UNIVERSIDAD DE MÁLAGA

A PERSPECTIVE ON THE PREPARATION OF VALUE-ADDED CARBON MATERIALS FROM LIGNIN

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Terma IQ UMA

The thermochemical conversion of lignin into different added-value carbon materials constitutes an alternative approach for valorization of this co-product that can be integrated in pulping and biorefinery processes. Such approach is based on the relatively high carbon content and the abundance of aromatic rings in the structure of raw and technical lignins.

The use of different electrospinning configurations (i.e. coaxial and triaxial needles) is the key for enabling a steady production of microsized lignin spheres, fibers and tubes.

Metal nanoparticles can be casted into the carbon fibers by adding the metallic precursor in the lignin solution, enabling the preparation of carbon-supported catalysts and electrocatalysts in fibrillary morphology in a one-step procedure.

Carbons with hierarchical pore structure have been also obtained from lignin using hard templating techniques with different type of zeolites.

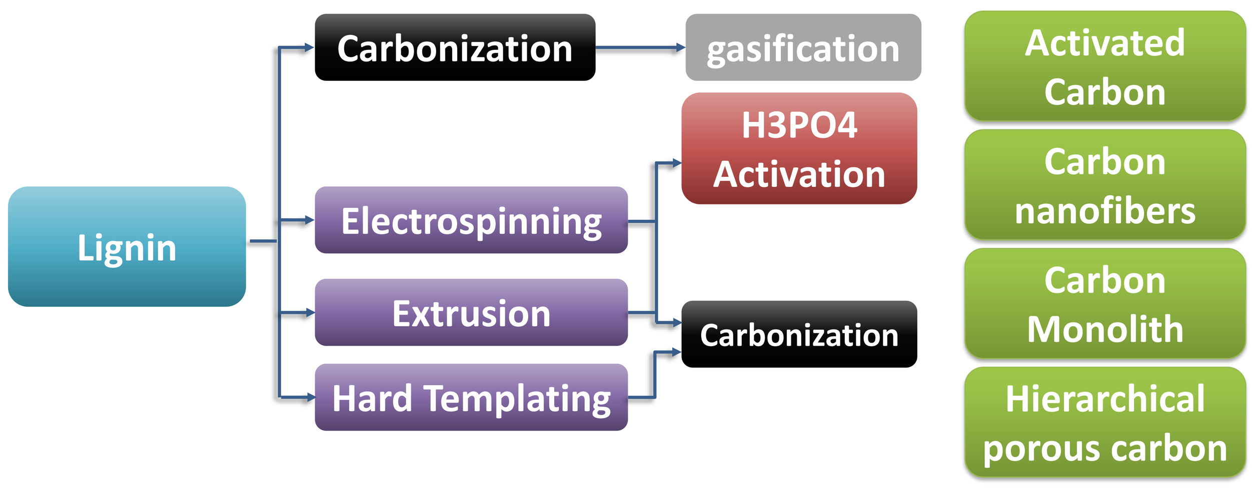
When alkalis are found in the parent lignin, physical activation with CO_2 is promoted. The presence of metal ions on the surface of the resulting activated carbons can serve as active phase for catalysis applications.

