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High temperature morphology of phenolic resin pyrolysis

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Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

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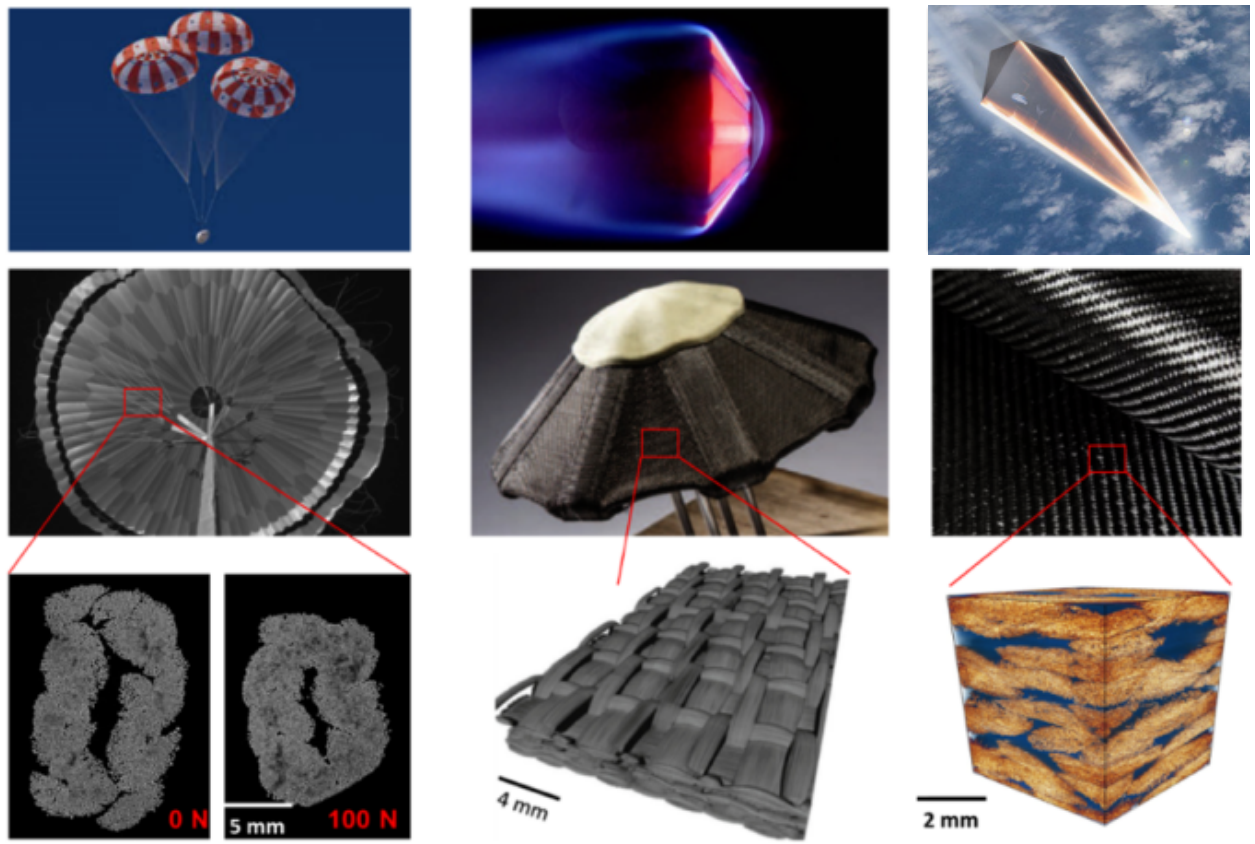
Overview

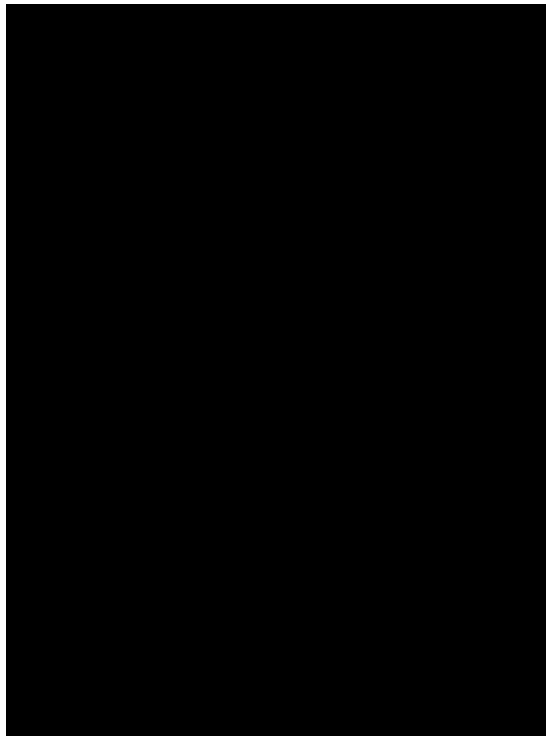
1. X-ray computed tomography (XCT) at the Advanced Light Source (ALS)
2. Resin introduction, SC-1008
3. In-situ XCT results
4. Outlook



Aerospace material systems and XCT

XCT at the ALS

X-ray system	Resolution [μm/px]	Field of View, $\varnothing$[mm]	Time/tomography	Capabilities
Xradia Bio-MCT	$0.9 - 10$	$1.5 - 10$	> 2 hours	*ex-situ*, static scanning
ALS 8.3.2 Beamline	$0.6 - 10$	$1.7 - 27$	30 s $-$ 30 min	*in-situ*, combined loading

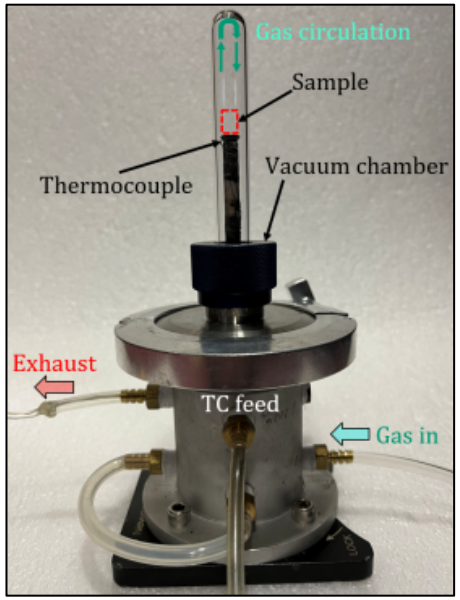


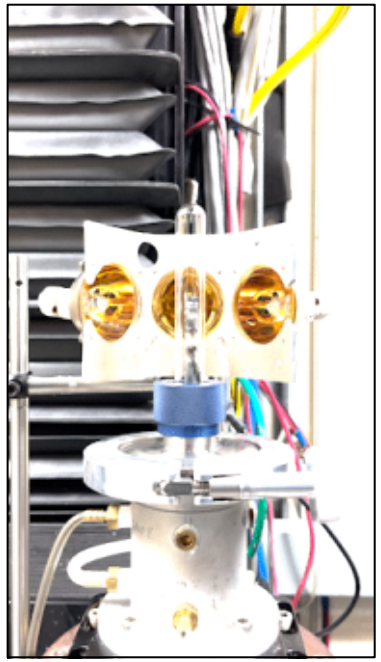
Synchrotron XCT of Astronaut

Courtesy of Dula Parkinson (Advanced Light Source)

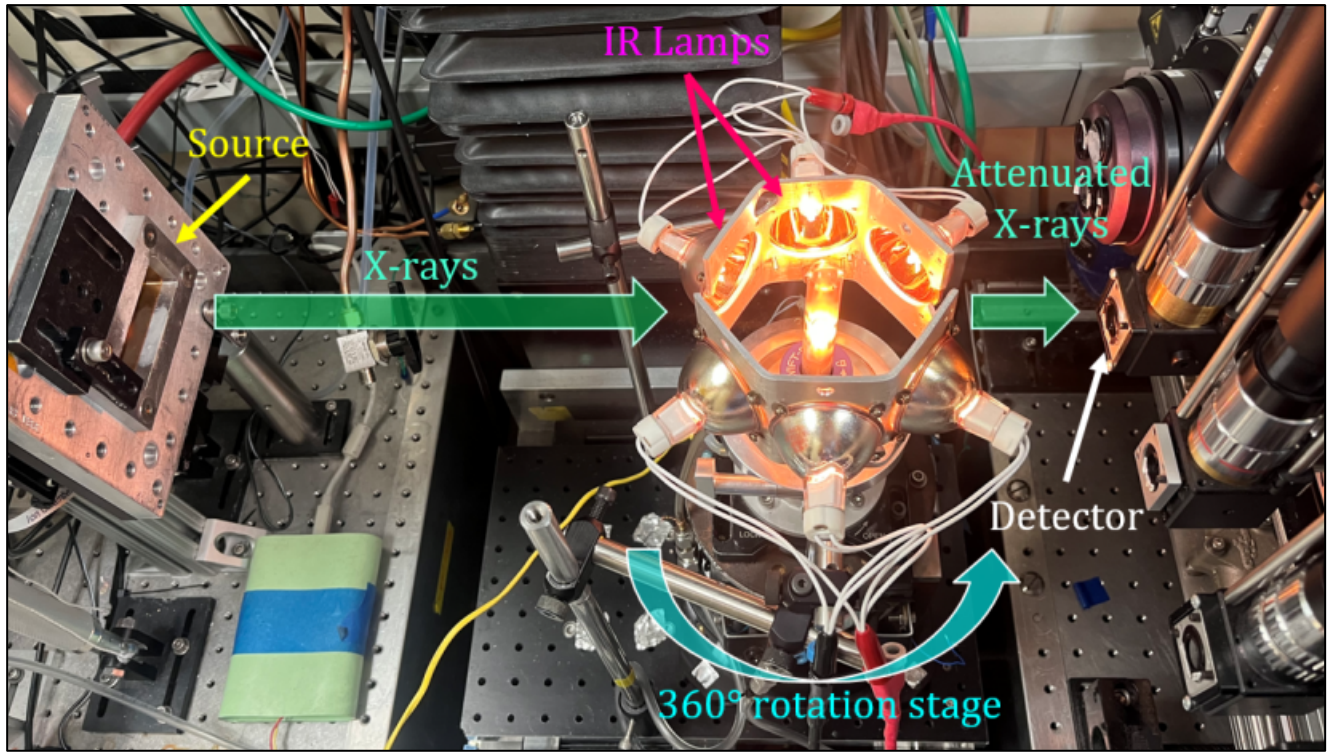
In-situ XCT at the ALS

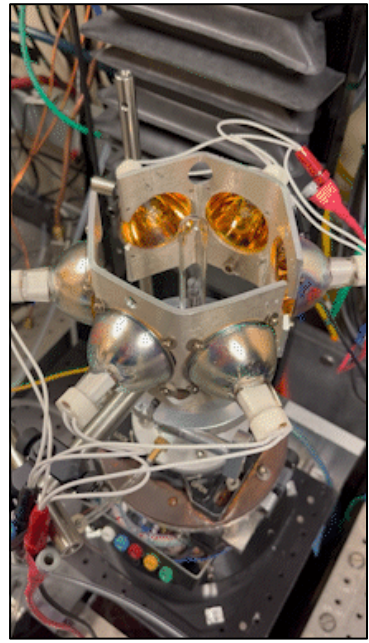
- **ALS Synchrotron** provides high flux of x-rays, allowing for ***in-situ*** XCT





