Towards resolving mechanisms of particle shrinking during biomass pyrolysis

via micro-computed tomography and *in-situ* radiography

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Introduction

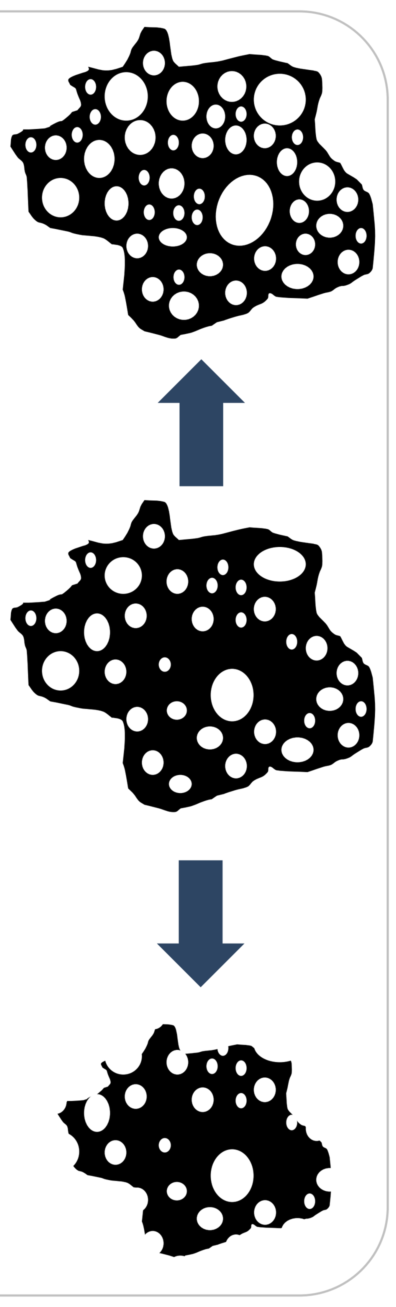
"What causes particle shrinkage and how can it be predicted?" is considered one of the top ten fundamental challenges of biomass pyrolysis for biofuels. [1]

Properly accounting for particle shrinkage is key to accurate morphological modelling of biomass pyrolysis. Such modelling would allow tailor-made chars to be produced with optimal properties for a variety of high-priority environmental applications such as air, water, and soil treatment, carbon capture and storage, and sustainable low-cost catalysis and energy storage. [2,3]

1. Uniform conversion
Assumes the entire volume of particle is in good contact with the atmosphere.
Volume loss is purely internal (porosity gain)

There are two conventional varieties of model for particle shrinking. [4,5]

2. Shrinking unreacted particle
Assumes only an infinitesimally-thin outer layer is in good contact with the atmosphere.
Volume loss is purely external (particle shrinking)



However, it is known that both internal and external volume loss occur simultaneously during pyrolysis. [5,6]

As a result, there have been several attempts to combine these conventional models, [5,6] but validation is lacking due to the challenging nature of imaging under controlled pyrolysis conditions (high temperature, constant heating rate, inert atmosphere, high gas-flow to remove produced volatiles from the reaction zone, etc.).

It is recognised that "*In situ* imaging… will provide unprecedented and much needed information for developing a new generation of models." [1]

Here, we attempt to close this knowledge gap using a combination of *in-situ* and *ex-situ* x-ray imaging techniques.

Methods

Using a novel purpose-built pyrolysis reactor, 6 mm tall beds of 1-2 mm particle size walnut and almond shells in 4 mm ID quartz tubes were convectively heated by a 3 LPM stream of pre-heated argon at precisely 6 °C/min to peak temperatures between 250 °C and 450 °C. During this pyrolysis process, x-ray images were acquired in a single plane. After pyrolysis, chars and representative raw samples were rotated continuously in the beam to acquire 3D tomograms of the reactants and products.