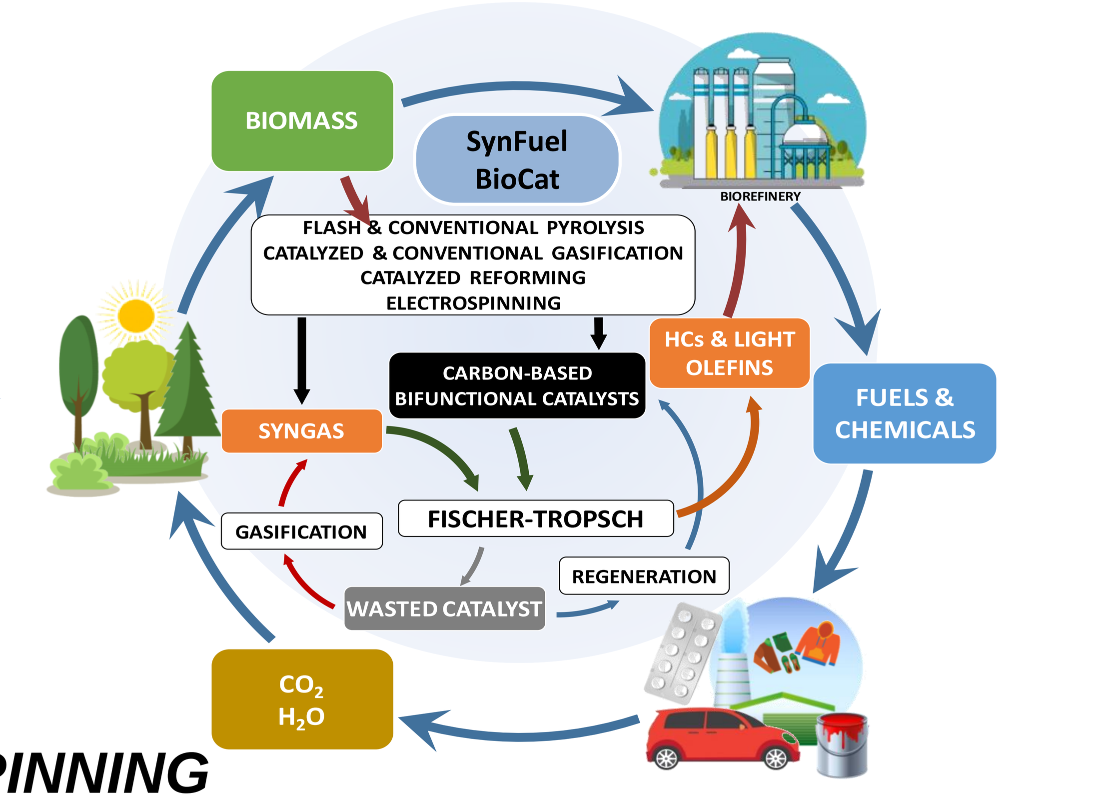
Preparation of binderless activated carbon monoliths from lignin is feasible by extrusion of H_3PO_4-lignin mixtures, obtaining porous monoliths with different number of channels.

Our research group is offering expertise in the preparation of carbon-based catalysts for lignin catalytic conversion into chemicals and bioproducts. These carbon-based catalysts can be prepared from lignin itself, increasing the sustainability and independence of such processes.

For more than 25 years, TERMA group from University of Malaga have explored lignin valorization through the preparation of different carbon materials

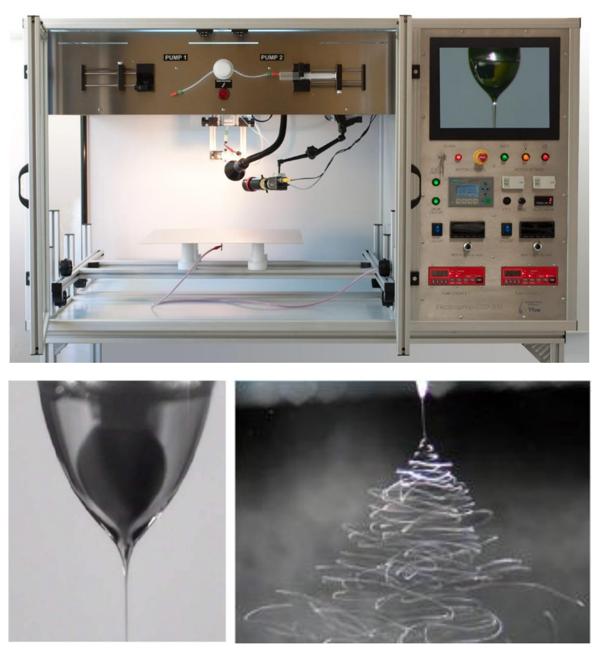
Our research group is currently focused on the preparation of carbon-based catalysts from lignin for syngas upgrading, catalytic pyrolysis, lignin depolymerization, steam reforming and Fischer-Tropsch synthesis