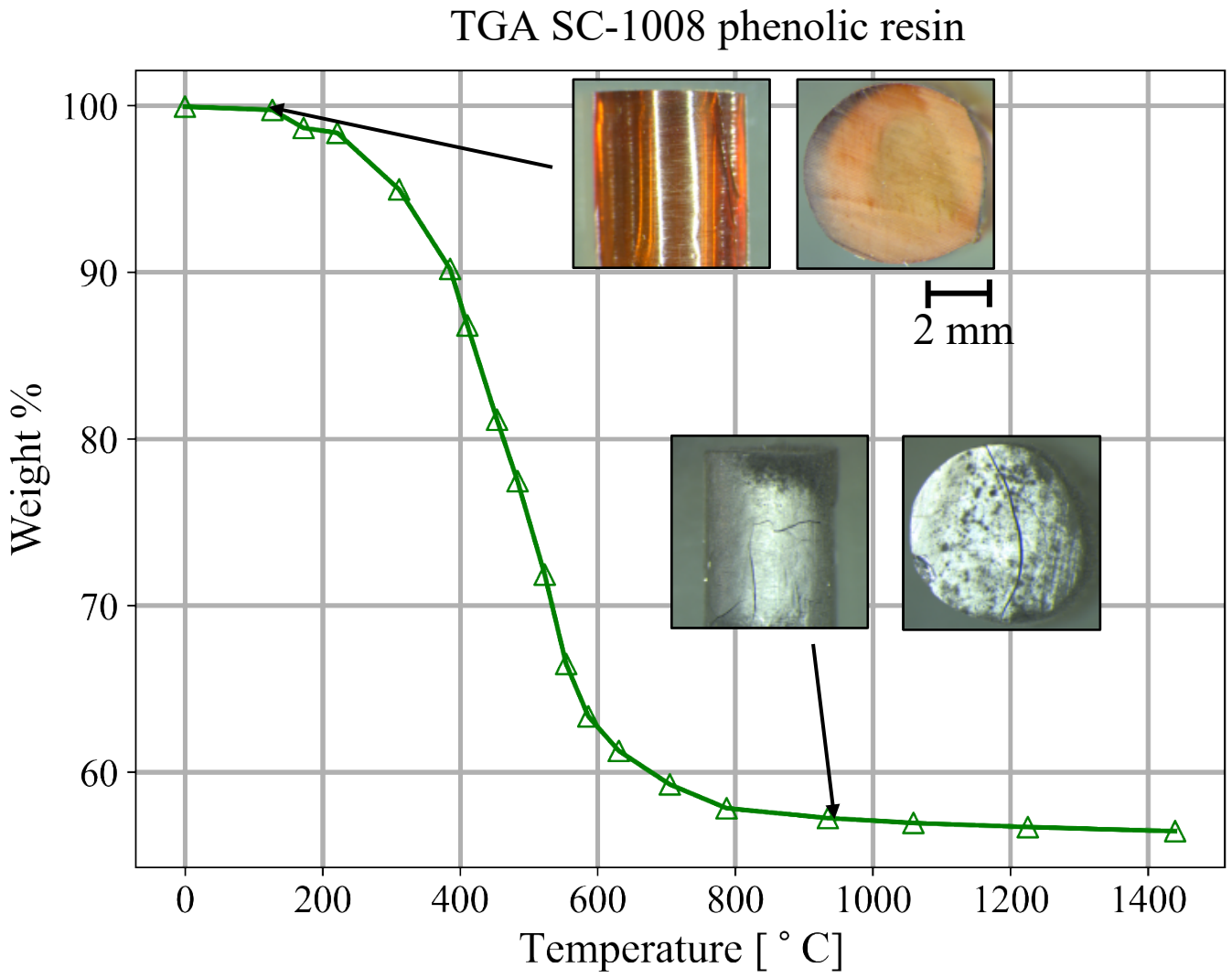
Controlled-environment chamber





Inside XCT hutch at ALS

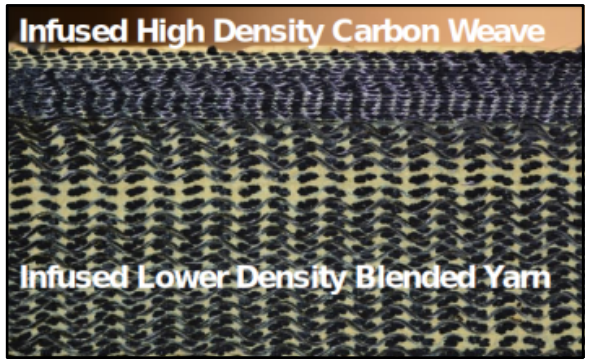
Resin systems

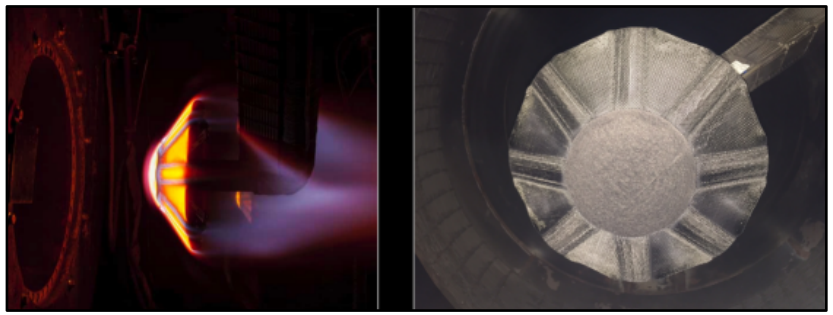


[TGA: Hernandez-Sanchez, 2021]

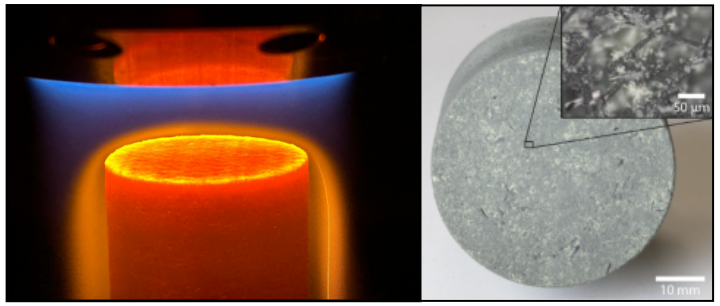
PICA
(*Stackpoole et al*)

HEEET
(*Ellerby et al*)



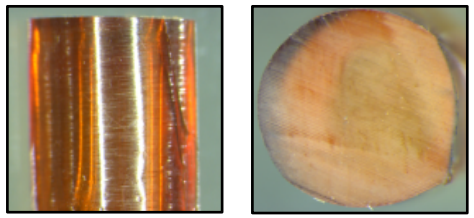


ADEPT
(*Venkatapathy et al*)

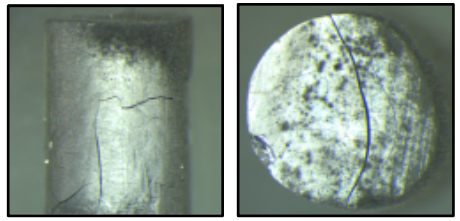


HARLEM
(*Varona & Univ. of Stuttgart, HEFDiG*)

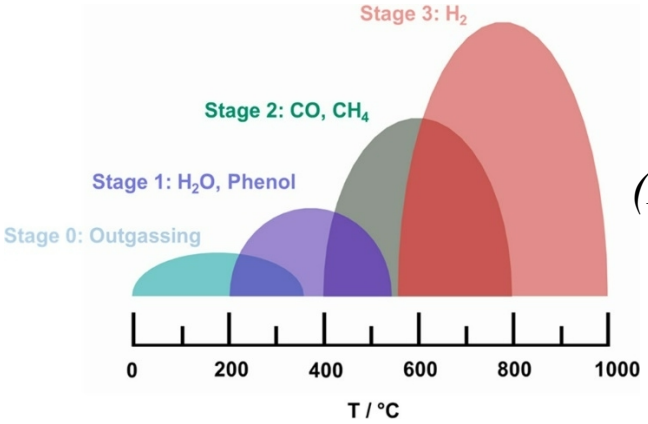
Resin chemistry



Virgin SC-1008

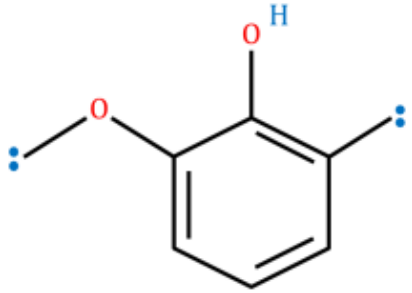


Pyrolyzed 1000 °C



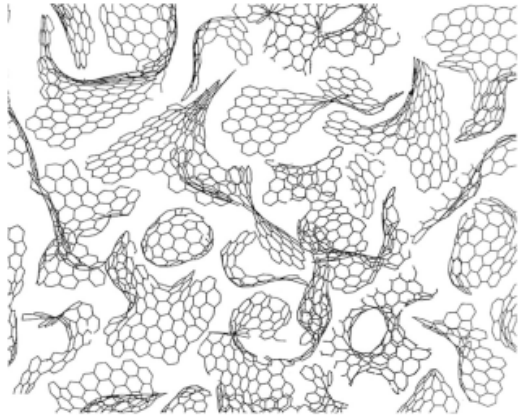
(Bessire et al.)

