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„Carbon Materials for Metal Production – Tradition and Progress“

AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

Highly Porous Carbon Adsorbents from Coal Tar Pitch and Waste Polymers

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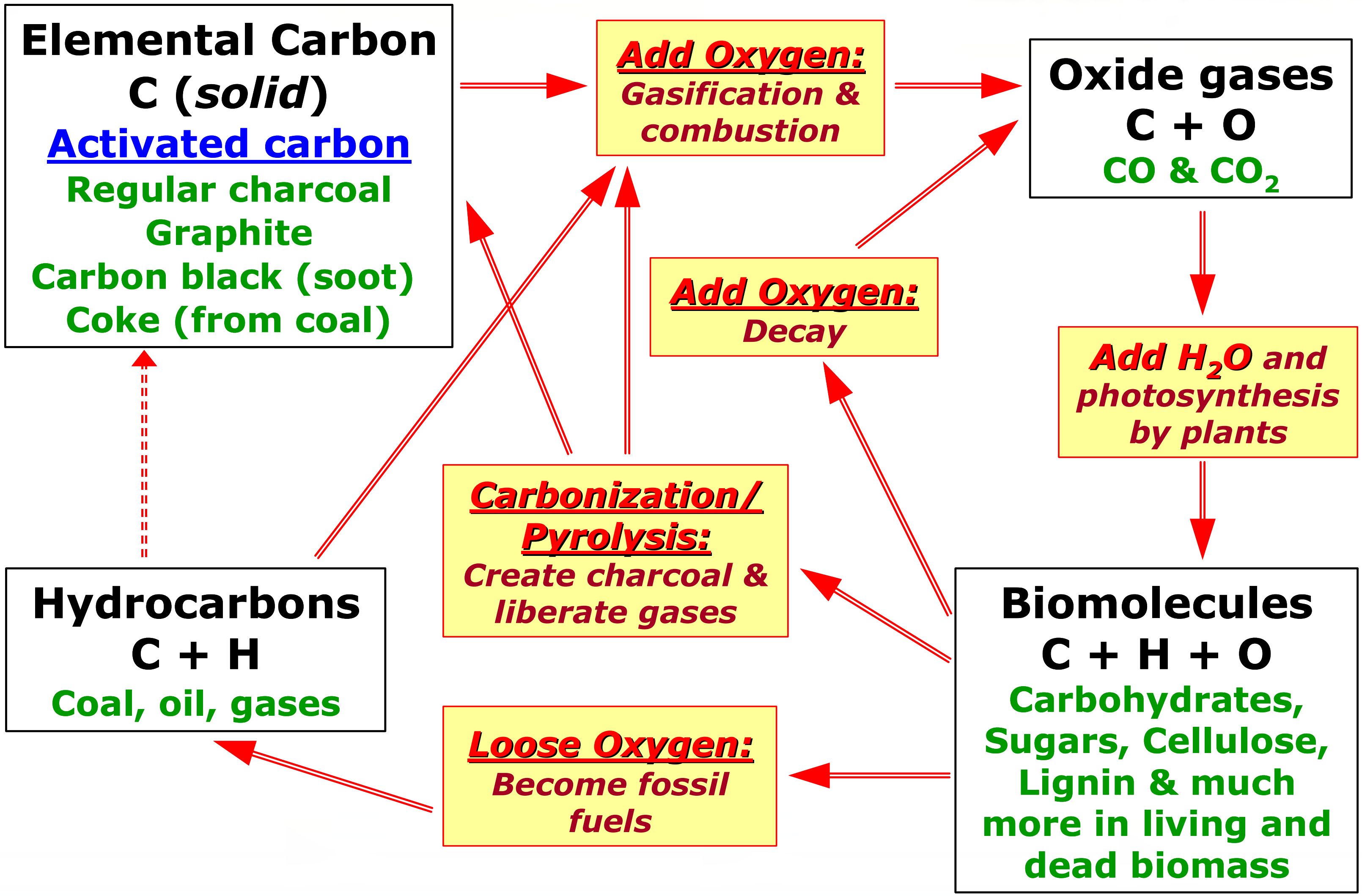
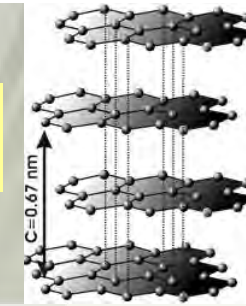
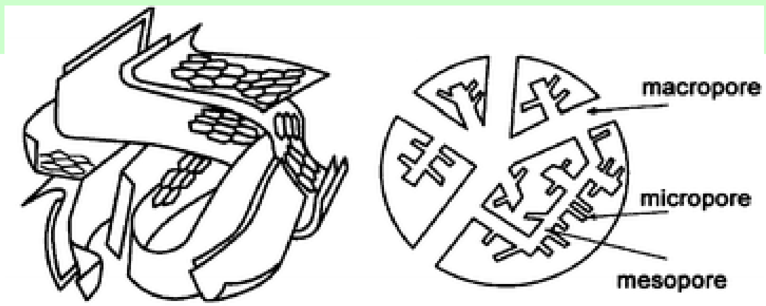
BASIC FORMS AND TRANSFORMATIONS OF CARBON