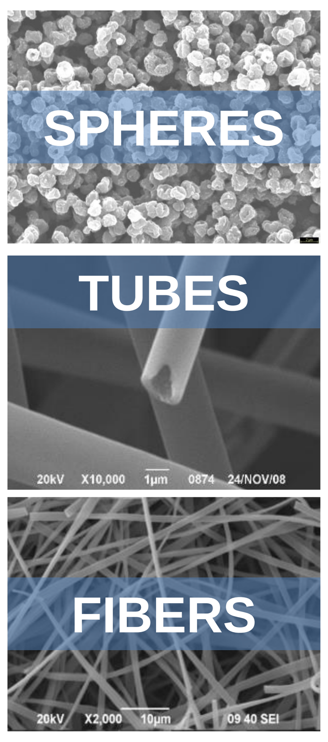




❖ CARBON NANOFIBERS, TUBES AND SPHERES BY ELECTROSPINNING

Electrospinning

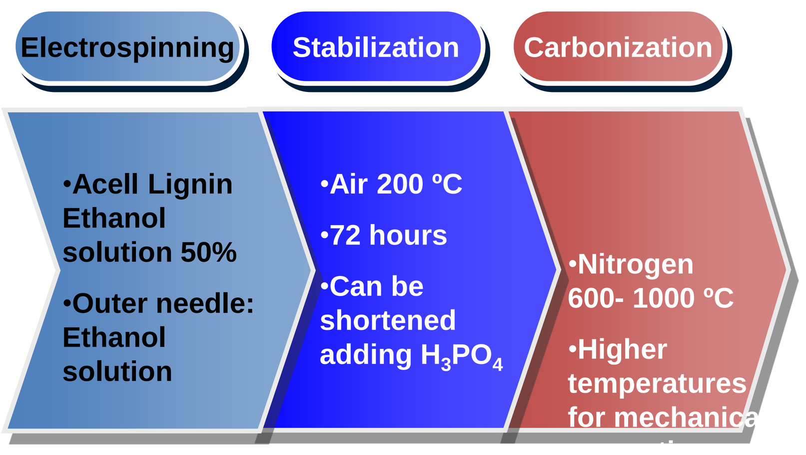


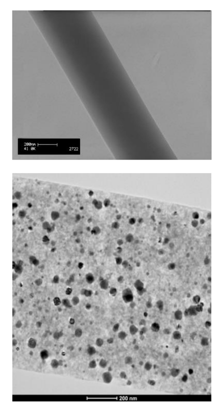


- Morphology is governed by voltage.
- Tubes can be obtained injecting oil through an inner needle.
- Metals can be loaded on the carbon fiber surface by adding salt into the lignin solution

Adv. Mater. (2007) 19, 4292
Carbon. (2010) 48, 696
Appl. Catal. B (2017) 211,18-30
J. Mater. Chem. A (2018) 6,1219-1233
Green Chemistry (2016) 18, 1506-1515
Catalysis Today (2022) 383, 308-319
Separation and Purification Technology (2020) 241, 116724

