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# Carbon materials from bio-based and tailored precursors

Carbon Fibre Future Directions Conference 2015
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- VTT

- High temperature carbonization
    - Cellulose based fibre precursors
    - Electrospun fibre precursors

- Hydrothermal carbonization (HTC)

- Modelling of cellulose carbonization

# VTT – Technology for business

**VTT Technical Research Centre of Finland Ltd is the leading research and technology company in the Nordic countries. We provide expert services for our domestic and international customers and partners, and for both private and public sectors. We use 4,000,000 hours of brainpower a year to develop new technological solutions.**

We develop new smart technologies, profitable solutions and innovative services. We cooperate with our customers to produce technology for business and build success and well-being for the benefit of society.

VTT is a non-profit organisation and a crucial part of Finland's innovation eco-system. VTT operates under the mandate of the Ministry of Employment and the Economy.


- Turnover 308 M€ (2013 VTT Group), personnel 2,600 (1.1.2015 VTT Group)
- Unique research and testing infrastructure
- Wide national and international cooperation network

*) Source: Roles, effectiveness, and impact of VTT, VTT & Technopolis Group, 2013.

# VTT 2015

VTT PROMOTES PROFITABILITY AND COMPETITIVENESS OF COMPANIES AND SOCIETY THROUGH INNOVATIONS

AGILE, COMPETITIVE

CUSTOMER-ORIENTED, FLEXIBLE

EFFICIENT, PROFITABLE

88 % of customers believed that a VTT project sped up or otherwise improved their R&D work*

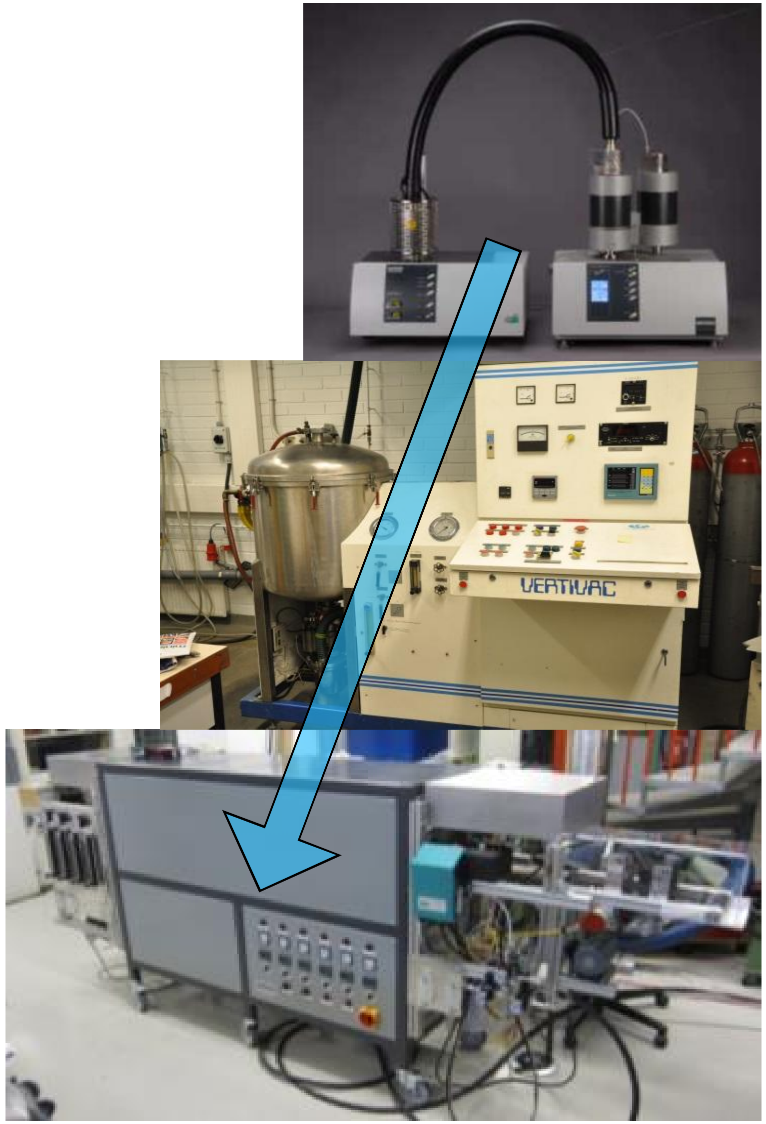
65 % believed that a VTT project had contributed positively towards the opening up of new business opportunities*

Nearly 70 % confirmed that new products, services or processes were created*

* Taloustutkimus Oy, VTT customer survey, 2014. Share of survey respondents who had this benefit as their goal in their VTT project and felt that the benefit was generated in the project.