$$(C_6H_8O_2)_x + \text{Heat} \rightarrow aC + bH_2O + cCO + dCO_2 + eH_2 + fCH_4 + (\ldots \text{VOCs})$$

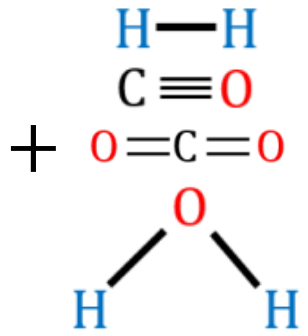


Phenolic formaldehyde (s)

Ar (g)
+
+ Heat



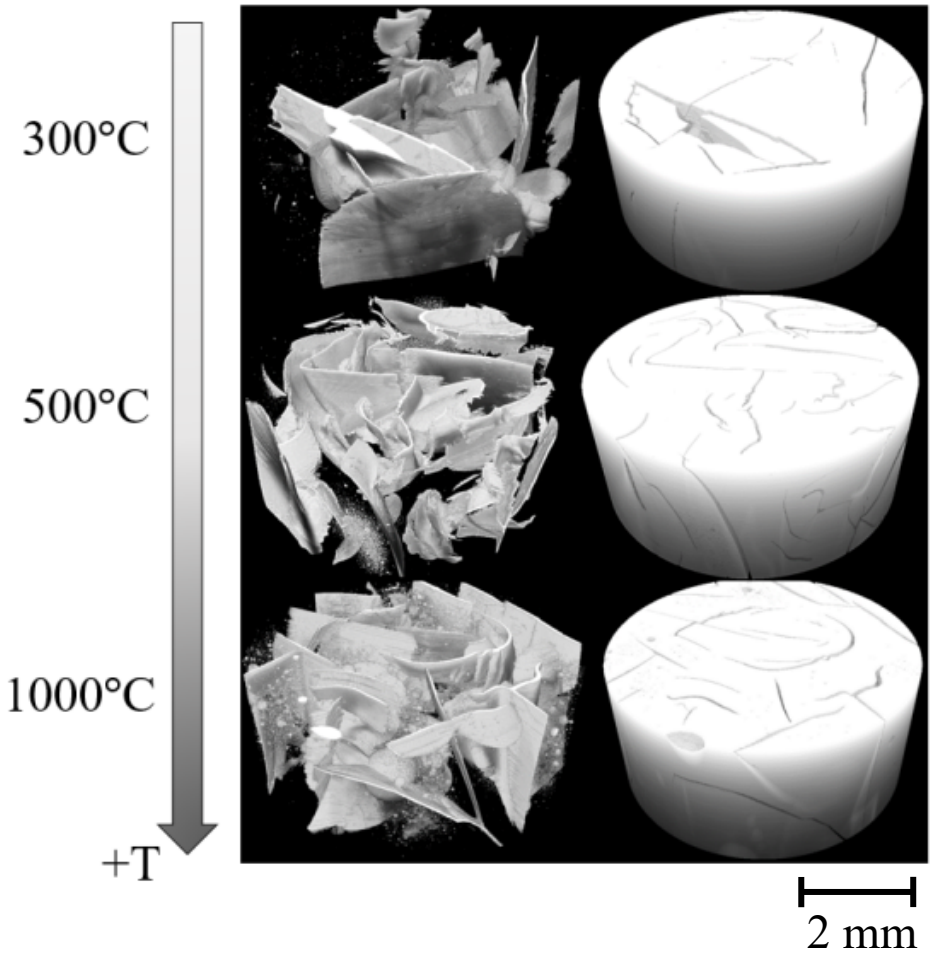
Glassy Carbon (s)
(Harris et al.)

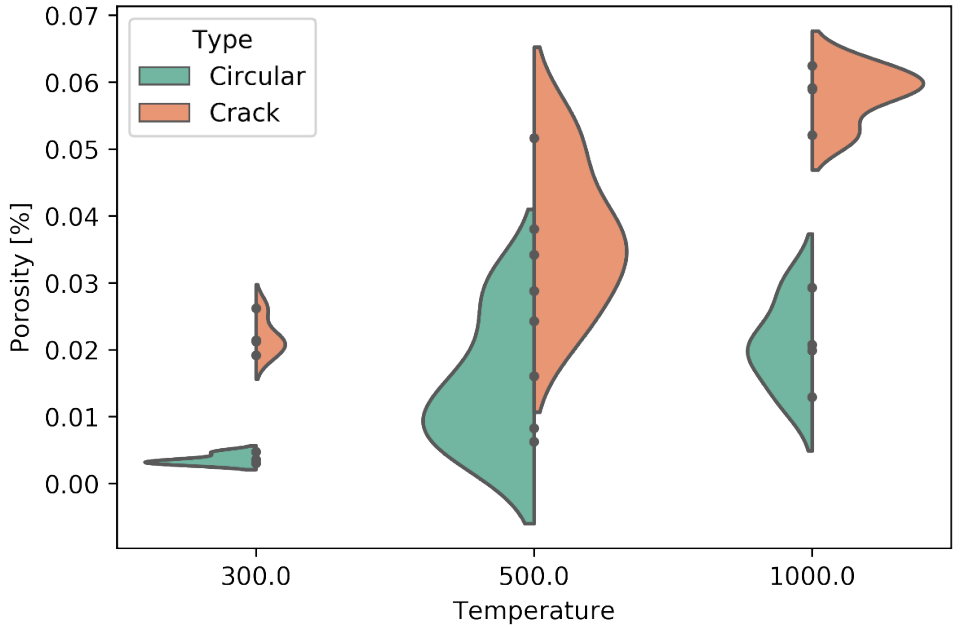


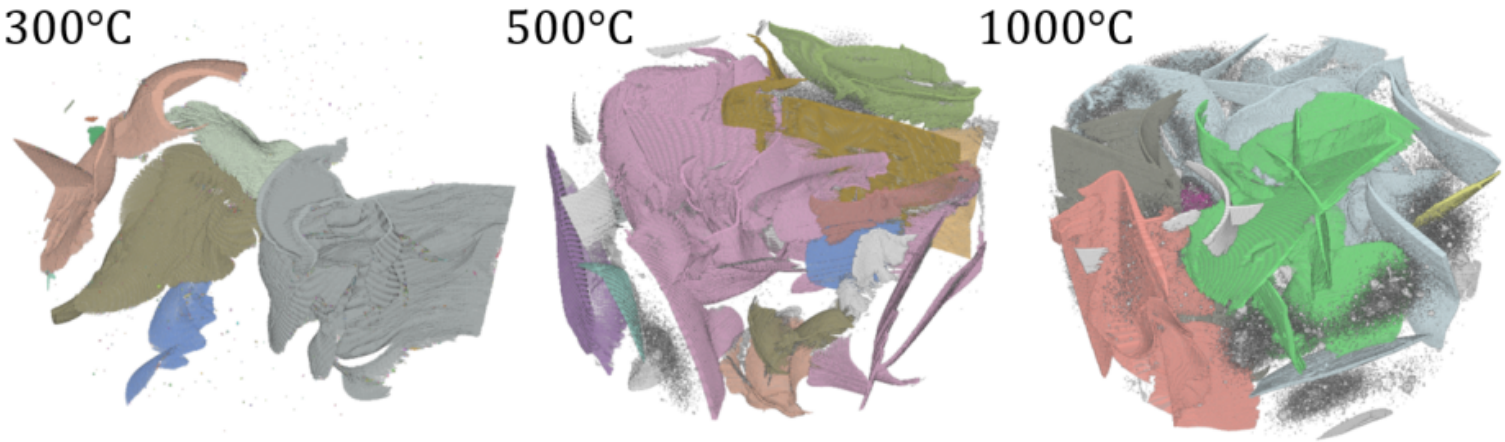
Pyrolysis products (g)

[Ouchi, 1965; Bessire, 2014; Bessire, 2017; Torres-Herrador, 2021]

