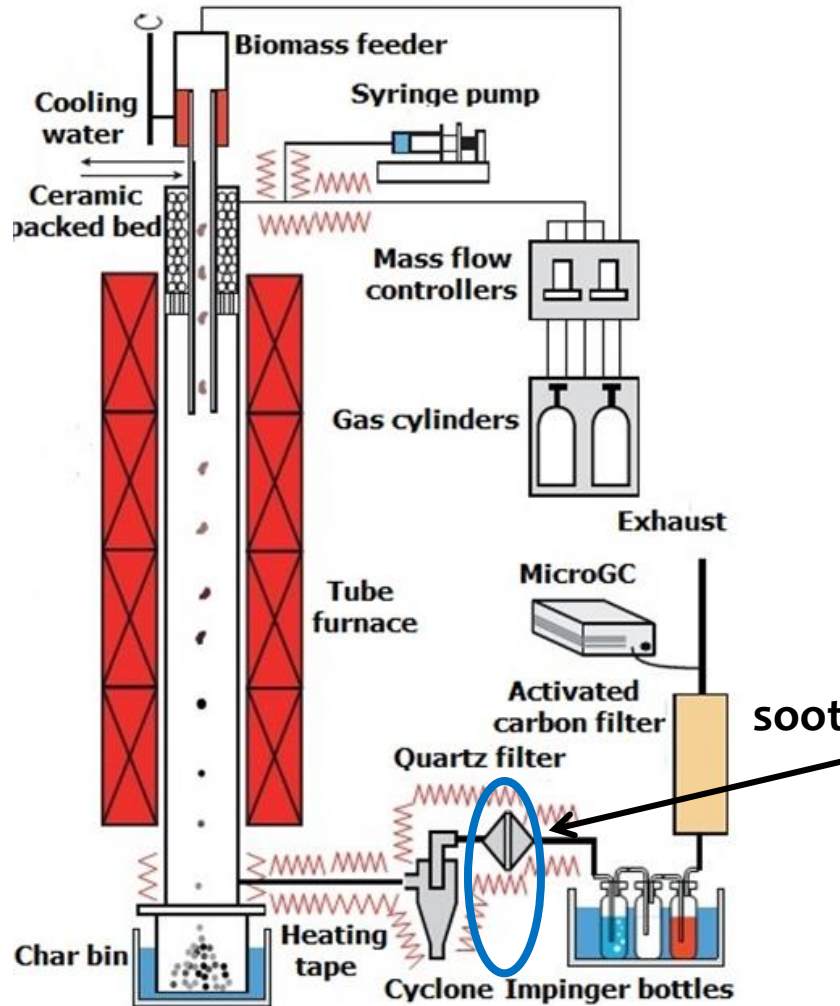
0.05-0.2 mm

Wheat straw



0.05-0.2 mm

Laminar drop tube furnace, 1250°C, 100% N₂



VOLVO tires



Pyrolysis
Scandinavia
Enviro Systems

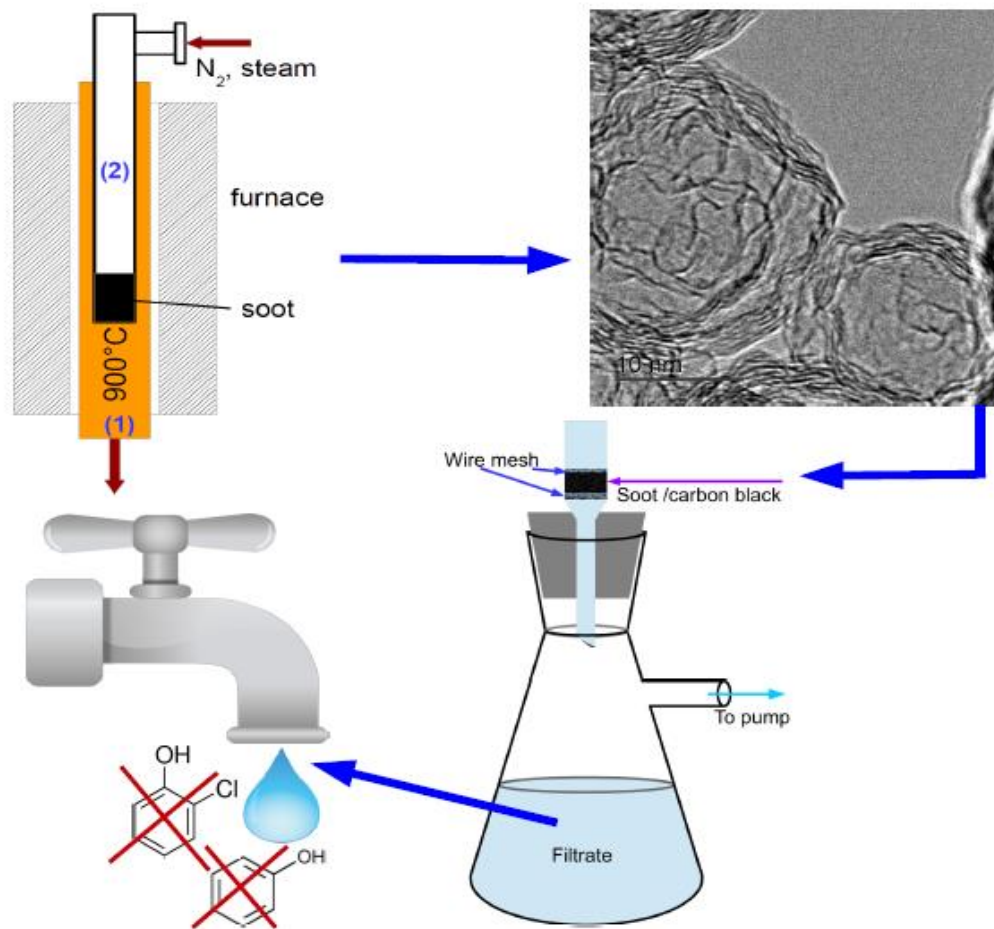