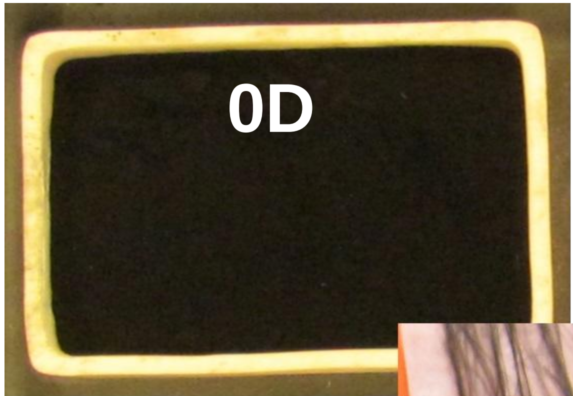
# High temperature carbonization

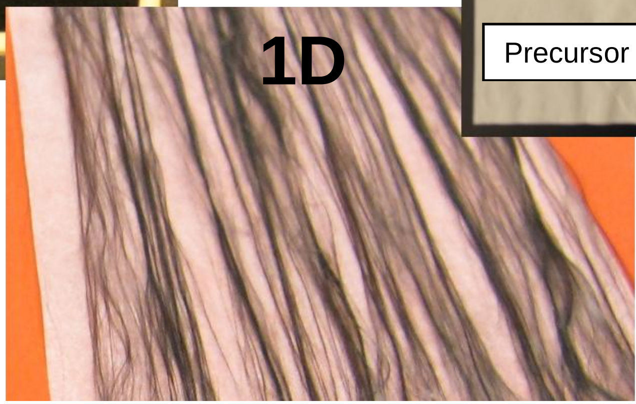
- Lab scale equipments available:
  - TG-DSC-MS
  - Several batch furnaces (up to 2200°C, even >2600°C)
    - 1ml - 2000ml
    - 0D, 1D, 2D, 3D
  - Continuous furnace (up to 1600°C)
    - Roll-to-roll process
    - Width 10cm (precursor), 5-6cm (finished product)
    - 1D, 2D
    - Partly automated process line
- Material yield depends on precursor
  - Typically for PAN ~60%
- Well-organized graphitic structure possible
- Majority of volatile impurities are removed
- Additionally: Functionalization of carbon materials, removal/adding of functional groups

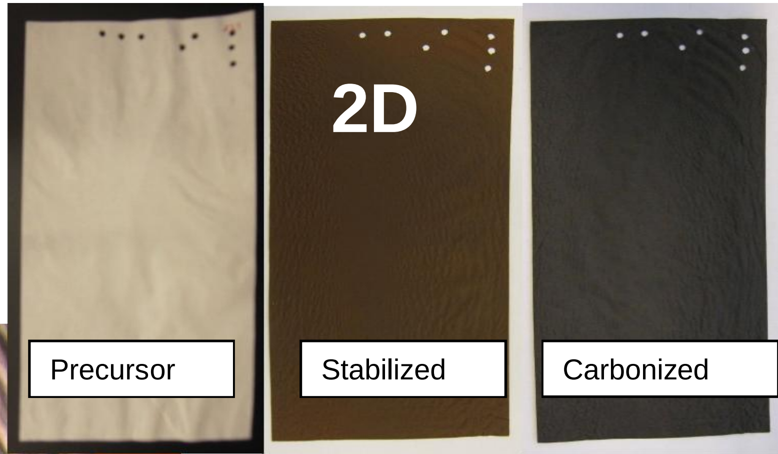


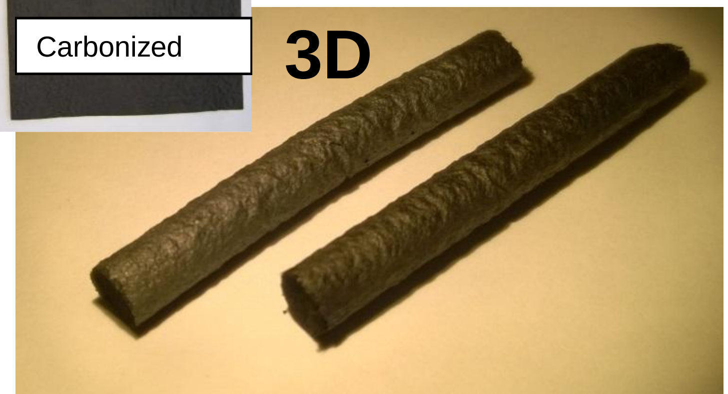
# Material examples

- Powders (0D), fibres & yarns (1D), felts & sheets (2D), 3D-objects
- Activated, graphitic, high strength, conductive carbons, carbon-carbon-composite
- Applications: catalysis, filtration, electrodes, adsorbents, etc…