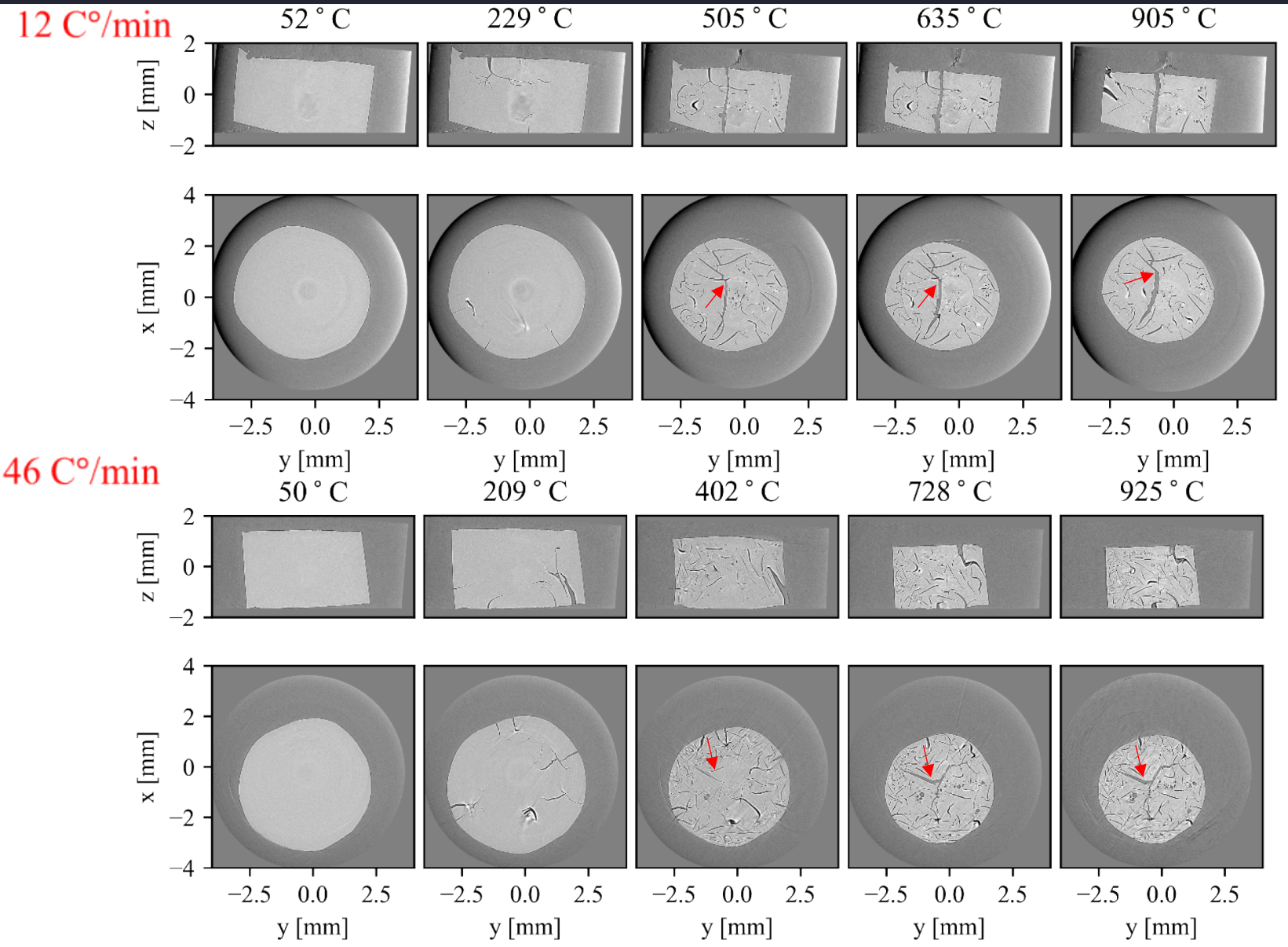
Resin ex-situ pyrolysis

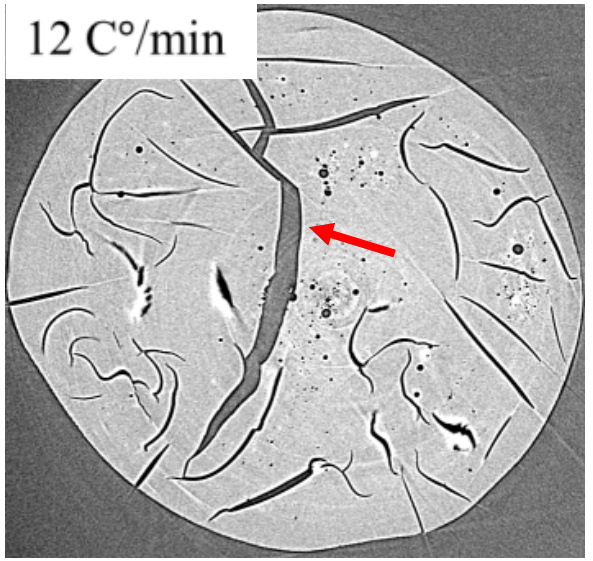


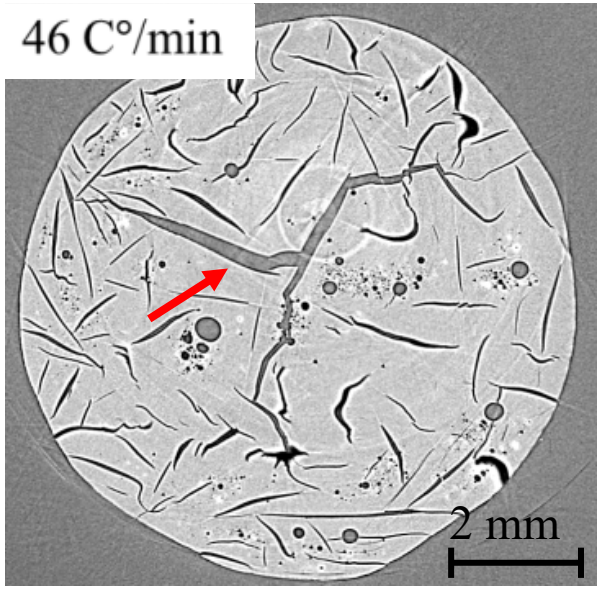




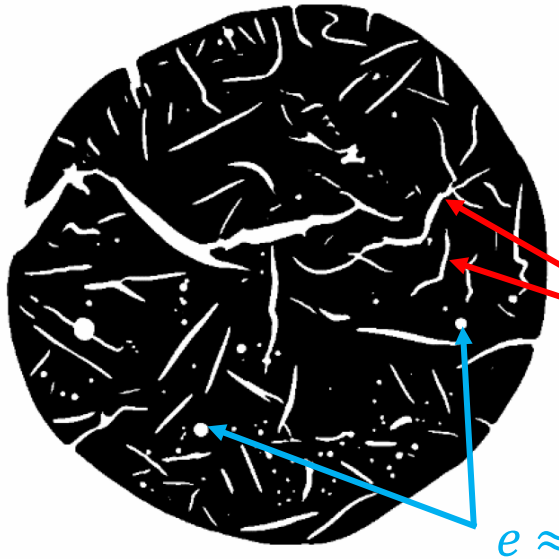
Resin in-situ pyrolysis





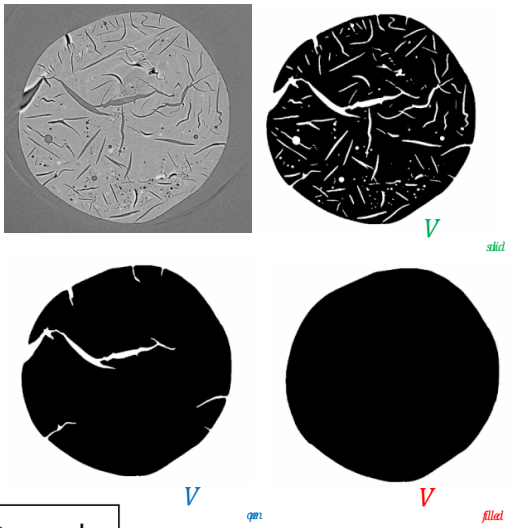


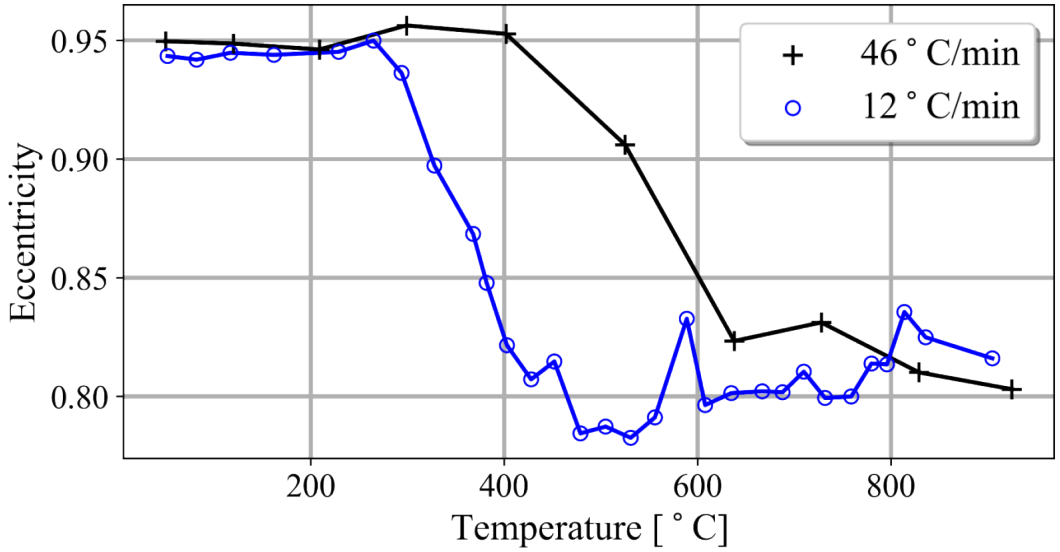
Results – Porosity

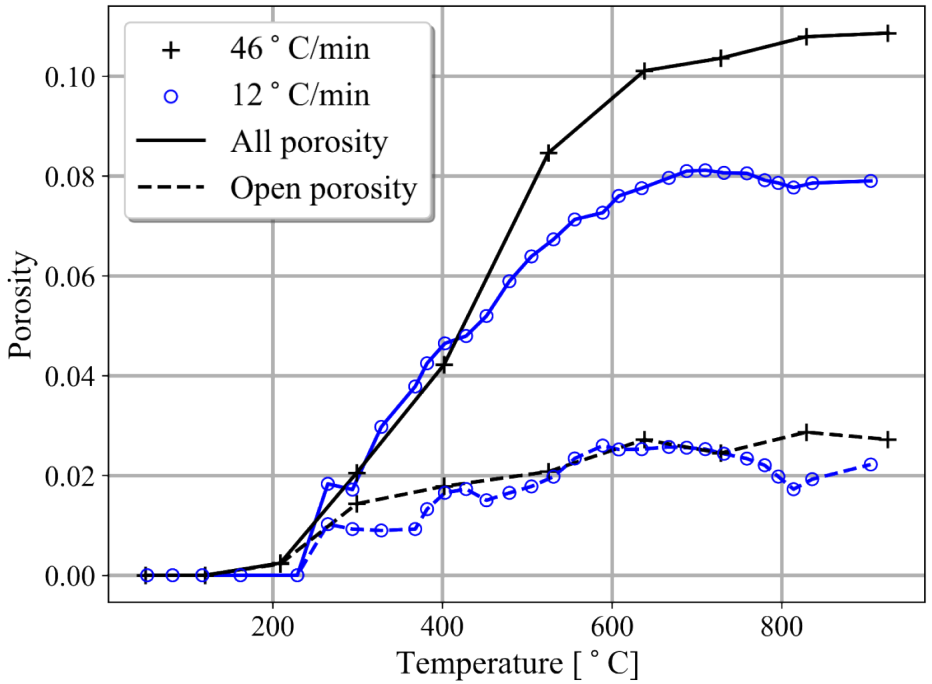


All porosity (open + closed), $\varepsilon_{all} = 1 - \frac{V_{solid}}{V_{filled}}$