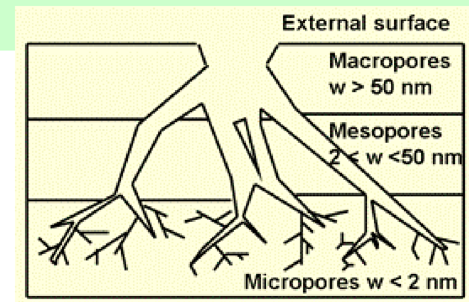


What is Activated Carbon?

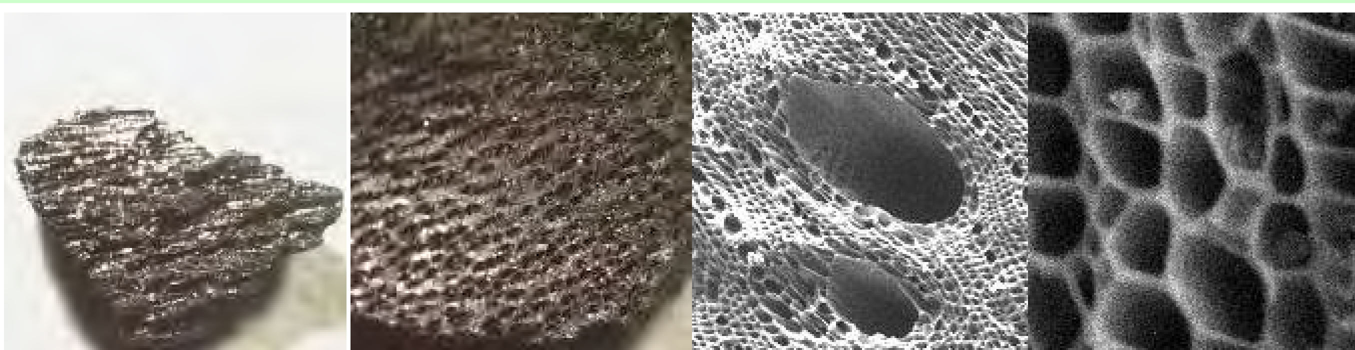


Highly porous, amorphous solid consisting of micro crystallites with a graphite lattice. It differs from graphite by having a random imperfect structure which is highly porous over a broad range of pore sizes.





Activated carbons have unique porous structures, large specific surface area and porosity, and various surface functional groups