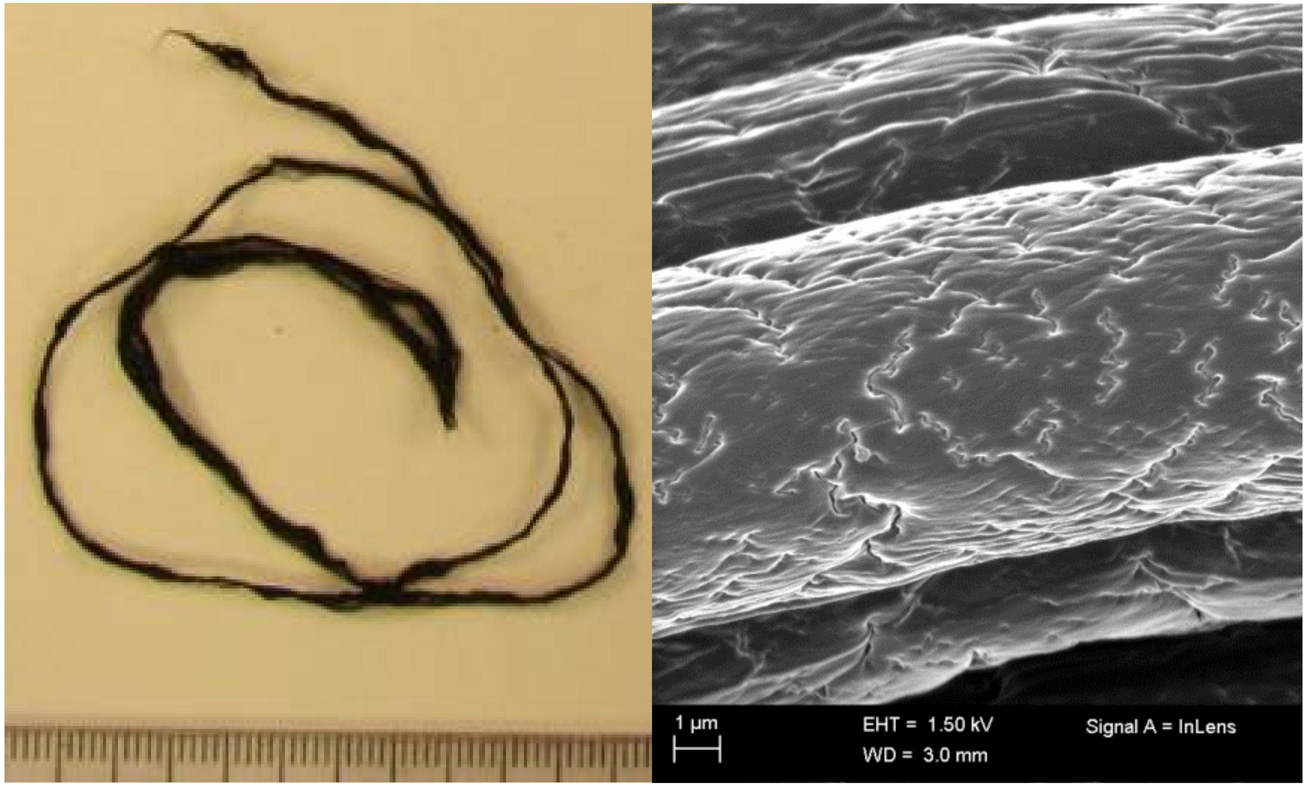



# Bio-based precursors

- Lignocellulosic materials: cellulose and lignin for carbon fibres
  - Advantages e.g.
    - Relatively high carbon content - suitable for precursors
    - Raw material abundantly available, raw material cost low compared to synthetics
  - Disadvantage e.g.
    - Complex molecular structure do not support formation of highly oriented carbon structure - costs for high performance material from bio-based precursors currently high
- Possible carbon applications of lignocellulosics
  - Non-structural carbons (particles, carbon black etc…)
  - Fibres for non-load-bearing applications
  - Activated carbon fibres e.g. for filters and personal protective equipment

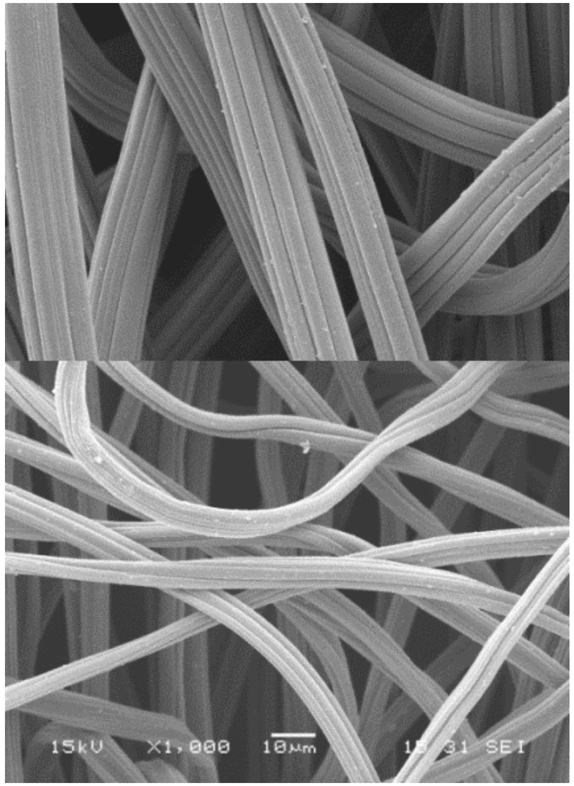
# Bio-based precursors

Carbonization of fibres…




AC fibres from wet-spun cellulosic fibres: cellulose carbamate and Biocelsol fibres, BET > 1000 $m^2$/g

…and as nonwovens.

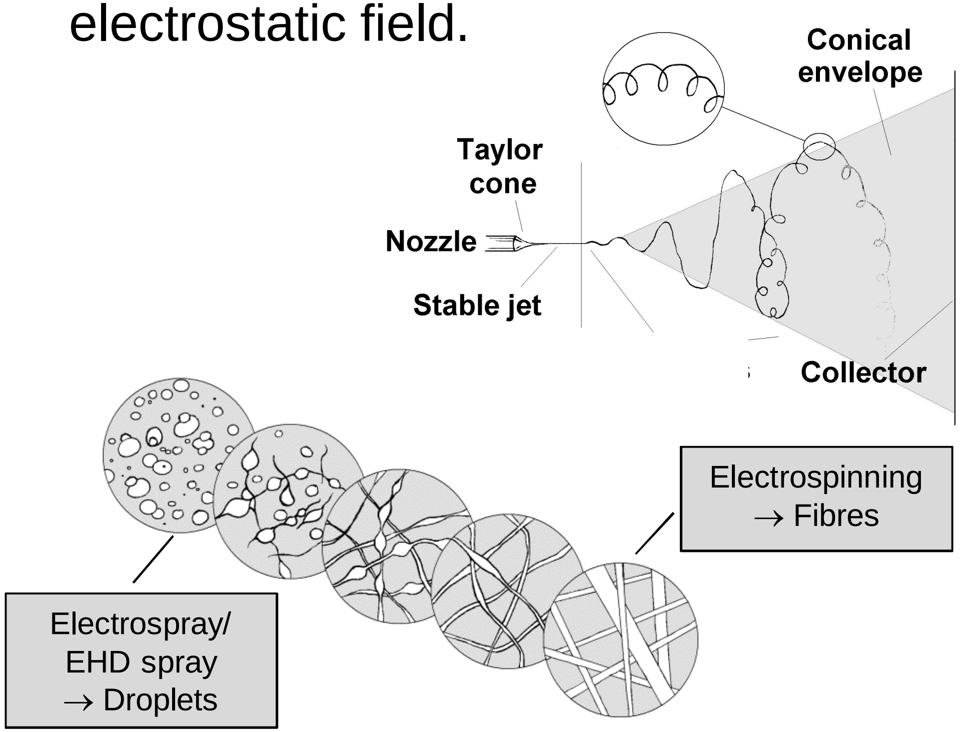



Viscose nonwoven precursor (up) and carbonized (down)