Alcell Lignin

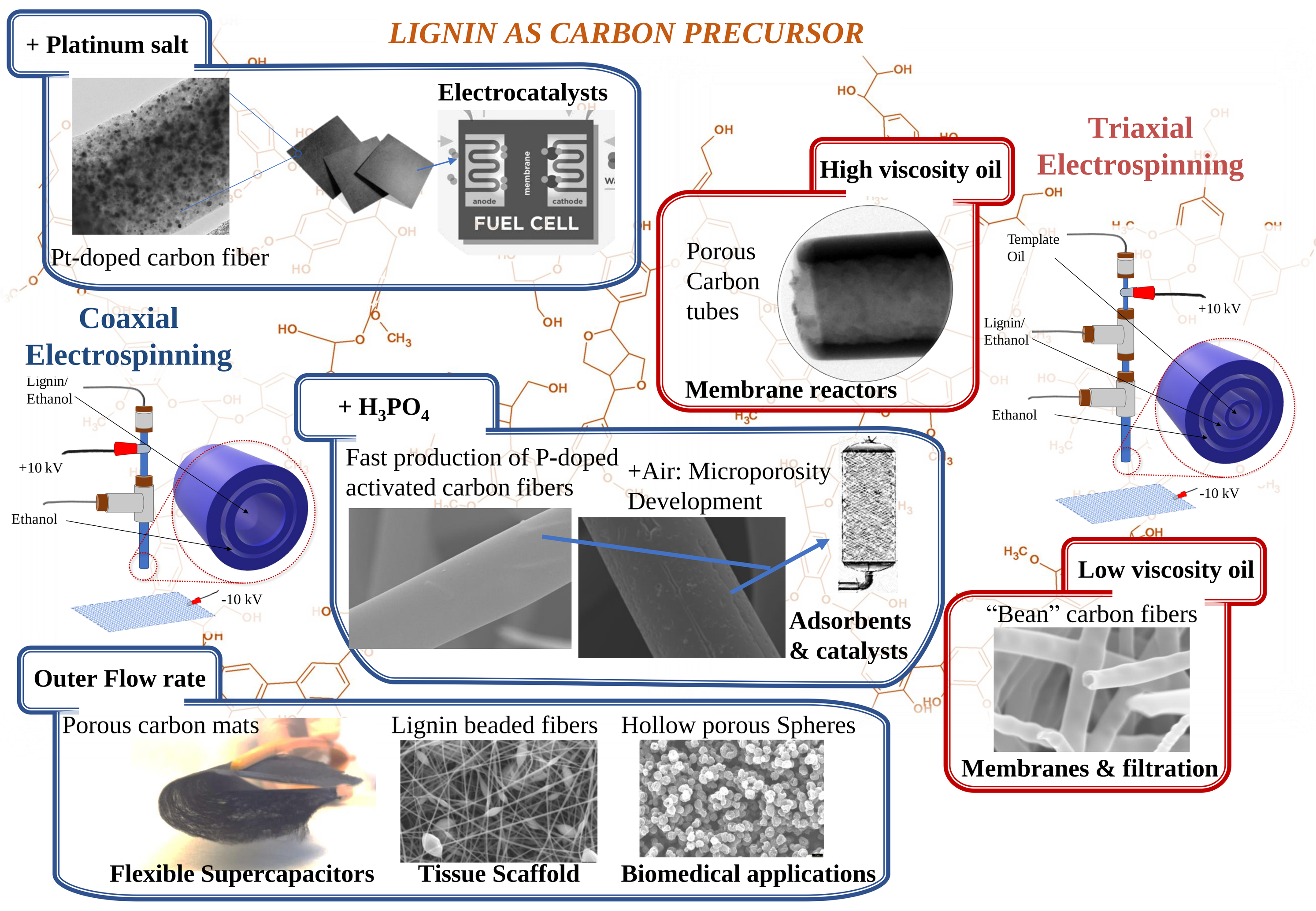




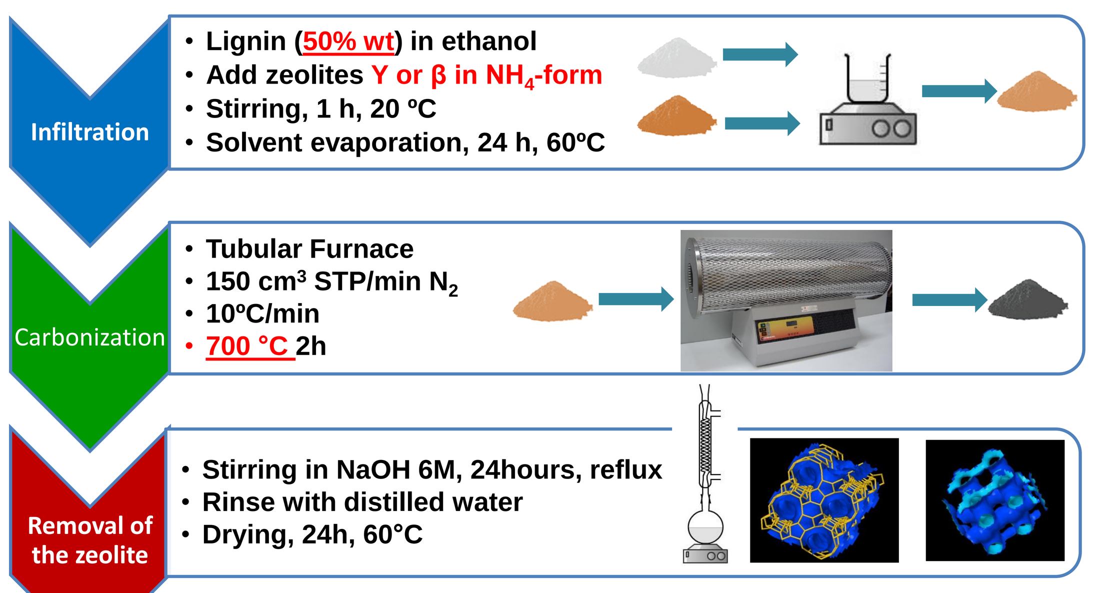
Carbon nanofibers

POTENTIAL APPLICATIONS FOR ELECTROSPUN LIGNIN-BASED CARBON FORMS

Front. Mater. (2019) 6:114

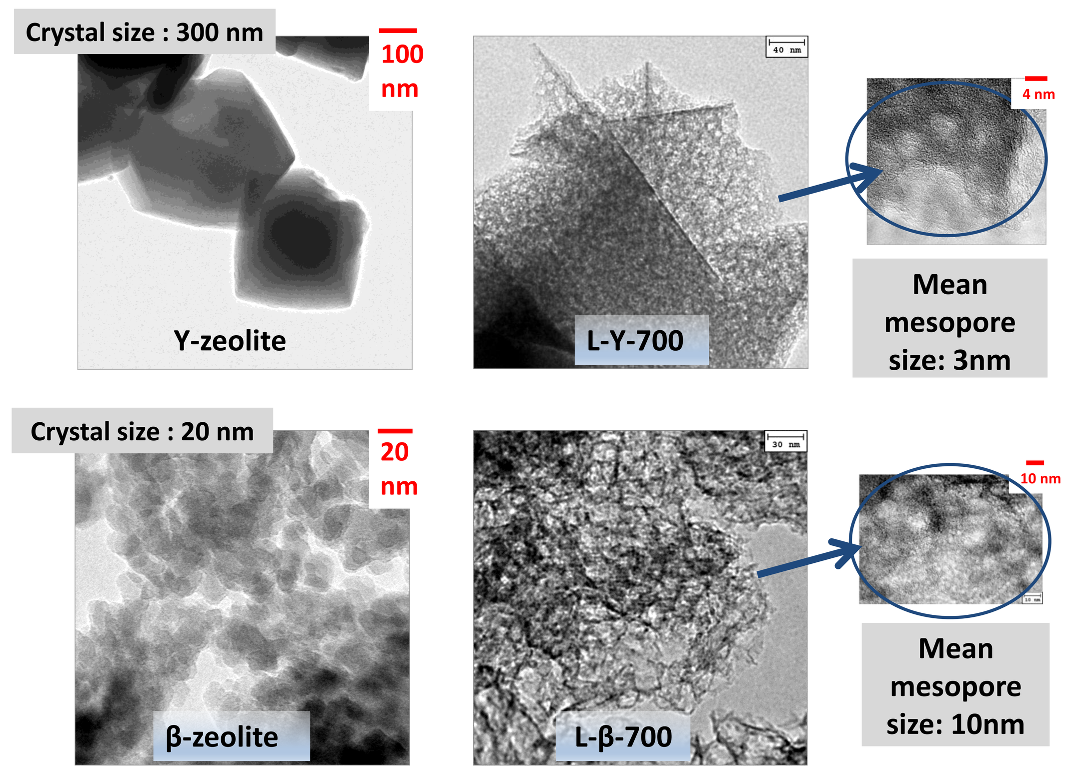


❖ POROUS CARBON BY HARD TEMPLATING

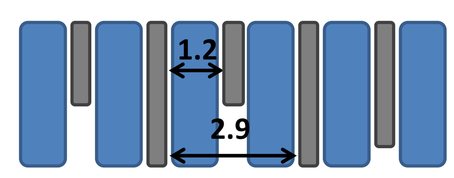


Microporous Mesoporous Mater 2014, 196, 68-78
ChemSusChem 2014, 7, 1458-1467
Journal of Power sources 326, 641-651

- Microporosity is conferred by lignin carbonization
- Mesoporosity is inherited from zeolite

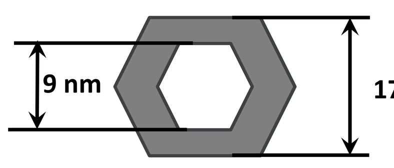


Y-zeolite: partial pore filling



Template	S_{BET} (m^2/g)	V_{mes} (cm^3/g)	V_{DR} (cm^3/g)
Y-zeolite	950	0.15	0.35
β-zeolite	865	0.85	0.32