Zoomed images of Carbon Surface and Pores *(zoom increases left to right)*

ACTIVATED CARBONS

Granulated

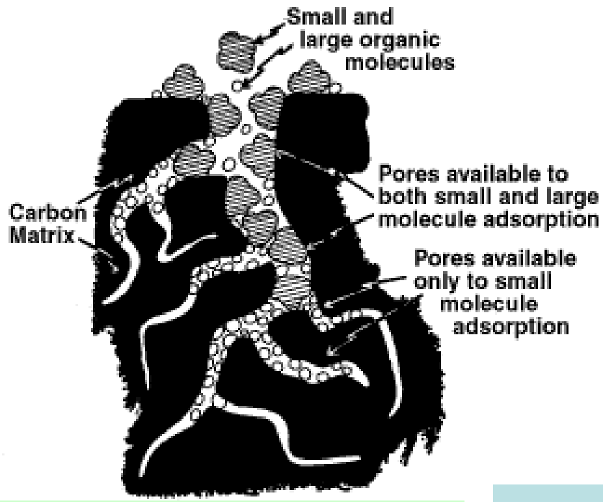
Crushed

Powdered

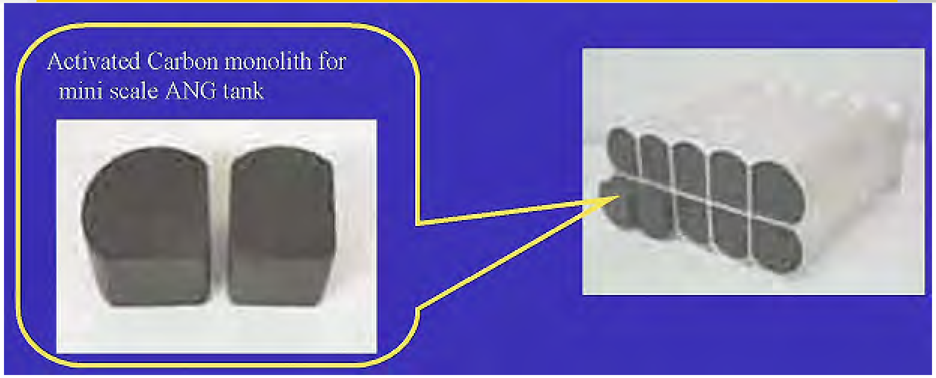
Monolithic forms of AC

AC fibers

Activated Carbon Applications

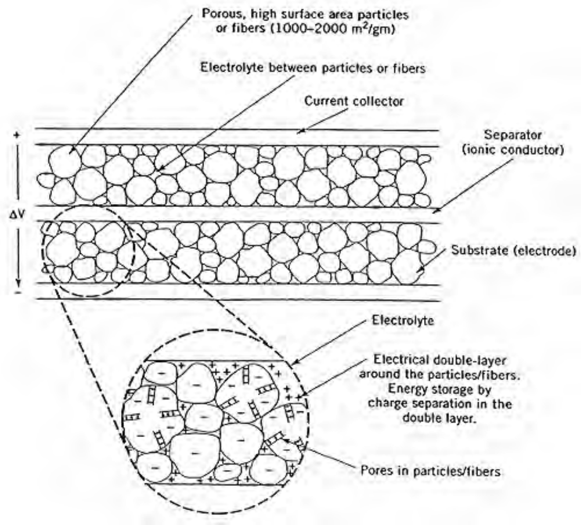


Natural gas, hydrogen storage



- Water treatment
- Air treatment
- Gas purification
- Gold purification
- Metal extraction
- Medicine
- Sewage treatment
- Gas masks
- Filter masks

Electrochemical applications (electrodes for fuel cells, supercapacitors)



Main Processes in the Production of Activated Carbon

SELECTION OF RAW MATERIALS

The choice of raw material has a large influence on the characteristics and performance of the AC, each producing an AC with differing surface areas, total pore volume, pore radius and pore volume distribution.

We should consider the following requirements:

- **Required properties of the final product**
- **Cost**
- **Availability**
- **Consistency of quality**
- **Purity**

Production of activated carbons comes from different carbonaceous materials like coal, wood, coconut shells, *etc.*

Main Processes in the Production of Activated Carbon

CARBONISATION

The raw materials are first ***carbonized*** via a controlled heating process at "*low*" temperature (200-300°C) in an oxygen-lean environment which keeps the material from burning. This process converts the raw material into a disordered carbon structure full of tiny pores.

ACTIVATION

The carbonized materials are then ***activated*** by steam (or chemical treatment). Steam activation is carried out at high temperature (700 - 1100°C) and the carbonized materials react with the steam to form carbon monoxide and hydrogen which exit as gases leaving behind a highly porous activated carbon material.

A porous structure is formed inside the carbonisates due to the partial gasification of the elemental carbon.

ACTIVATED CARBONS PREPARATION

RAW MATERIALS

COAL - TAR PITCH (CTP)

POLYMERS:

PAN – *polyacrylonitryle*
PET - *poly(ethylene terephthalate)*
PF - *phenol/formaldehyde resin*
PC – *polycarbonate*
PMMA - *poly(methylenemethacrylate)*

HOMOGENIZATION OF COMPOSITES

- **Compositions with different pitch/polymer ratios were prepared in the conditions allowing to obtain homogeneous and stable mixtures.**
- **Depending on the polymer type, the components were homogenized in the temperature 423-523K, during 0.5-2.5 h.**