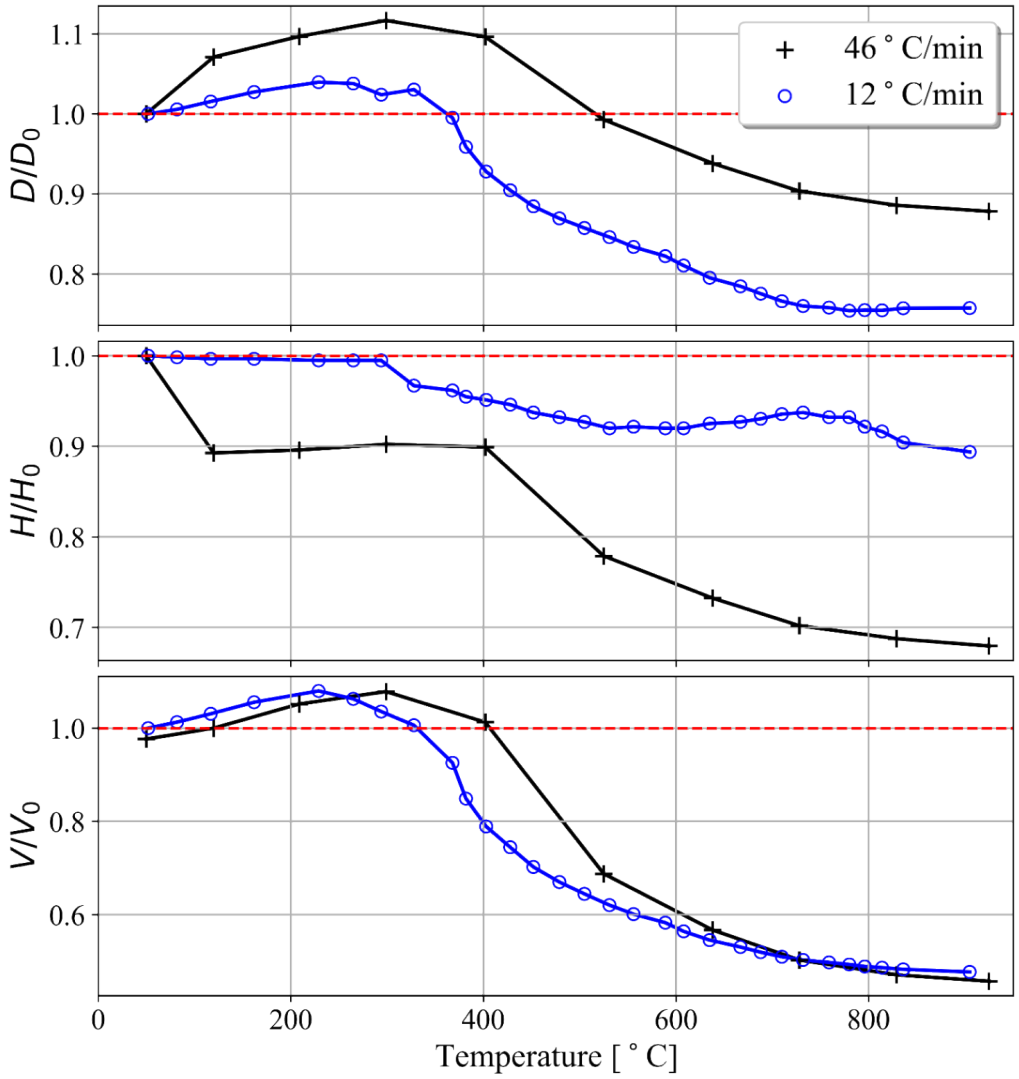
Open porosity, $\varepsilon_{open} = 1 - \frac{V_{open}}{V_{filled}}$