(BioPreCarb) project: VTT and Tampere University of Technology, 2013-2015, funded by Tekes

# Electrospinning

**Electrospinning:**
Sub-µm and nanosized fibres from viscoelastic polymer solutions in electrostatic field.

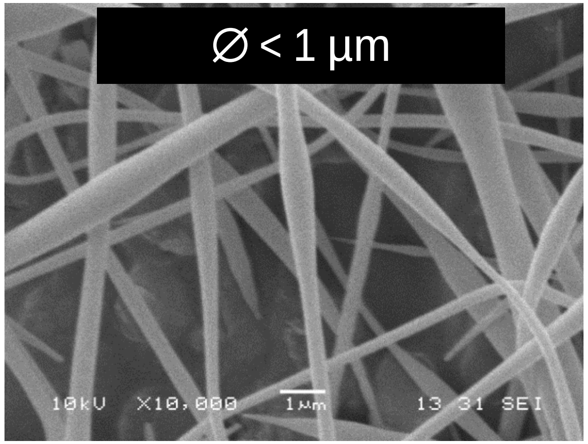


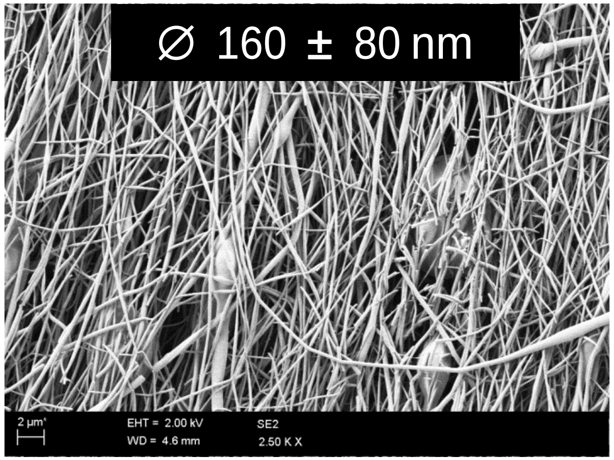

Advantages of electrospun precursors:

- Large surface area → needed for certain applications, e.g. catalyst carriers
- Thin diameter → can enhance crystallinity and thus electrical conductivity and mechanical strength
- Orientation of polymer chains → enable stabilization and carbonization in lower temperatures

# Electrospinning

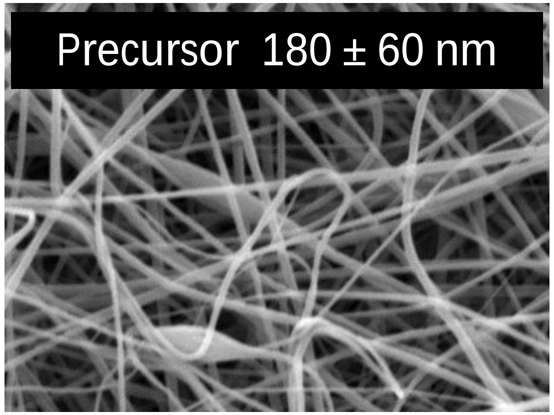
Electrospun lignin precursor fibres

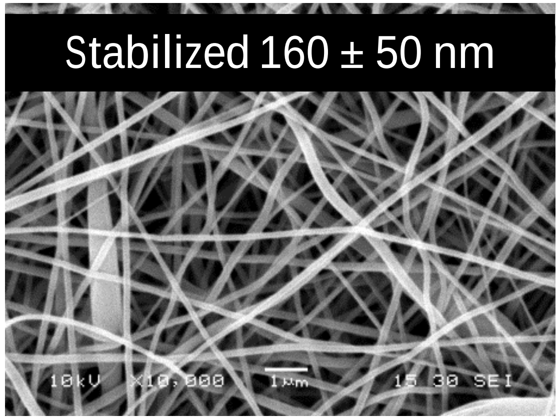


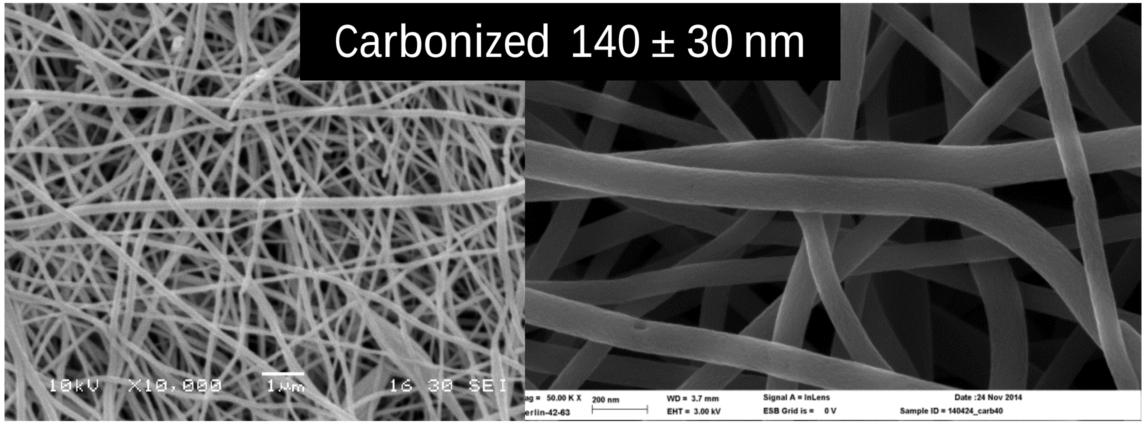




BioPreCarb project (up), VTT basic funding (down)