ACTIVATED CARBONS PREPARATION

CARBONISATION

Primary carbonization

Heating to 793K
N_2 atmosphere

Secondary carbonization

Heating to 793K,
then to 1123K

ACTIVATION

Selective gasification with

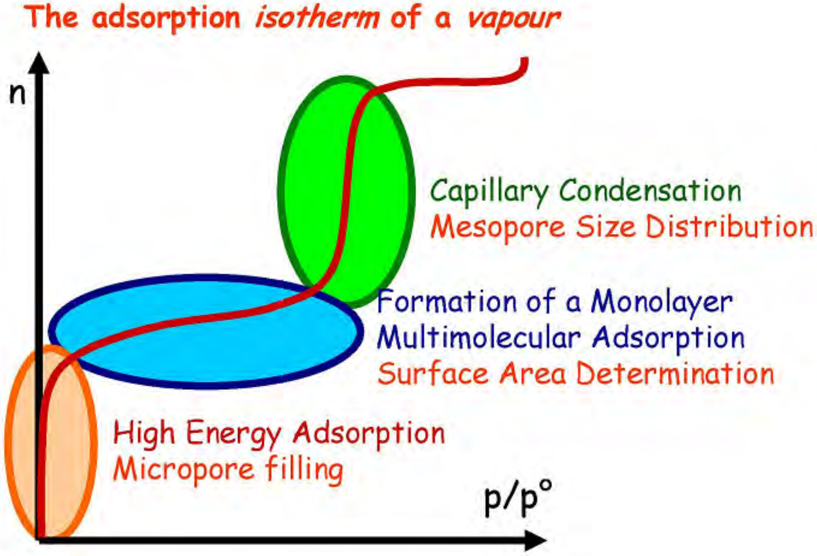
steam (1073K)
or
carbon dioxide (1123K)
to 50% burn-off

Chemical activation with KOH

Heating of KOH and product of the primary carbonization (mass ratio of 4:1) in N_2 atmosphere to 1073K

The textural properties of the activated carbons were determined using physical adsorption of gases (N_2 at 77K and CO_2 at 273K) using a Quantachrome Autosorb 1C analyzer

INTERPRETATION OF EXPERIMENTAL DATA



- NIST 2006, *Porosity and Specific Surface Area Measurements for Solid Materials*.

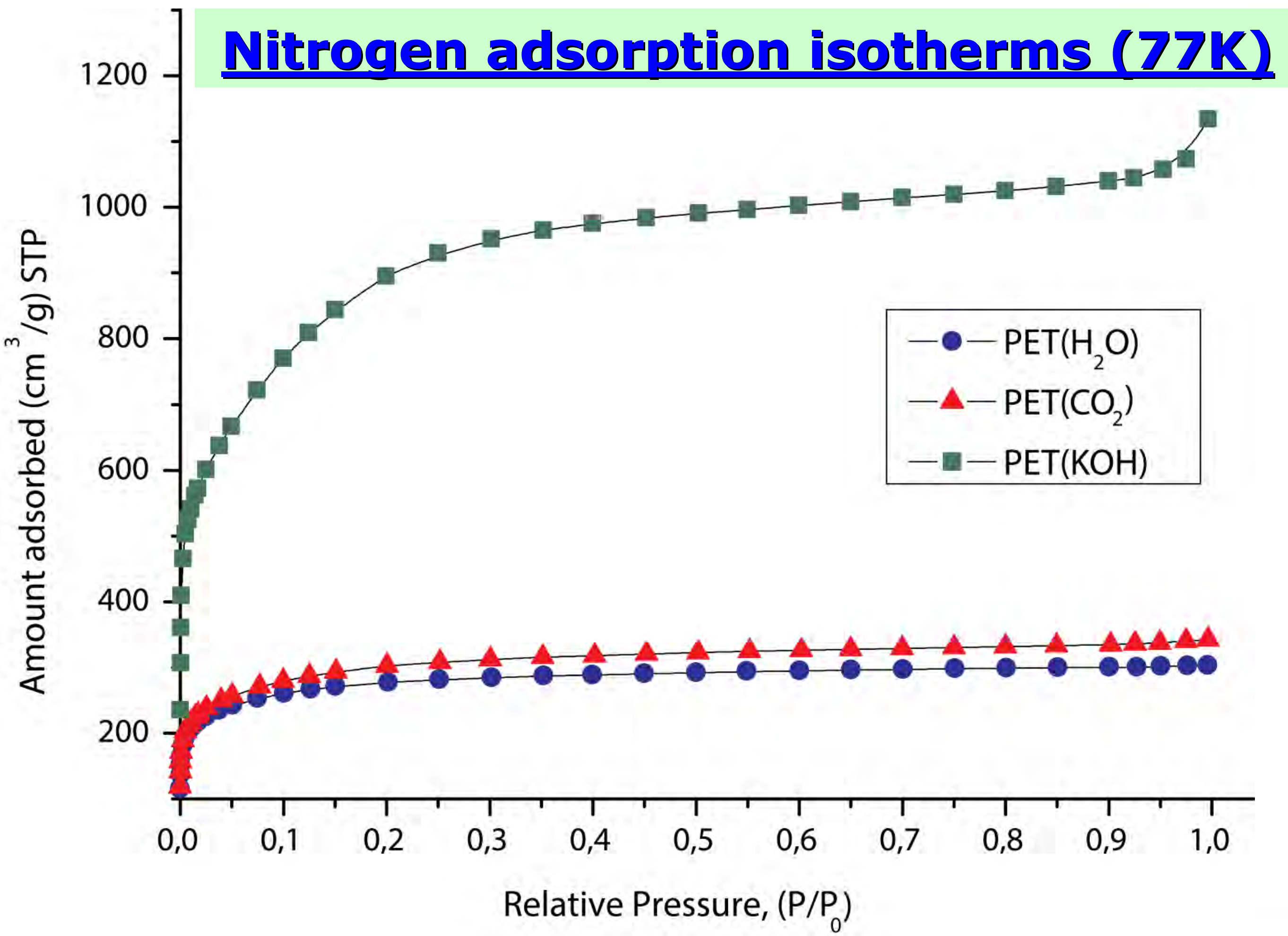
- ISO 9277: 2010, *Determination of the specific surface area of solids by gas adsorption - BET method*.