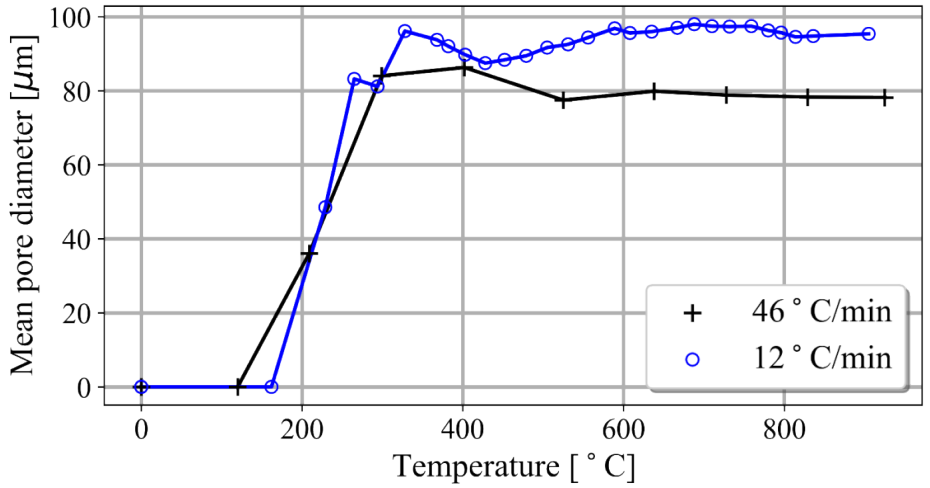


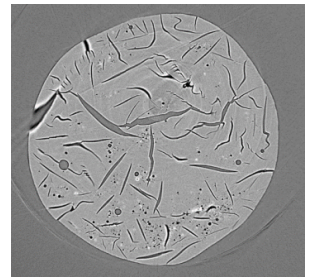




Results – Shrink and swell

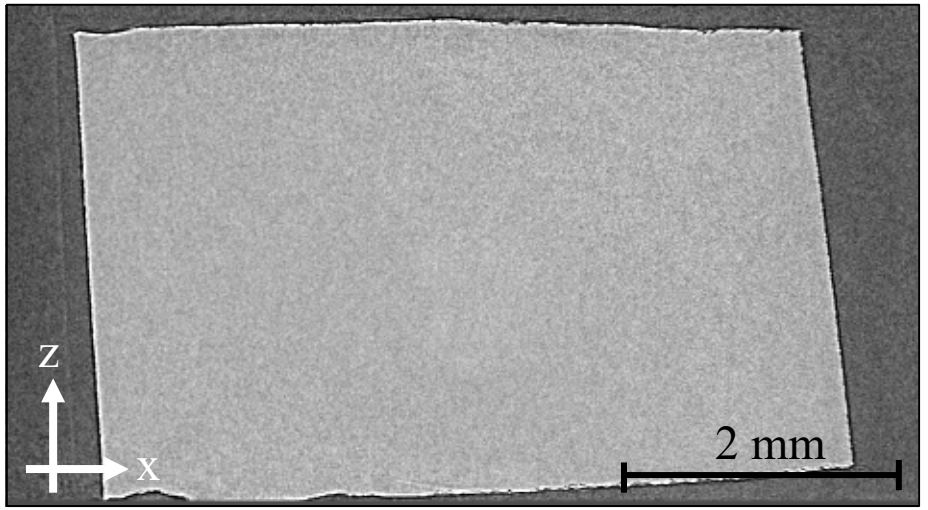


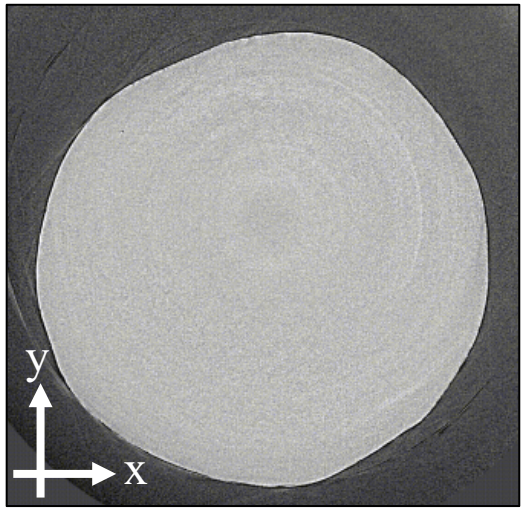




V_{solid}

Microstructure evolution of SC-1008





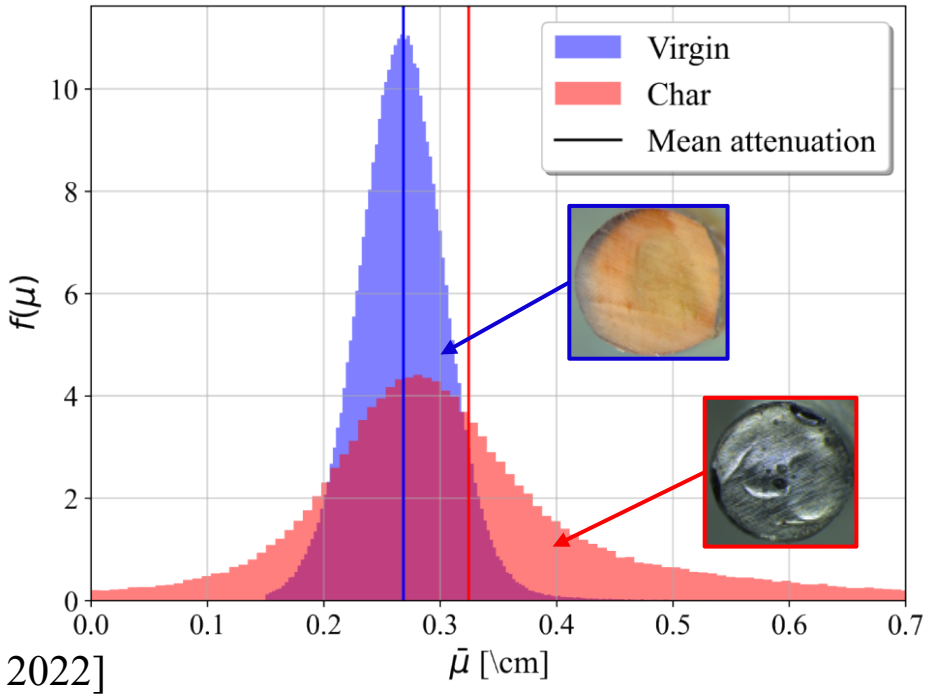
Results – Density and mass loss

(1) Mean attenuation (Beer-Lambert law), $\frac{I}{I_0} = e^{(-\mu t)}$

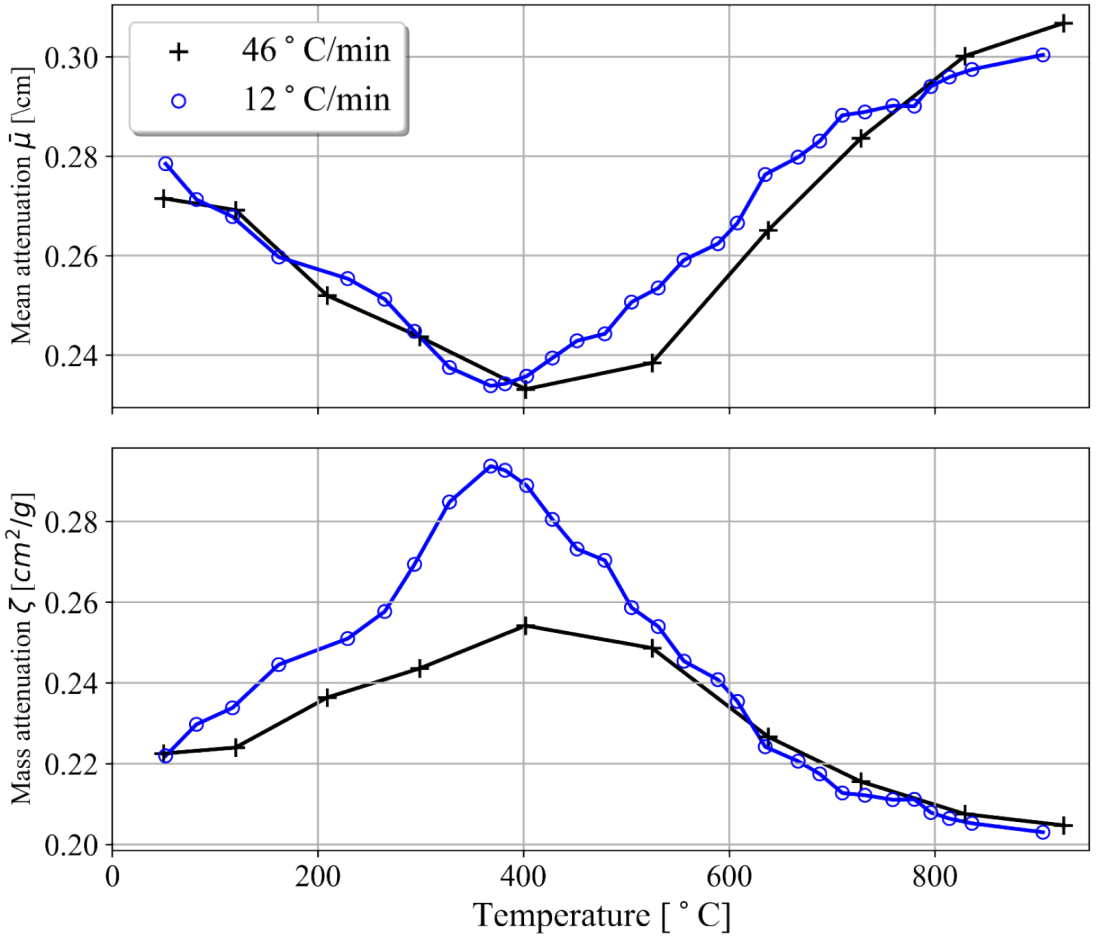
(2) X-ray linear attenuation, $\mu(x,t) = \rho * \zeta$

(3) Volume fraction of char material, $\bar{X}_c = \frac{\mu_0 - \bar{\mu}}{\mu_0 - \mu_c}$

(4) Mean mass attenuation coefficient, $\bar{\zeta} = \frac{\bar{\mu}}{\bar{\rho}} = \frac{\mu_0 - \bar{X}_c(\mu_0 - \mu_c)}{\rho_0 - \bar{X}_c(\rho_0 - \rho_c)}$



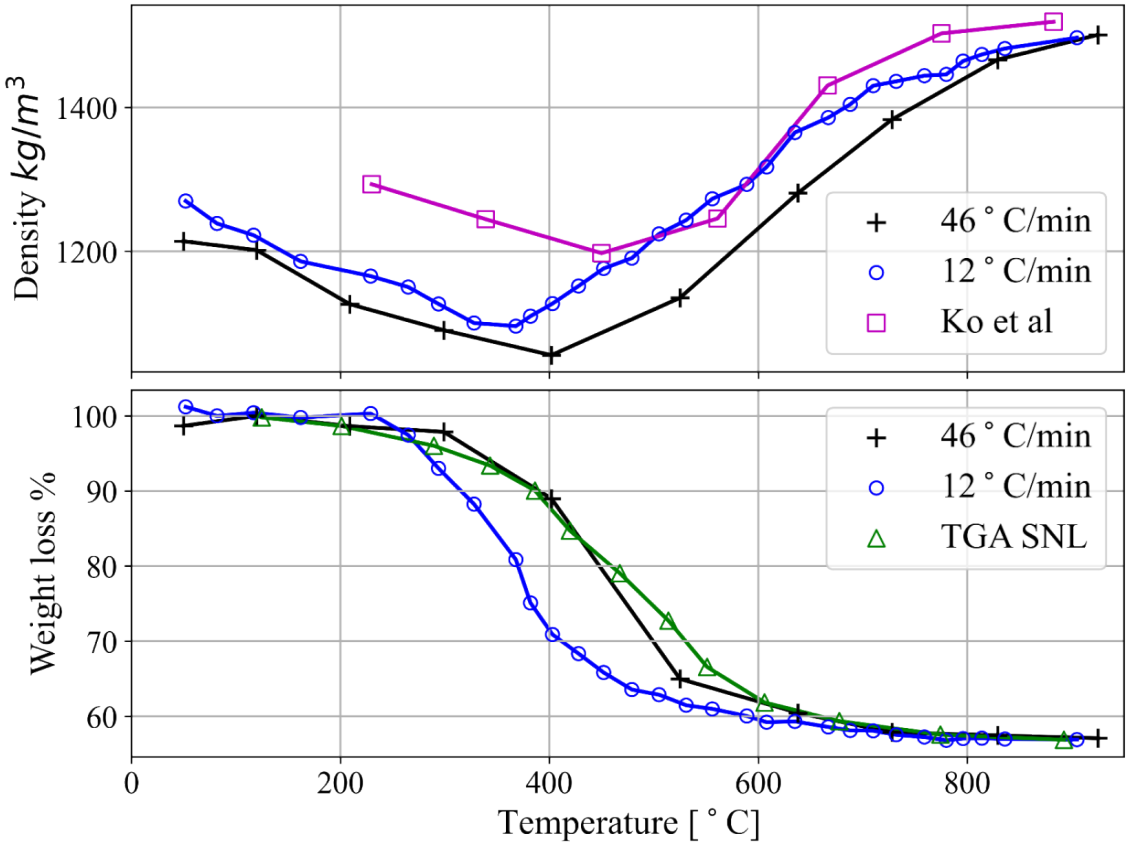
[Boigné, 2022]



Results – Density and mass loss

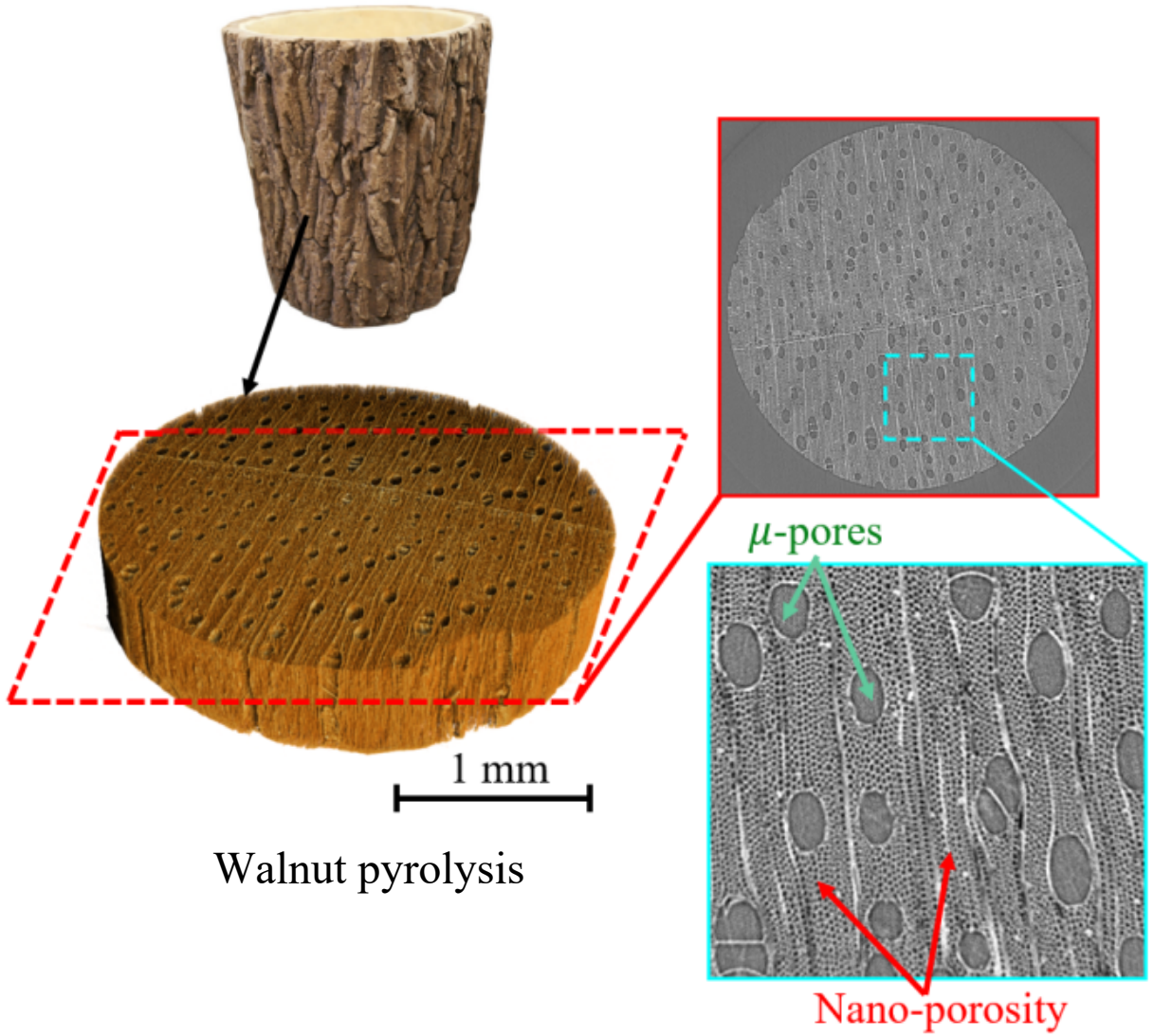
Heating rate	12 °C/min	46 °C/min
Number of tomographies	31	11
Virgin density ρ_0 $[kg/m^3]$	1238.84	1201.76
Virgin X-ray mass attenuation ζ_0 $[cm^2/g]$	0.218	0.224
Virgin mean attenuation μ_0 [/cm]	0.271	0.269
Char density ρ_c $[kg/m^3]$	1514.11	1508.66
Char X-ray mass attenuation ζ_c $[cm^2/g]$	0.201	0.204
Char mean attenuation μ_c [/cm]	0.304	0.308
Volatile matter $Y_p = 1 - m_c/m_0$ [wt%]	43.2	43.2
Extent of volume shrinkage $\gamma = V_c/V_0$ [%]	46.5	45.2
Temperature at 40% mass loss [°C]	595	630