Carbonization of electrospun PAN fibres



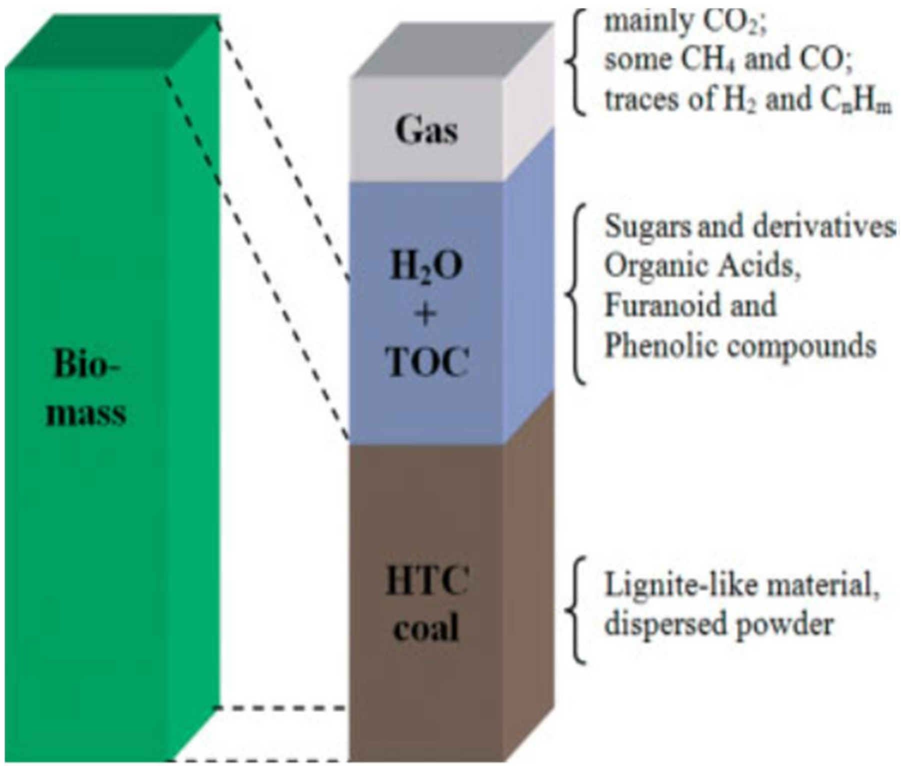




CATAPULT (novel CATAlyst structures employing Pt at Ultra Low and zero loadings for auTomotive MEAs) project; Funded by EC FP7, Fuel Cells and Hydrogen Joint Technology Initiative, grant agreement n°.325268)

# Hydrothermal carbonization (HTC)

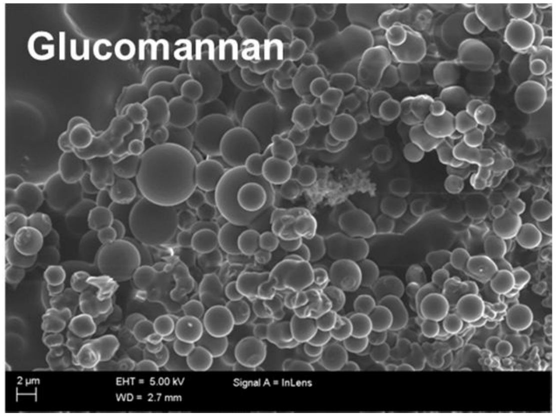
- HTC process
  - Wet organic raw material
  - Temperatures ~180-220 °C
  - Self generated pressures < 50 bars
  - Residence time few hours
- Wide range of organic materials
  - Virgin e.g. wood, leaves, cellulose, lignocellulosic materials
  - Recycled/waste e.g. biosludge, municipal waste, animal manure
- Environmentally friendly process
  - Mild processing conditions
  - Exothermic process - further utilization of energy
  - Possibility to recirculate water
  - $CO_2$ neutral
- Facilities at VTT
  - Several lab scale (500 ml-2 L) to semi-pilot scale (10 L) high-pressure reactors

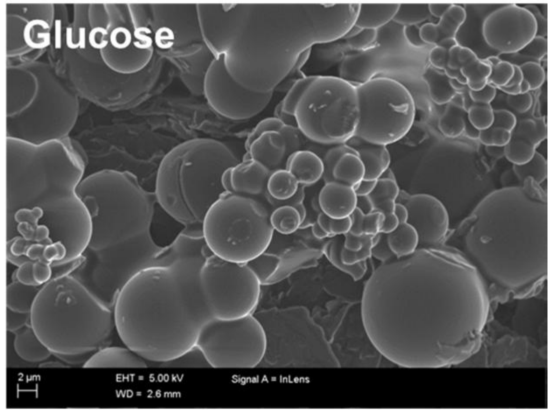


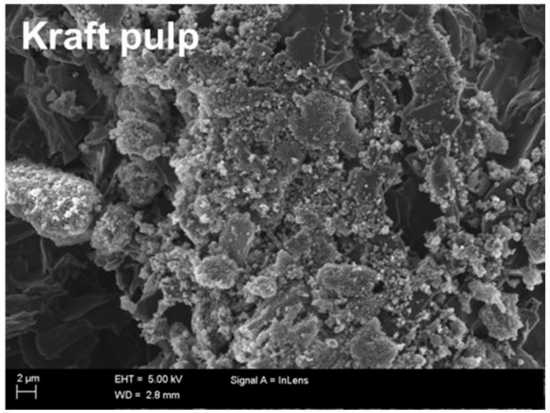

Products of hydrothermal carbonisation of biomass, separated according to their state of aggregation (Funke and Ziegler 2010)