- ISO 15901-1: 2005, *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 1: Mercury porosimetry.*

- ISO 15901-2: 2006, *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 2: Analysis of mesopores and macropores by gas adsorption.*

ISO 15901-3: 2007, *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption — Part 3: Analysis of micropores by gas adsorption.*

Influence of activating agent on porous texture of activated carbons composites 50% CTP + 50% PET



Influence of activating agent on porous texture of activated carbons composites 50% CTP + 50% PET

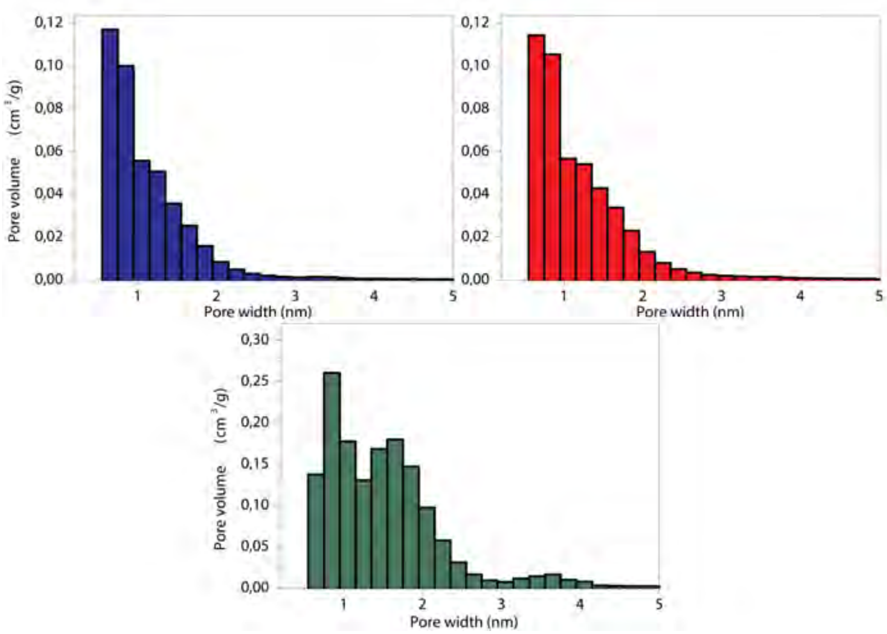
Porous texture of activated carbons from PET

Activating agent	H_2O	CO_2	KOH
N_2 ad-/desorption isotherm (77K)			
BET surface area, m^2/g	1042	1122	3265
Dubinin-Radushkevich volume of micropores, cm^3/g	0.385	0.403	1.060
Dubinin-Radushkevich surface area of micropores, m^2/g	1080	1145	2983
DFT volume of pores: 0.35÷2 nm, cm^3/g	0.319	0.441	1.282
DFT surface area of pores: 0.35÷2 nm, m^2/g	816	1028	2424
DFT volume of pores: 2÷40 nm, cm^3/g	0.112	0.044	0,275
DFT surface area of pores: 2÷40 nm, m^2/g	185	26	167
CO_2 adsorption isotherm (273K)			
DFT volume of pores: 0.35÷1.5 nm, cm^3/g	0.230	0.229	0.503
DFT surface area of pores: 0.35÷1.5 nm, m^2/g	709	710	1287