Morphological evolution SC-1008



[Ko, 2001]

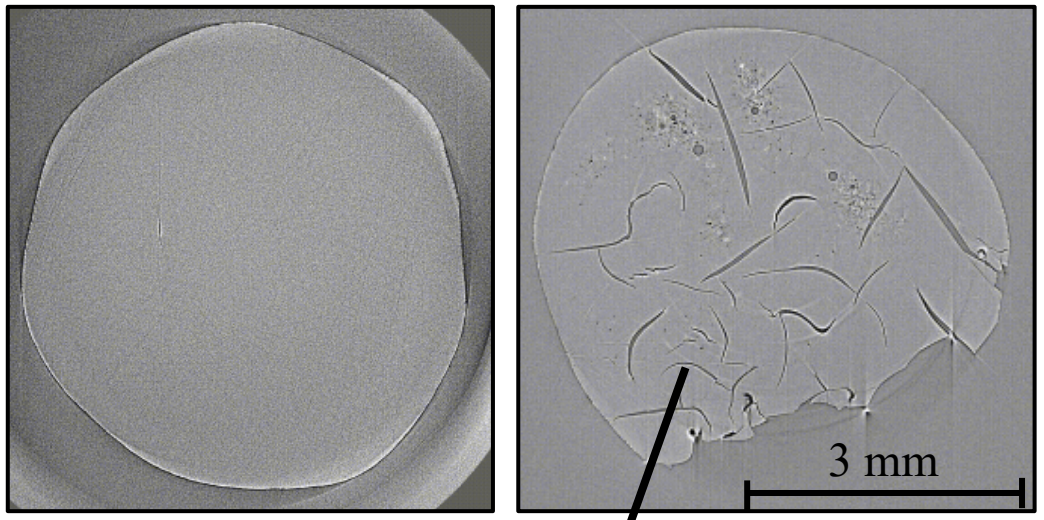
Outlook

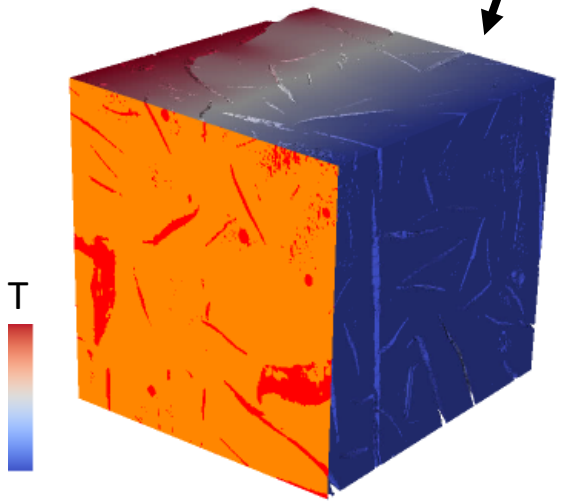


Walnut pyrolysis

Oxidation of virgin

Oxidation of pre-char





Effective property simulations

Acknowledgements

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

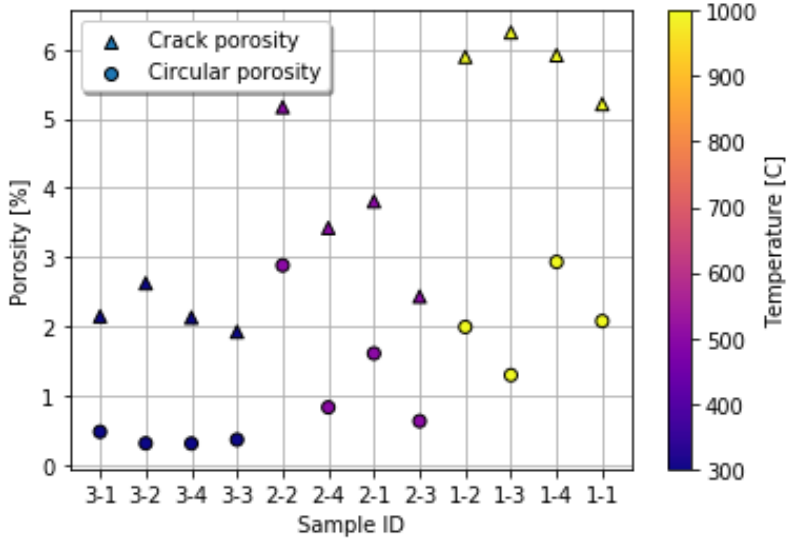
Supplementary

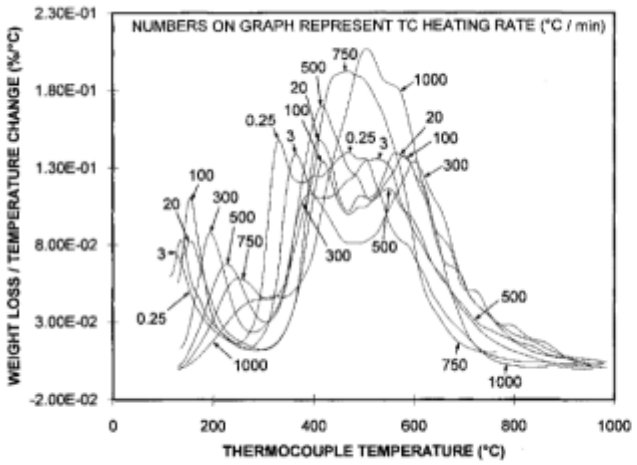
$$\mu(x,t) = \rho\zeta$$

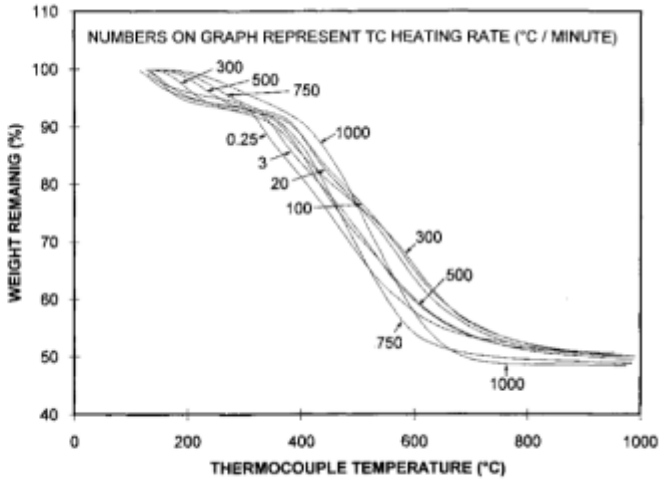
$$\int \mu dV = \int \zeta \rho dV$$

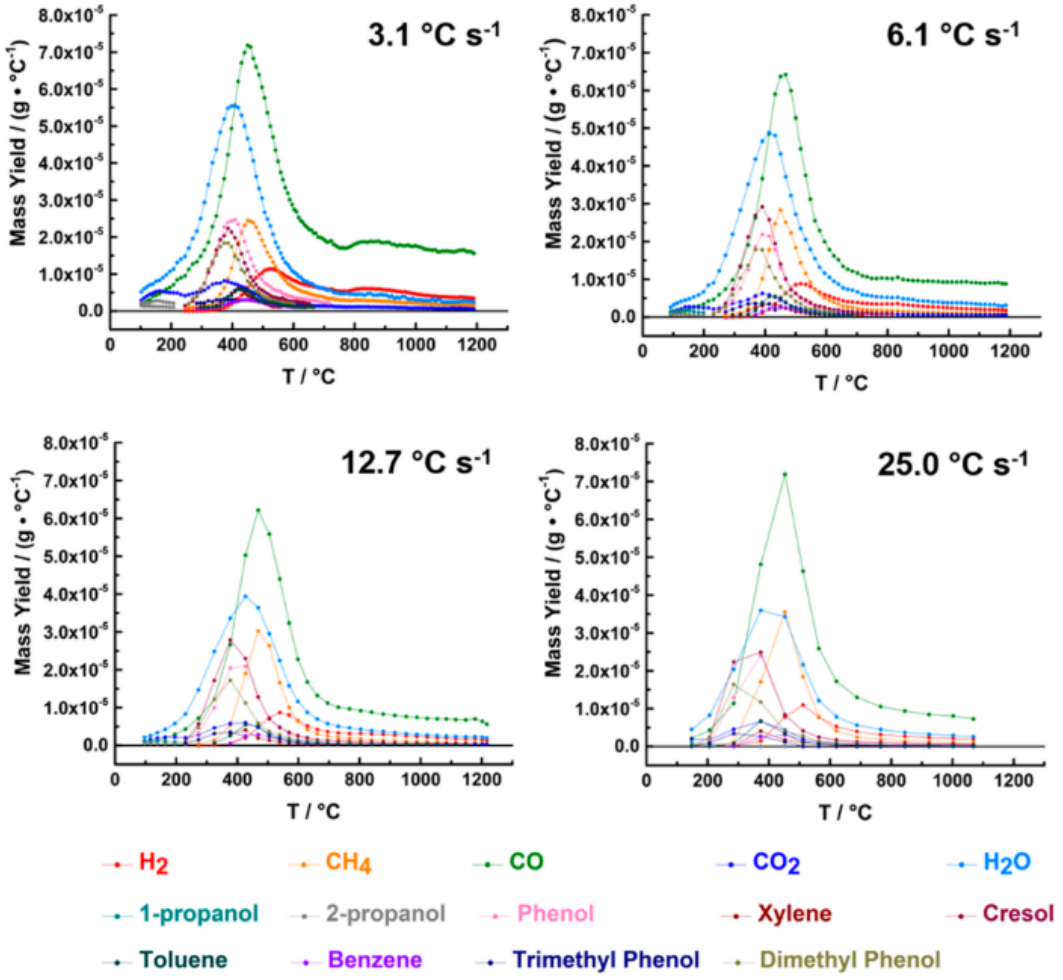
$$\int \mu dV = \bar{\zeta} * \int \rho dV$$