Tire carbon black



20-200 nm

Experimental setup

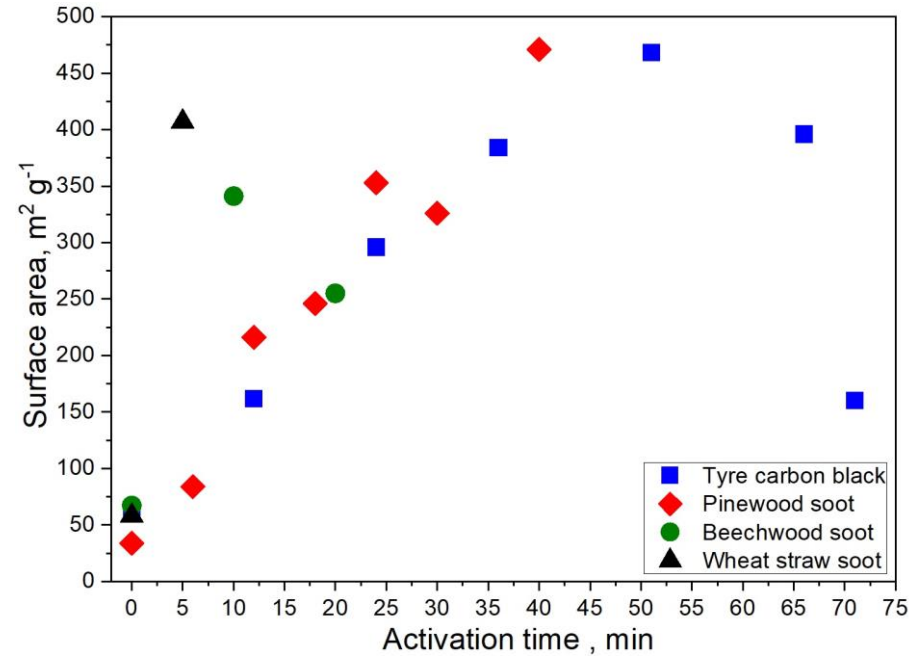
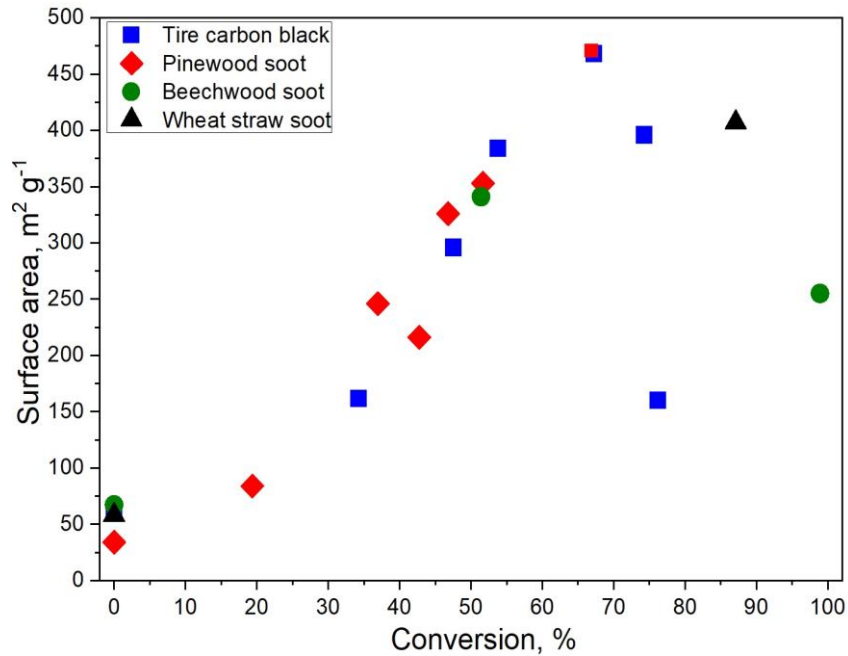
Steam activation furnace and filtration setup