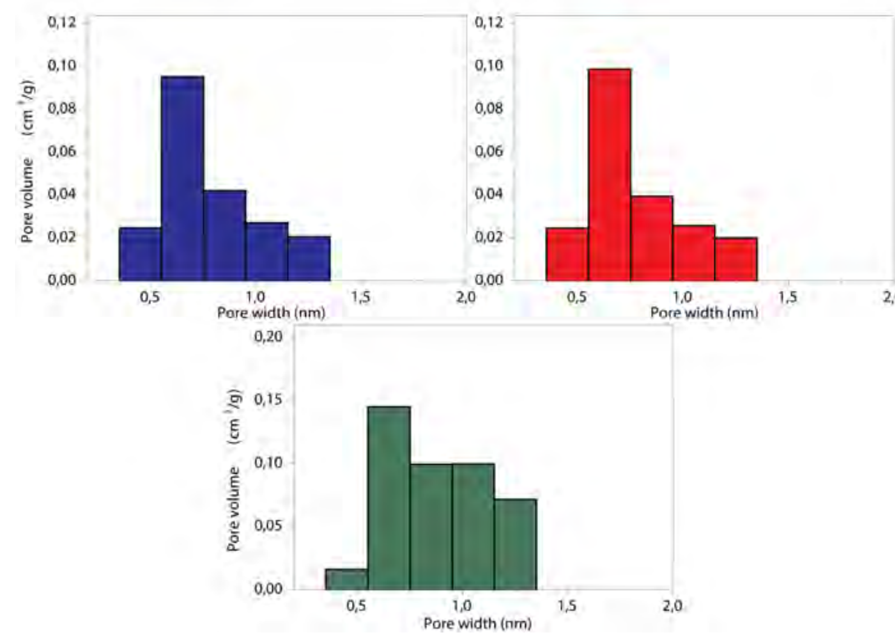
Influence of activating agent on porous texture of activated carbons composites 50% CTP + 50% PET

Pore size distribution for activated carbons from PET

N_2 adsorption isotherms (77K)



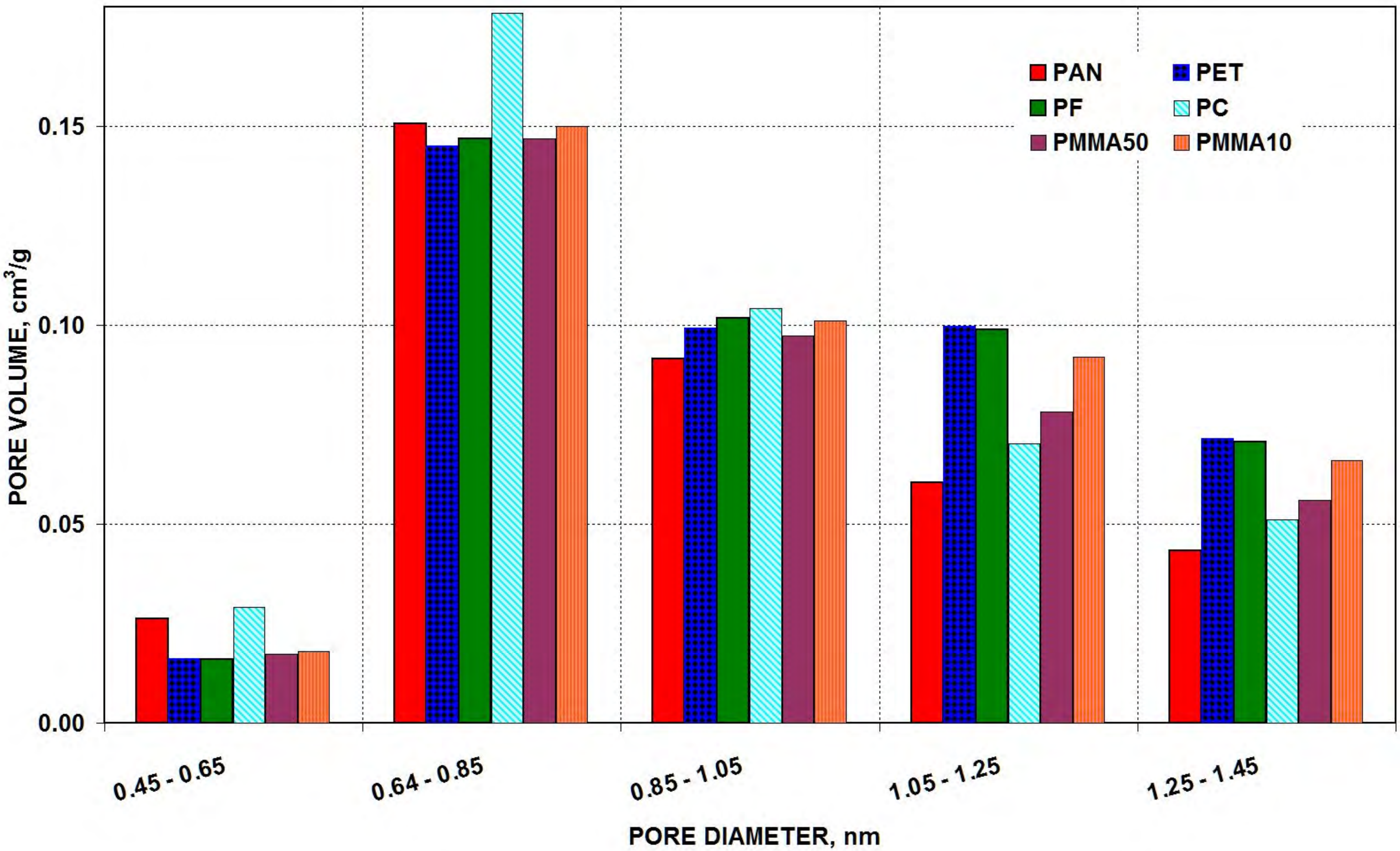
CO_2 adsorption isotherms (273K)