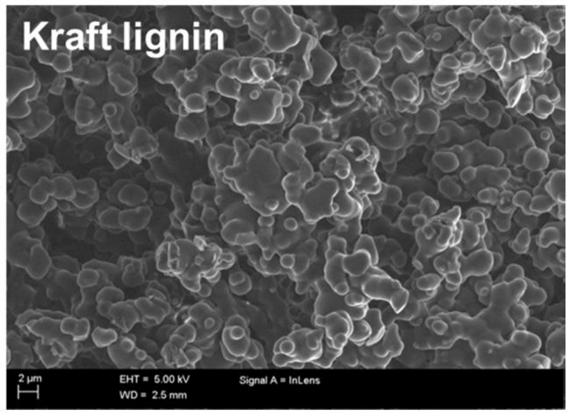
# HTC carbonaceous particles

- Produces carbonaceous particles with different shape and size
- The majority of the particles in nanoscale
- Degree of carbonization ~70 %
- Mass yields between ~ 30 and 70 %
- Suitable applications e.g. as adsorbents for water purification, in energy storage, in heterogeneous catalysts, as solid fuels, as soil fertilizers, as additives in lubricants



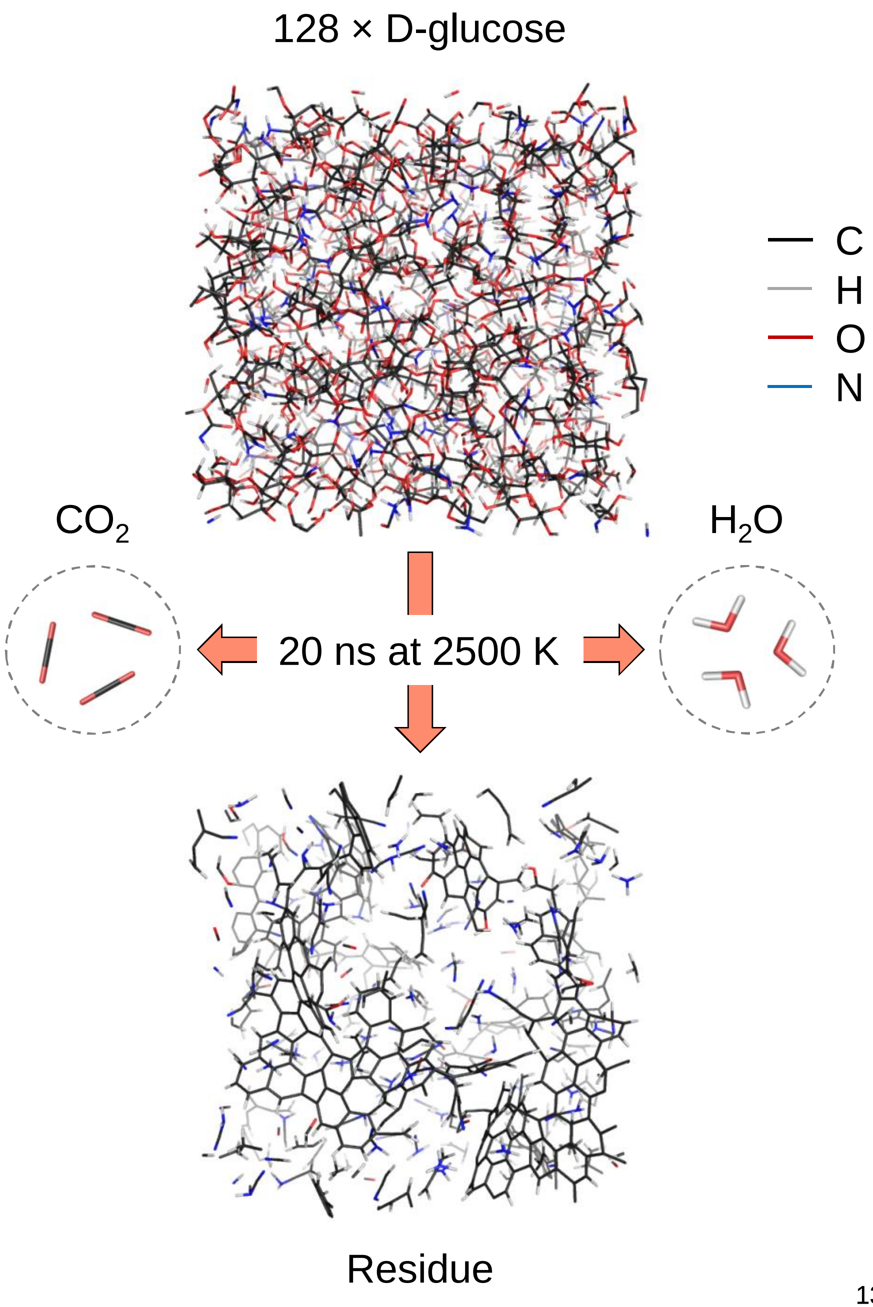




SEM images Mari Honkanen TUT

Grönberg V, Wikberg, H., Hentze, H.P., Harlin, A. and Jääskeläinen, A.-S., Process for the hydrothermal treatment of high molar mass biomaterials, WO2014096544 A1 (2012).
Wikberg, H., Grönberg, V., Jermakka, J., Kemppainen, K., Kleen, M., Laine, C., Paasikallio, V. and Oasmaa, A., Hydrothermal Refining of Biomass – An Overview and Future Perspectives, Accepted to TAPPI journal (2015).