Thermogravimetric analyzer with a steam generator



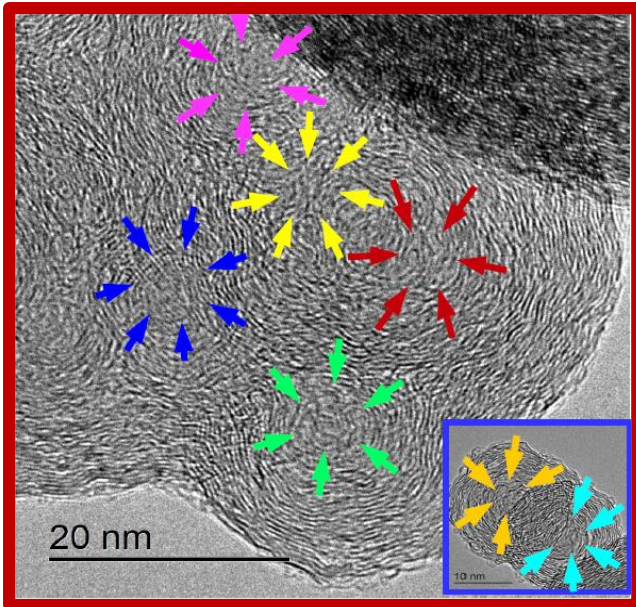
Surface area of over conversion and activation time



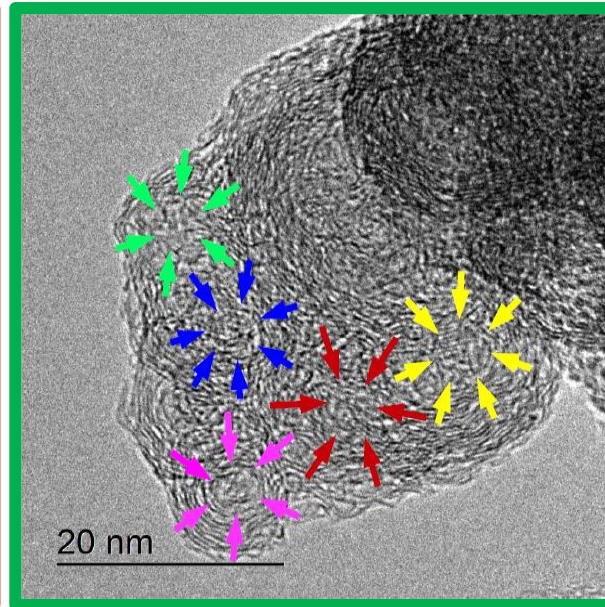
- Pinewood soot and tire carbon black required the activation time to be in the range of 40-50 min to obtain the highest specific surface area of $470 \text{ m}^2 \text{g}^{-1}$
- The 5-20 min steam activation of beechwood and wheat straw soot led to the higher specific surface areas (260 and $400 \text{ m}^2 \text{g}^{-1}$) at about 90 % carbon conversion
- The high content of alkali metals in beechwood and wheat straw soot caused the formation of the highest surface area and large macropores during the first 10 min of steam activation