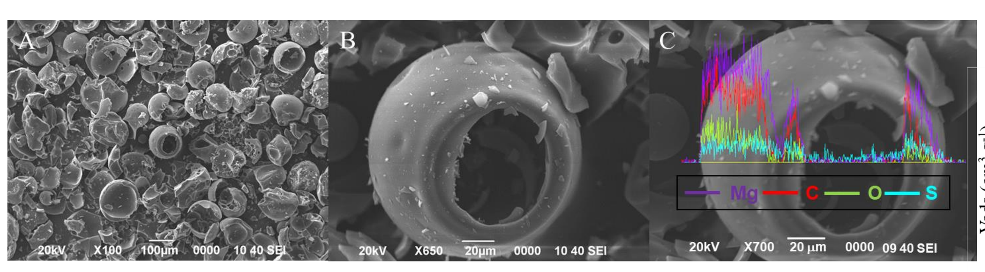
β-zeolite: partial crystal filling + voidage between crystal

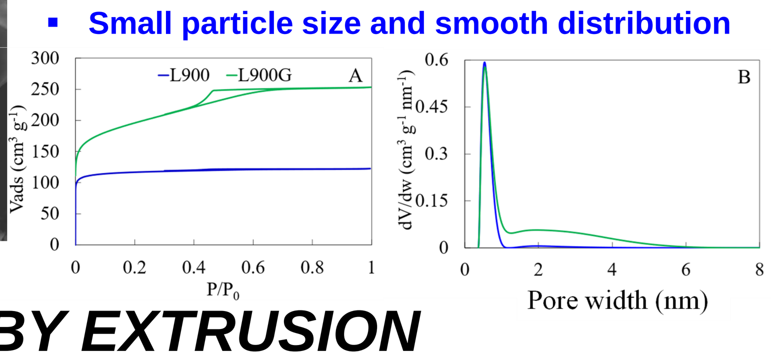


❖ ACTIVATED CARBONS BY PHYSICAL ACTIVATION (SEE POSTER OF GARCIA-ROLLAN FOR H3PO4 ACTIVATION)

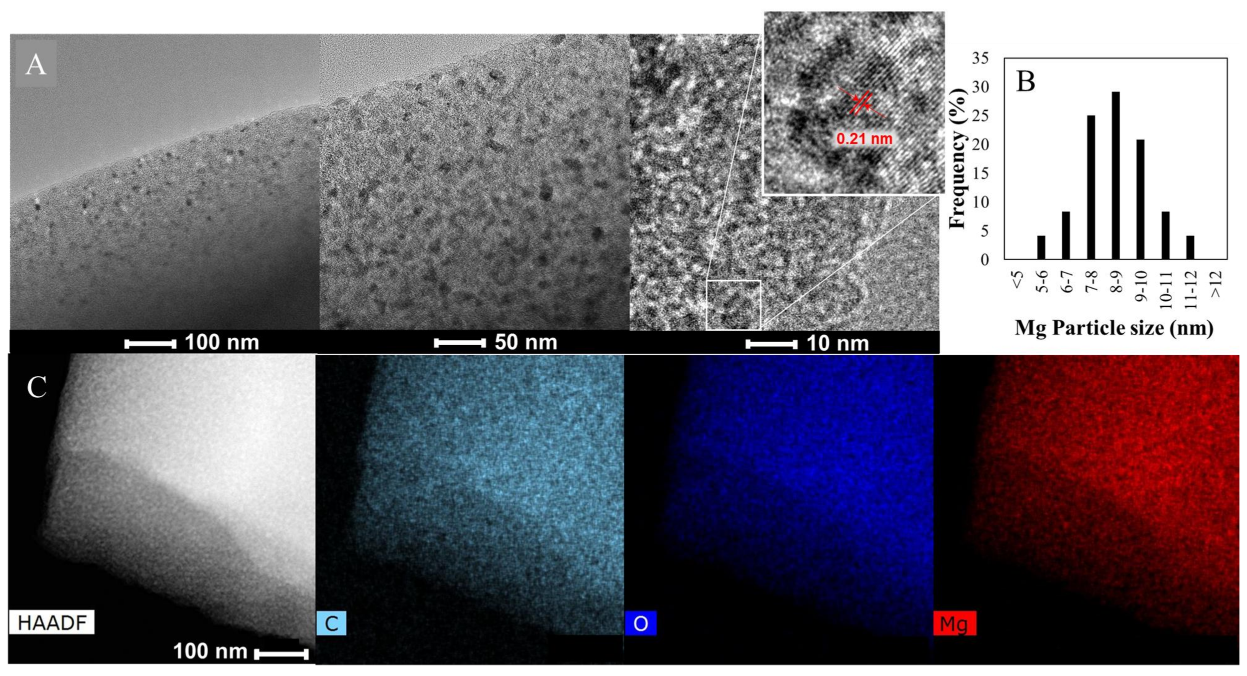
Magnesium lignosulfonate → 1. N_2, 900°C 2 h; 2. CO_2, 750°C, 0.5 h → BASIC CATALYST