# Modelling

- Reactive Molecular Dynamics (RMD) modelling of the high-temperature carbonization of D-glucose
    - non-crystalline system of 128 D-glucose molecules with added functional groups/molecules (carbamoyl, CO, $H_2$)
    - ReaxFF reactive force field for the description of interatomic forces
    - series of 20 ns NVT ensemble simulations at 2500 K
    - removal of inert gaseous species at regular intervals
- Virtual measurements
    - carbon yield, i.e. $m_1/m_0$
    - five- and six-carbon ring count
    - observations on graphene sheet growth mechanisms
    - elemental and molecular composition



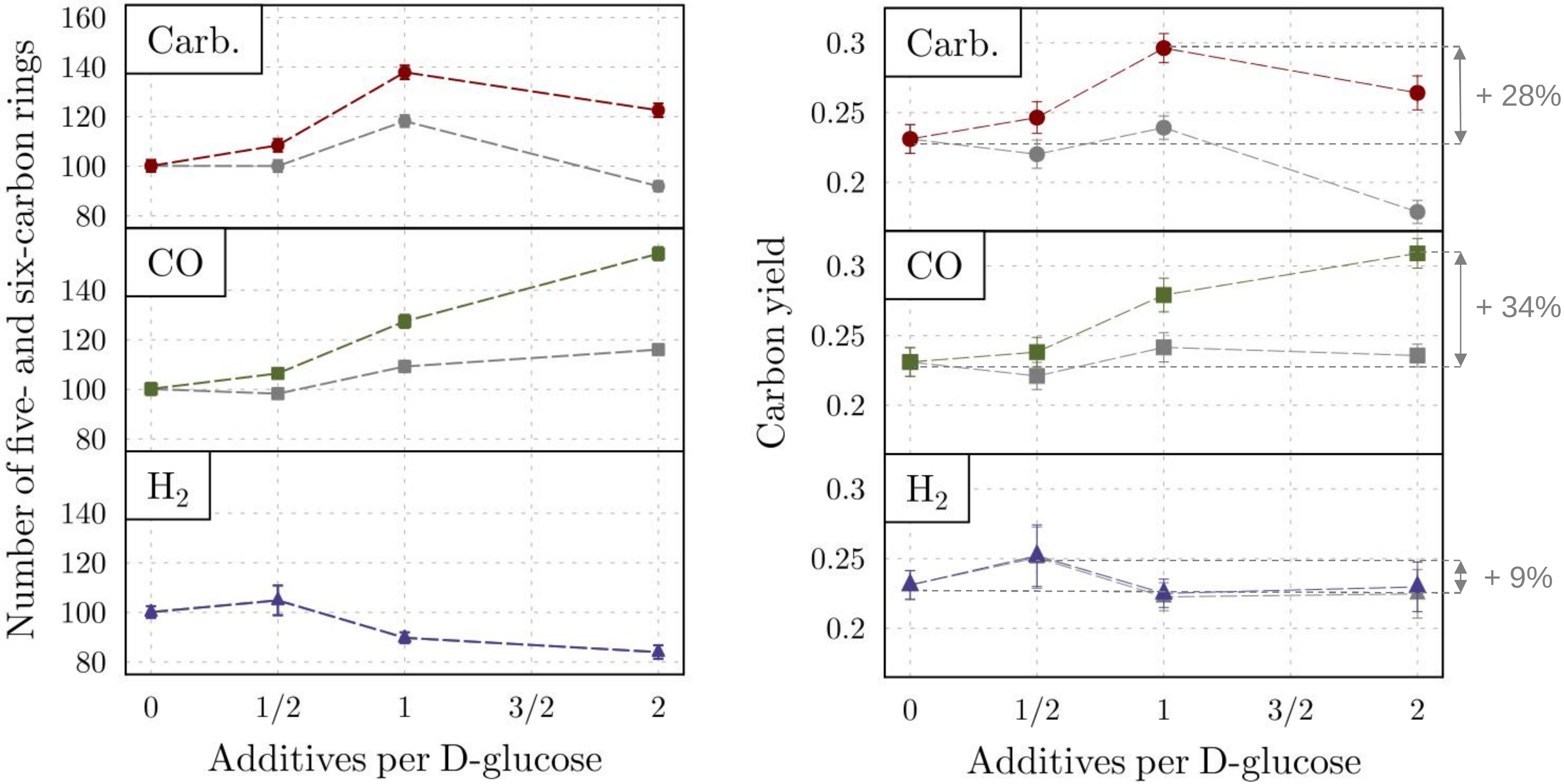
# Modelling

absolute values / residue mass compared to the 128 × D-glucose case

scaled values / residue mass compared to the respective additive case

5- and 6-carbon ring production

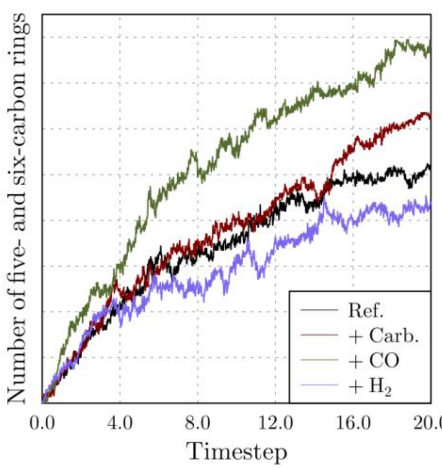
Carbon yield

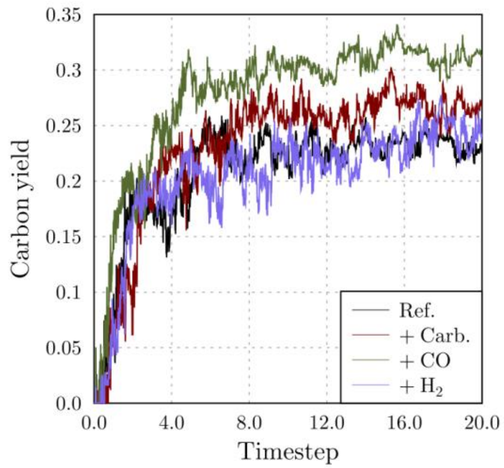