Influence of precursor polymers on porous texture of composites activated with KOH

Precursor polymer	PAN	PET	PF	PC	PMMA50	PMMA10
N_2 ad-/desorption isotherm, 77K						
BET Surface Area, [m^2/g]	2225	3265	3345	2330	3134	2917
Total Pore Volume, [cm^3/g]	1.198	1.635	1.747	1.021	1.539	1.439
Volume of micropores, [cm^3/g]	0.813	1.06	1.062	0.824	1.017	0.949
Surface area of micropores, [m^2/g]	2283	2983	2989	2313	2875	2670
Volume of mesopores, [cm^3/g]	0.179	0.328	0.258	0.063	0.162	0.127
Surface area of mesopores, [m^2/g]	143	167	214	40	102	80
Average radius of mesopores, [nm]	1.7	2.2	1.5	1.7	1.7	1.7
DFT Volume of pores (0,35-40 nm), [cm^3/g]	1.113	1.557	1.633	0.939	1.43	1.334
DFT Surface area of pores (0,35-40 nm), [m^2/g]	2009	2591	2598	2076	2488	2312
CO_2 adsorption isotherm, 273K						
DFT Volume of pores (0,35-40 nm), [cm^3/g]	0.417	0.503	0.506	0.486	0.453	0.493
DFT Surface area of pores (0,35-40 nm), [m^2/g]	1174	1287	1296	1370	1201	1287
Monte-Carlo pore volume, [cm^3/g]	0.482	0.518	0.541	0.542	0.486	0.526
Monte-Carlo surface area, [m^2/g]	1229	1265	1304	1400	1212	1292