Nanostructure of steam activated carbon

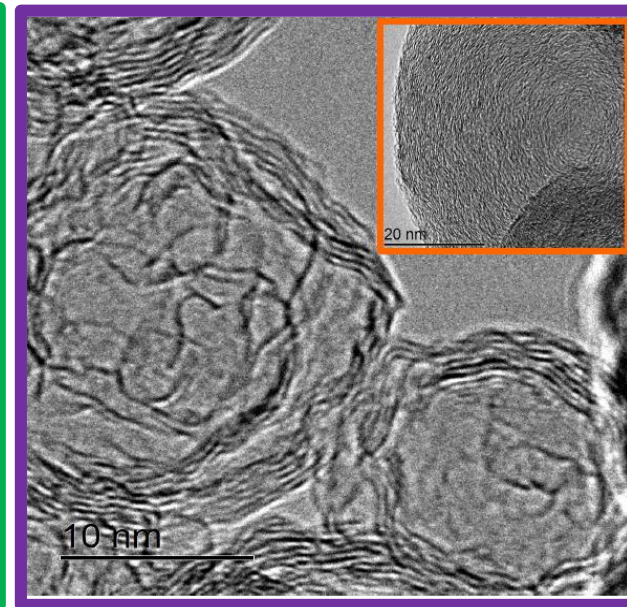
Activated pinewood soot



Activated tire carbon black



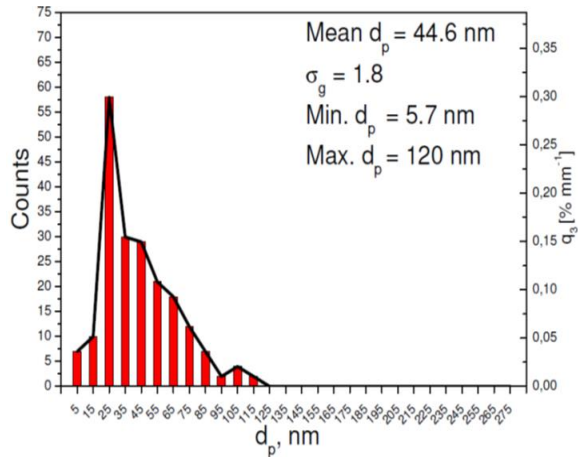
Activated beechwood soot



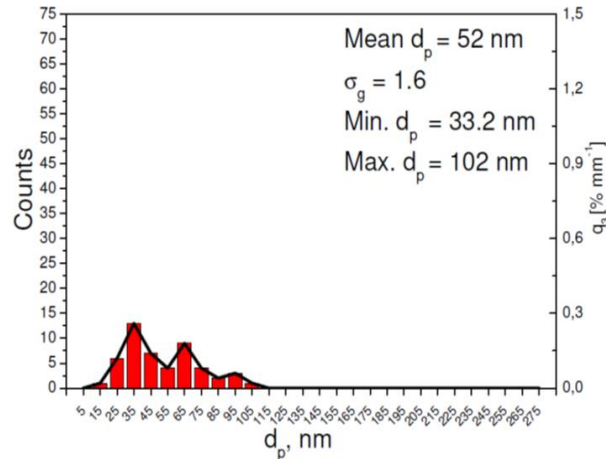
- Steam activated pinewood soot and tire carbon black particles did not contain macropores, whereas steam activated soot from high alkali containing wheat straw and beechwood showed a greater macroporosity
- The less ordered activated soot particles exhibited a lower packing density of graphene segments than the non-treated soot samples
- Non-treated samples and steam activated soot and tire carbon black exhibited a nanostructure resembling carbon black based on the curvature (0.83-0.88) and separation distance (0.33-0.35 nm)