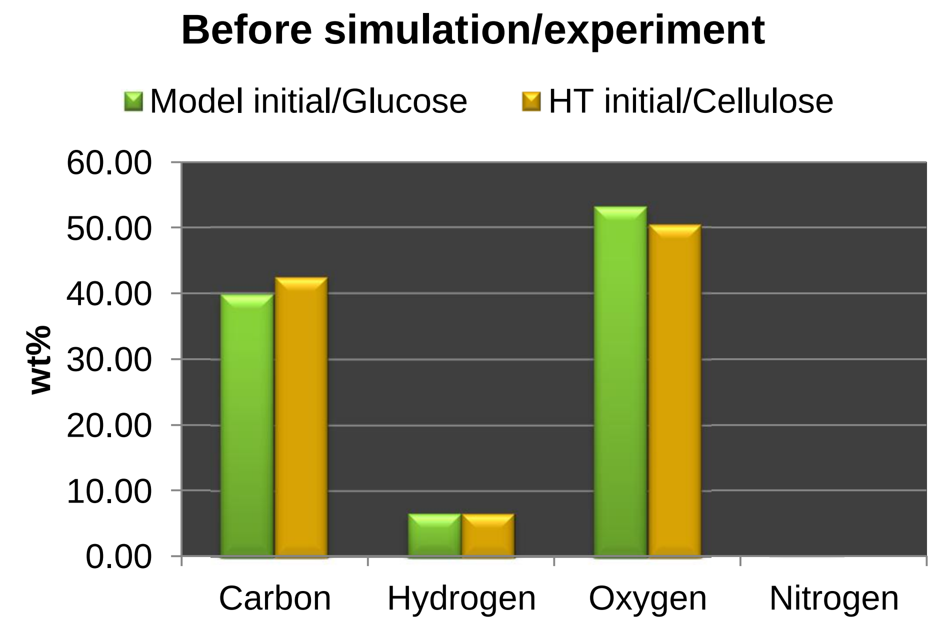
# Modelling

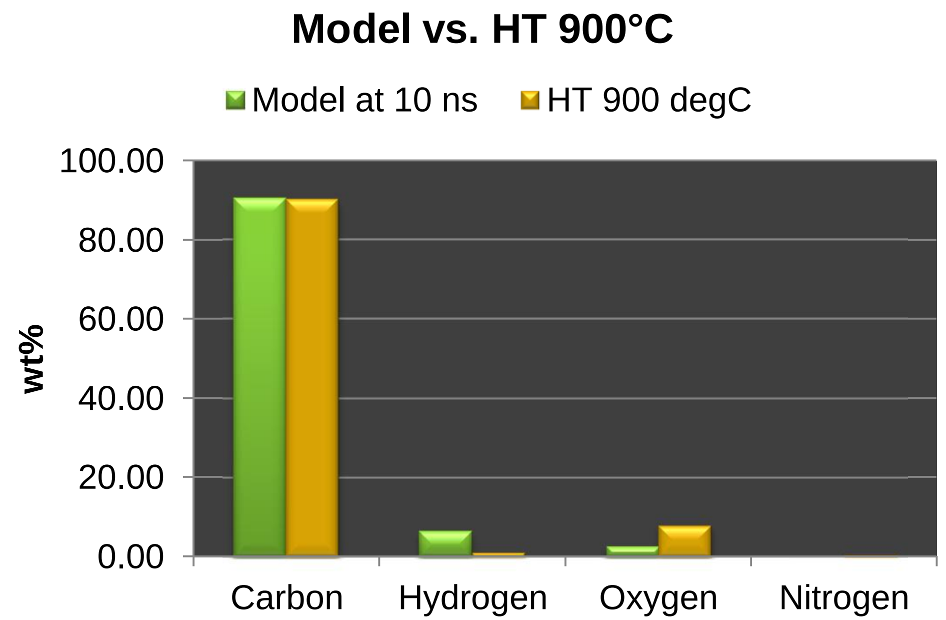
- Observations

1. added carbamoyl groups or CO promotes the growth of PAHs
2. added $H_2$ has a neutral/negative effect on the growth of PAHs
3. carbon content of the final residue is in agreement with the experiments
4. saturation of carbon yield is observed before 10 ns, while the number of carbon rings (i.e. quality of residue) continues to grow throughout the simulation.



# Summary

- VTT has wide expertise in carbonization of bio-based and tailored materials
- High temperature carbonization facilities enable processing of all types of precursors in lab scale and continuous roll-to-roll furnace for fibres and sheets
- HTC enables production of various types of carbonaceous particles and is especially interesting option for utilization of side streams
- We have modelling experience in carbonization of cellulose


TECHNOLOGY FOR BUSINESS