$$\bar{\mu} = \bar{\zeta} * m$$
$$\rightarrow m \approx \bar{\mu}/\bar{\zeta}$$



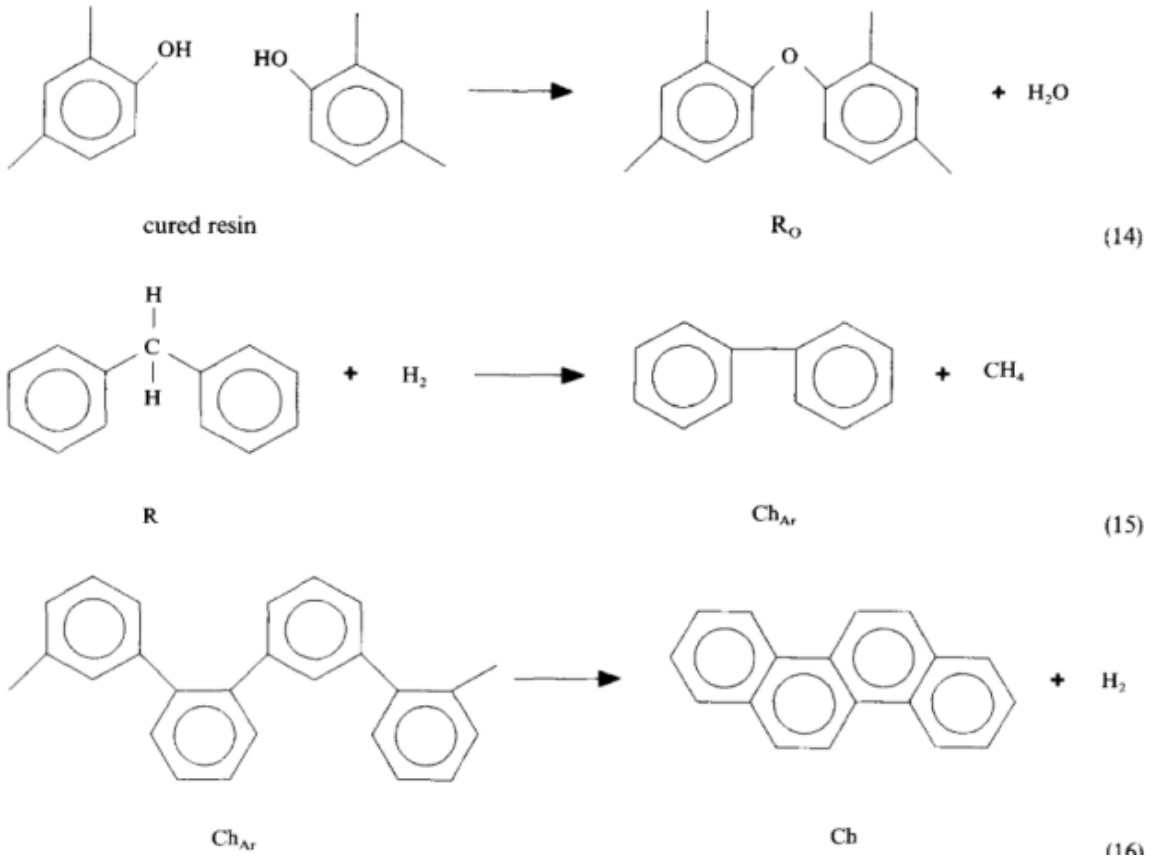






[Bessire, 2017; Stokes, 1995]

Supplementary



[Trick, 1995]

Supplementary

Approximating temperature gradient:

$$\rho = 1238.84 \frac{kg}{m^3}$$

$$C_p = 1180 \frac{J}{kg * K}$$

$$V = 5.89E - 7$$

$$\frac{dT}{dt} = 4.75K/s$$

$$A_s = 8.64E - 5$$

$$q'' = \rho C_p V * \frac{dT}{dt} * 1/A_s = 4734.34\, W/m^2$$

$$T^* = \frac{k(T - T_i)}{q''L} = 0.5$$

$$\Delta T = 0.5 * \frac{q''L}{k}$$

$$\Delta T = 0.5 * \frac{\left(\frac{0.473W}{cm^2}\right) * 0.25cm}{\frac{0.001W}{cmK}} = \mathbf{60K}$$

Largest temperature gradient being 60K

Approximating time for quasi-steady state:

$$Fo = 0.5$$

$$t = 0.5 * \frac{L^2}{\alpha}$$

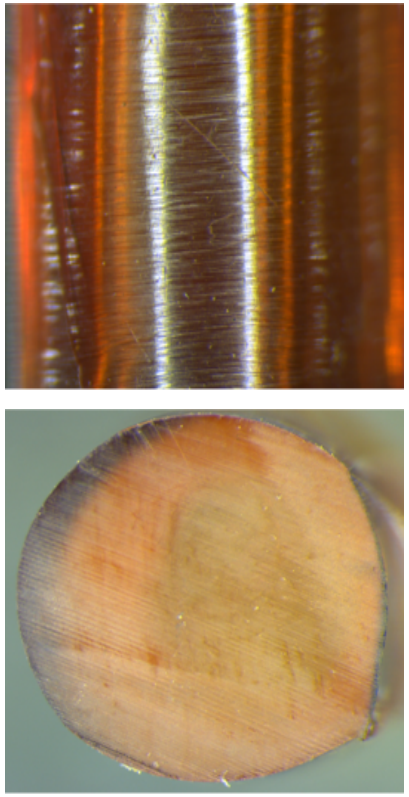
$$t = 0.5 * \frac{(2.5mm)^2}{\frac{0.167mm^2}{s}} = \mathbf{18\ sec}$$

Quasi steady state reached quickly compared to timescale of each tomography (~1 tomo per 1.5 min)

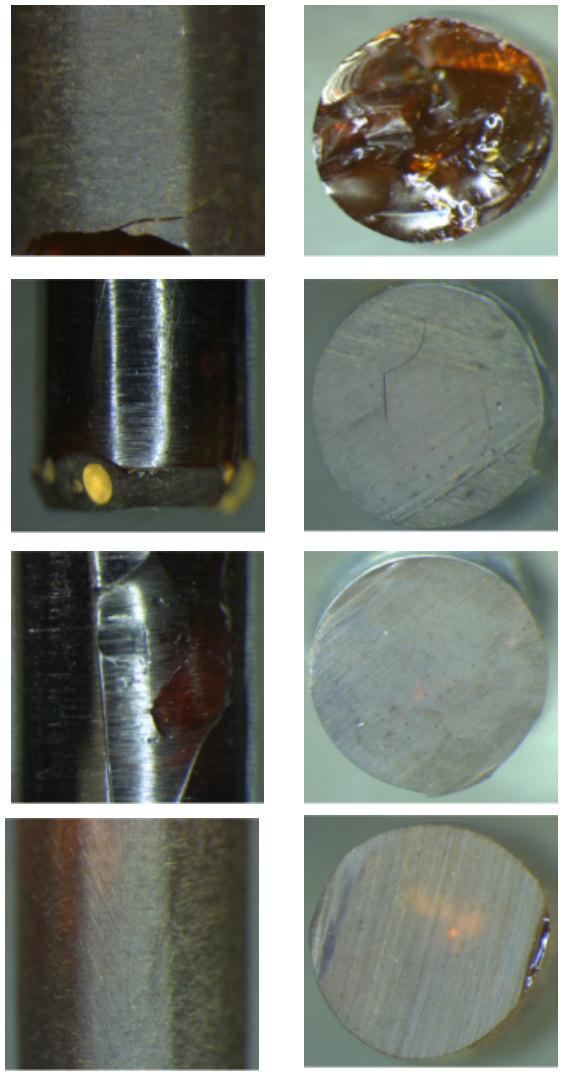
[Engerer, 2018]

Supplementary

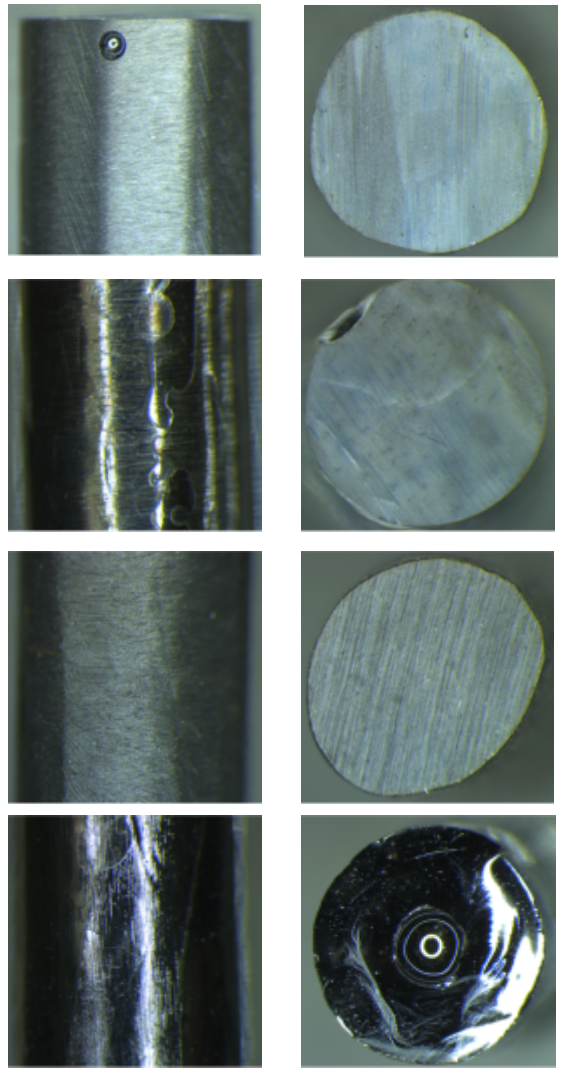
Virgin



300C



500C



1000C