Particle size of steam activated carbon

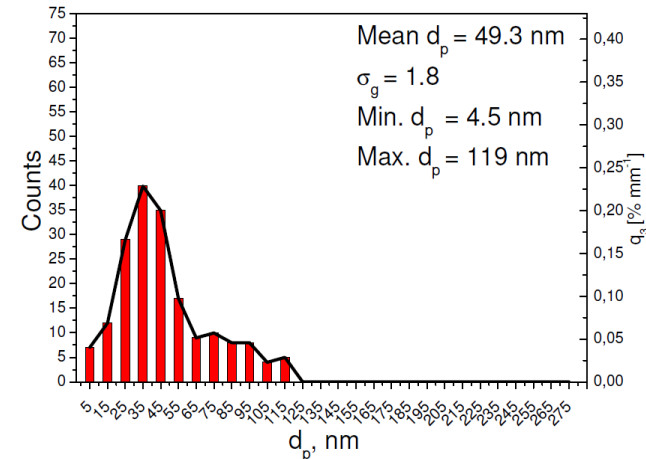
Activated tire carbon black



Non-treated beechwood soot



Activated beechwood soot

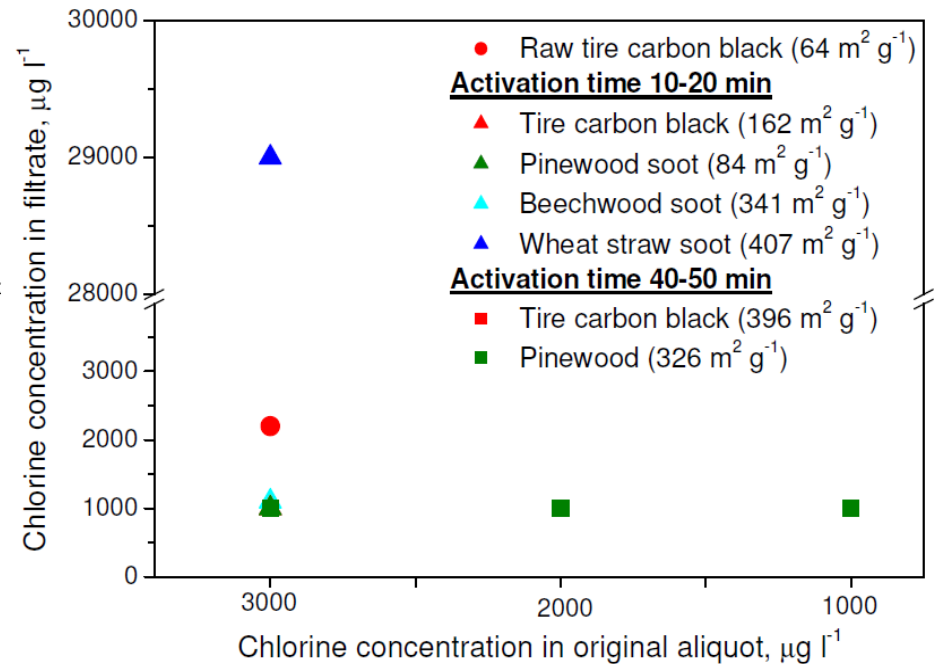
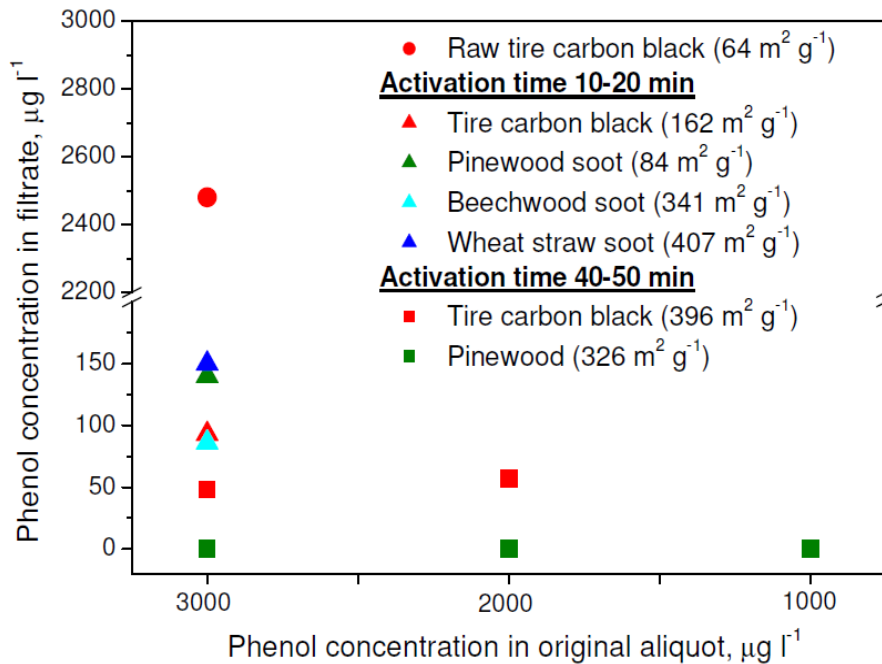