IPA decomposition results: 50% conv at 325 °C, acetone selectivity >95%

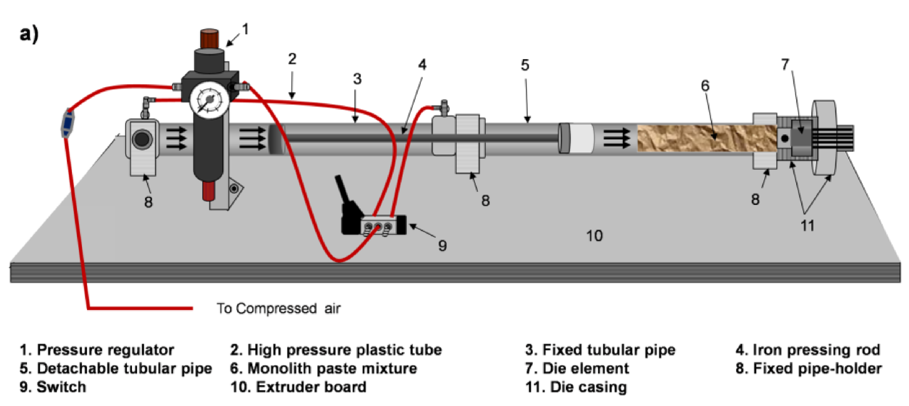


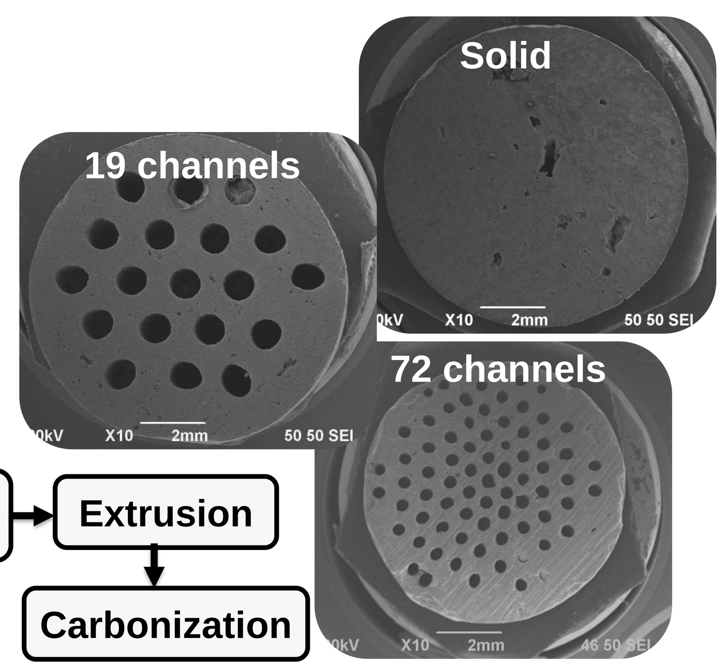


- Carbonization of cation-containing lignosulfonates produces metal-loaded porous carbons
- CO_2 activation increases surface area and metal content (18% Mg in this example)
- Small particle size and smooth distribution



❖ POROUS CARBON MONOLITHS BY EXTRUSION





Kraft Lignin / Alcell Lignin → Mixing with H_3PO_4 1:1 weight ratio → 1:1 Mixing → Extrusion → Air treatment 3°C/min, 250 °C → Carbonization

Lignin	S_{BET} m^2/g	V_t cm^3/g	V_{meso} cm^3/g	C (%)	O (%)	P (%)	ρ_{Tavg}^{He} (g/cm³)	compression strength (MPa)
Alcell	1054	0.49	0.02	87.3	9.0	3.7	1.77	7.56
Kraft	682	0.28	0.09	78.4	16.7	4.5	1.85	4.12

IPA decomposition results: 50% conv at 250 °C, propylene selectivity >90%

- Lignin-H_3PO_4 mixtures can be extruded
- Air stabilization step was optimized to minimize lignin swelling
- Highly dense microporous monoliths with acid character

Materials 2019, 12, 2394
Journal of the Taiwan Institute of Chemical Engineers (2019) 97, 480-488