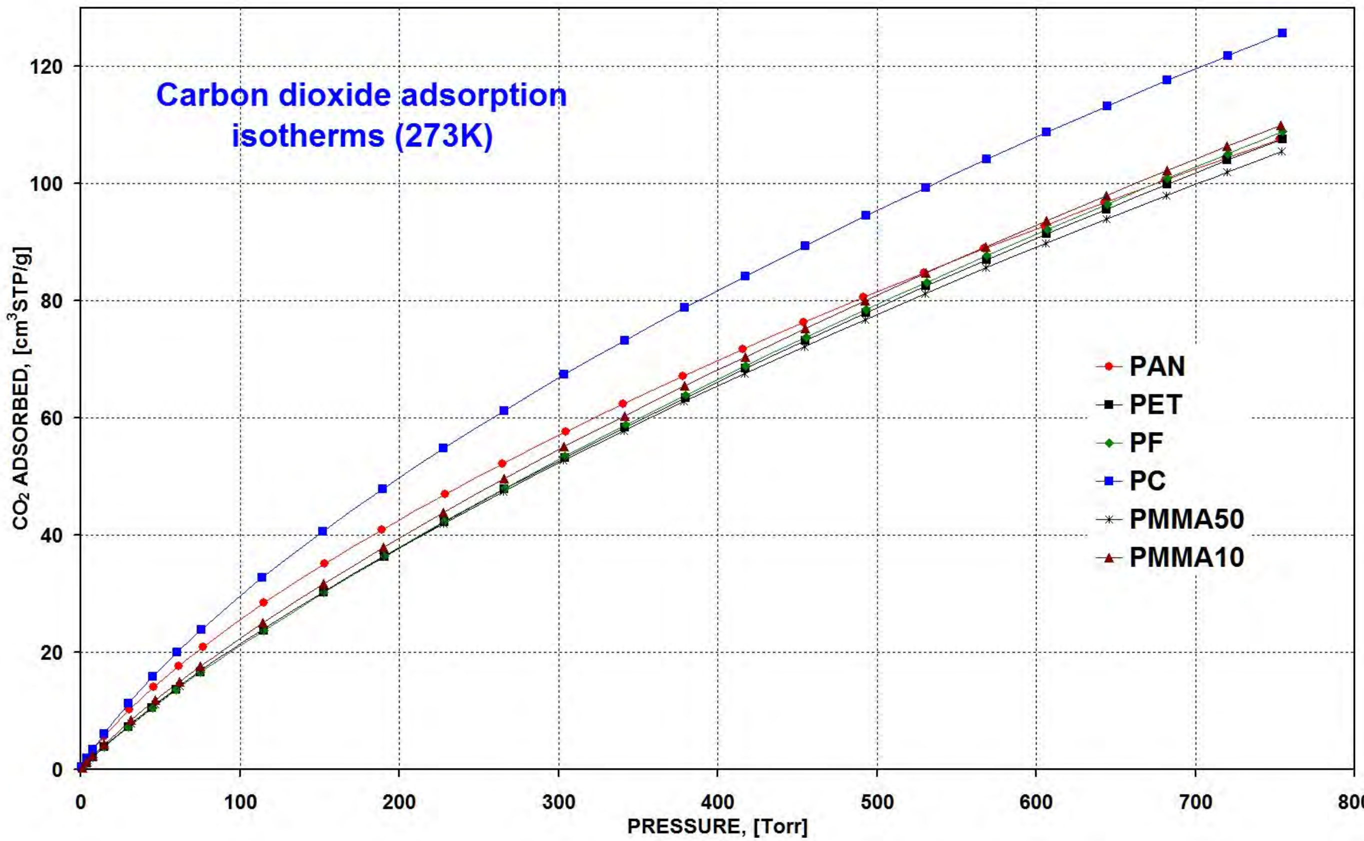
PSD of activated carbons from coal-tar pitch and polymer composites activated with KOH



Acid-base properties of AC's
(Boehm titration method)

Polymer	Activating agent	Acidic groups [meq/g]				Basic groups [meq/g]
		Total	Carboxylic	Lactonic	Phenolic	
PET	CO_2	0.58	0.38	0.10	0.10	0.35
PET	H_2O	0.55	0.42	0.05	0.08	0.44
PET	KOH	0.56	0.18	0.10	0.28	1.49
PET	K_2CO_3	0.44	0.13	0.08	0.23	0.94
PET	$MgCO_3$	0.33	0.05	0.09	0.19	1.45
PMMA	CO_2	0.43	0.21	0.10	0.12	0.39
PMMA	H_2O	0.50	0.10	0.32	0.18	0.65
PMMA	KOH	0.66	0.13	0.16	0.37	0.99
PF	CO_2	0.67	0.25	0.21	0.21	0.35
PF	H_2O	1.27	0.35	0.25	0.67	0.73
PC	CO_2	0.40	0.07	0.13	0.20	0.85
PC	H_2O	0.34	0.09	0.07	0.18	1.02
PC	KOH	1.32	0.17	0.15	1.00	0.98
PAN	CO_2	0.23	0.05	0.04	0.14	0.62
PAN	H_2O	1.30	0.46	0.35	0.49	1.10
PAN	KOH	1.05	0.32	0.40	0.33	0.98

CO_2 adsorption isotherms on activated carbons from coal-tar pitch and polymer composites activated with KOH



The samples seems to be a suitable adsorbent for carbon dioxide because its adsorption properties are dependent on its pore texture and chemical surface characteristics determined by the amount and type of heteroatoms existed in the acid, basic, or neutral form of organic functional groups.

CONCLUSIONS

- Activated carbons of coal-tar pitch and polymer waste origin can be converted to highly porous products with essentially high micropore volume and relatively small volume of mesopores.

- In spite of the high carbon content of the precursors, the porous structure developed during the preparation is strongly influenced by the original matrix structure of the polymers, as well as greatly depends on the carbonization and activation conditions.

- A good combination of activating agent, ratio of activating agent/precursor and carbonisation/activation temperature allows the production of activated carbons with specific chemical and structural characteristics, which are properties very important for identifying an application.

- Waste polymers are promising activated carbon precursors for two reasons. First, they contain a high percentage of carbon and second, they are readily available in a relatively pure state from waste recovery.

Thank you for your attention