- The calculated geometric mean diameters of non-treated and steam activated samples varied from 20.6 to 78.6 nm
- The differences in particle size of non-treated and activated samples were small, except for the tire carbon black

Porosity of steam activated carbon

Sample	Activation	Cumulative pore volume	Mean pore diameter		Porosity
			Micropore	Mesopore	
	min	cm ³ g ⁻¹	nm	nm	%
Tire carbon black	0	0.4	1.6	19.2	47.4
	10	0.4	1.5	20.1	47.6
	65	0.6	1.5	19.2	55.1
Pinewood soot	0	0.3	1.5	17.5	41.1
	10	0.7	1.5	17.5	61.8
	30	1.3	1.5	12.2	73.7
Beechwood soot	0	0.4	1.5	19.2	44.3
	10	0.5	1.5	17.5	53.8

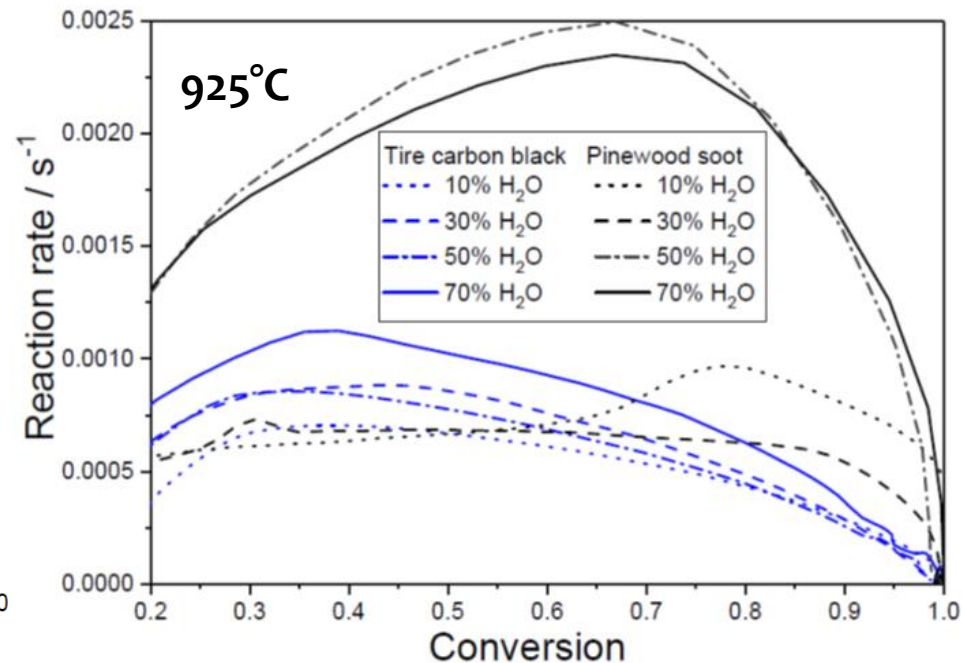
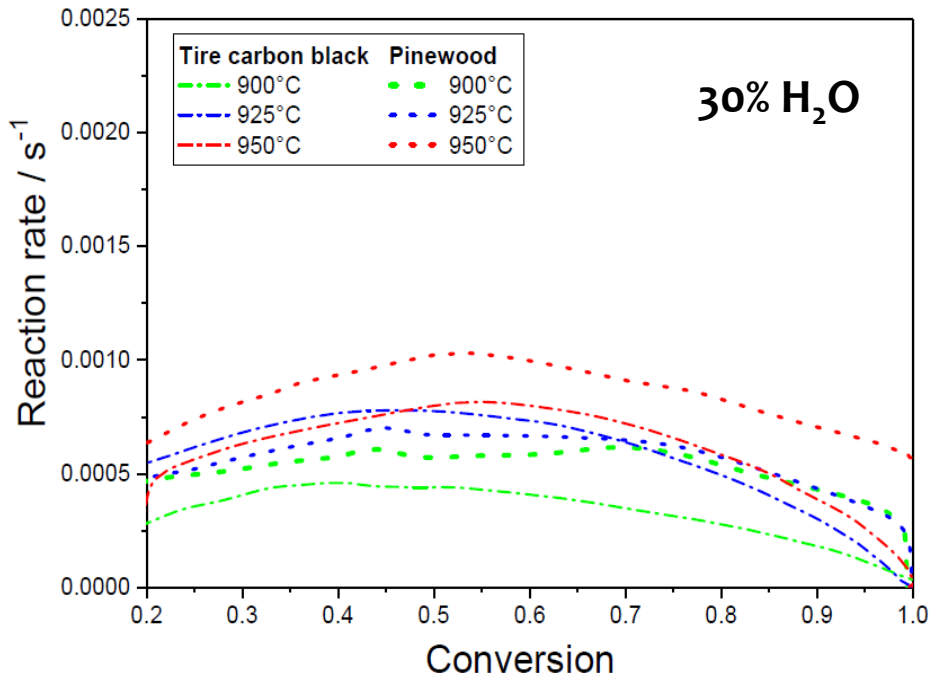
Filtration efficiency



- The use of non-treated tire carbon black as a sorbent removed chlorine and phenol from aqueous solution with the efficiency of 81.6 % and 73 %
- The activated carbon samples showed the filtration efficiency of about 95 % for both compounds
- The activation time of biomass soot and tire carbon black was the main factor influencing the filtration efficiency.

Kinetic parameters using TGA with the steam generator

- ❖ Isothermal kinetic analysis
- ❖ 7 mg of carbon / each experiment
- ❖ Heating from 85 to 900, 925 and 950°C at a constant heating rate of 10°C min⁻¹
- ❖ Steam in 10, 30, 50, and 70% mole was used and N₂ (30 ml min⁻¹) as a protective gas
- ❖ The steam activation of carbon was mainly kinetically controlled, and to a minor extent controlled by the external diffusion
- ❖ Optimum conditions were determined with the varying temperature and steam concentration
- ❖ Random pore model was used for the experimental data fitting



Conclusion

- ❖ This work has demonstrated a novel method for removing toxic chemicals - phenol and chlorine - from water using steam activation.
- ❖ Steam activation leads to significantly higher filter efficiencies compared to untreated materials with filter efficiencies as high as 95 % (both phenol and chlorine) for steam activated materials compared to 81.6 % (chlorine) and 73 % (phenol) for the untreated carbon material.
- ❖ A twenty-fold decrease in phenol and chlorine concentrations was observed using carbon black and pinewood biomass soot.
- ❖ The calculated kinetic parameters derived from the steam TGA experiments were calculated. The used model is able to fit the tire carbon black and soot conversion results and predict the experimentally determined reaction rate.
- ❖ Overall, this work shows great promise for using these waste streams as cheaper alternatives for cleaning wastewater, which is of great importance for water remediation issues.



Thank you!



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