Results

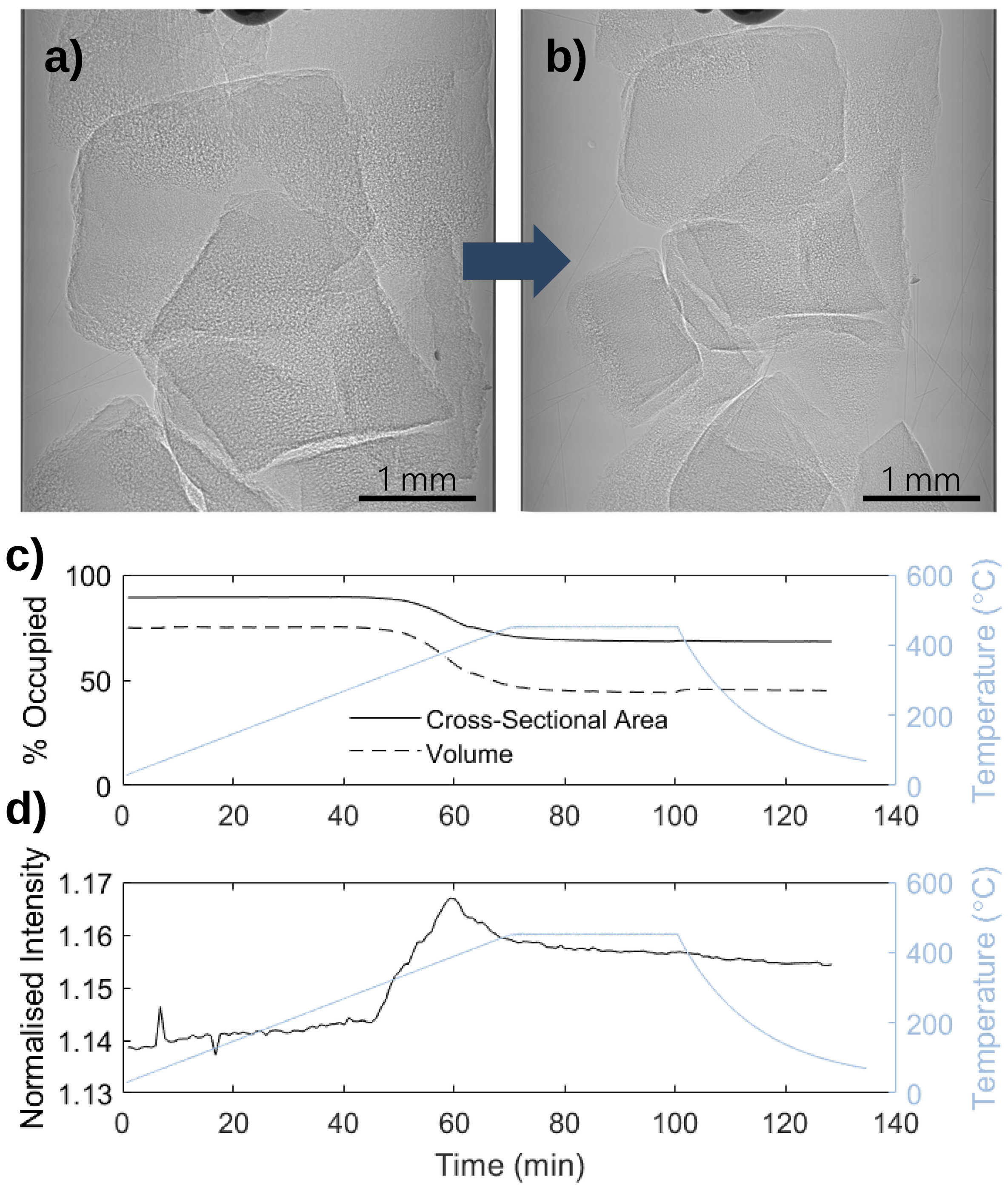
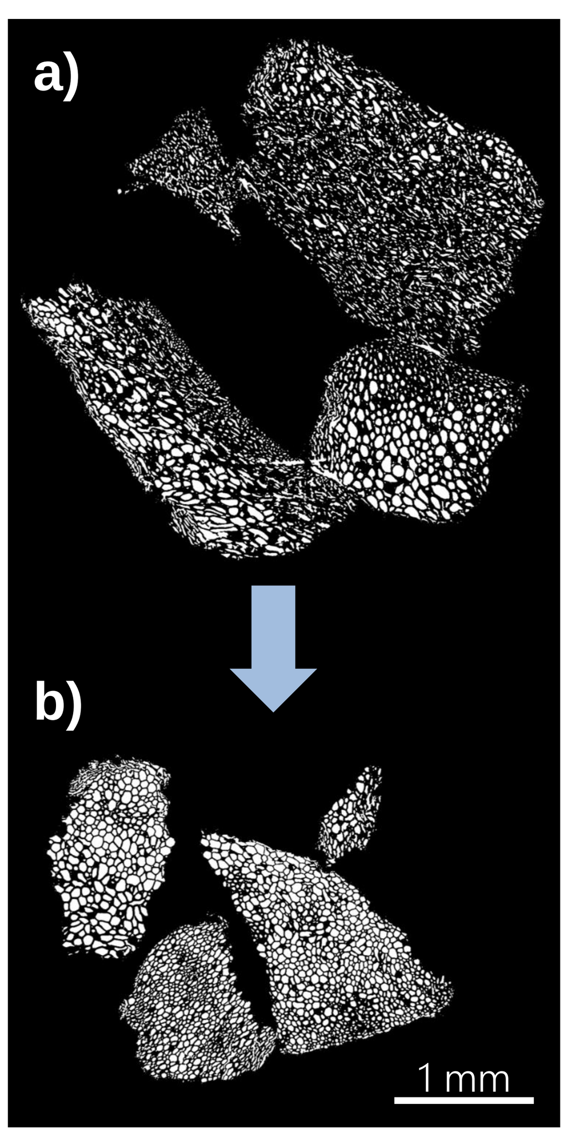


Figure 1. In-situ radiographs of walnut shells (a) before and (b) after pyrolysis to 450 °C, and corresponding (c) approximated volume loss and (d) normalised average pixel intensity of the bed.



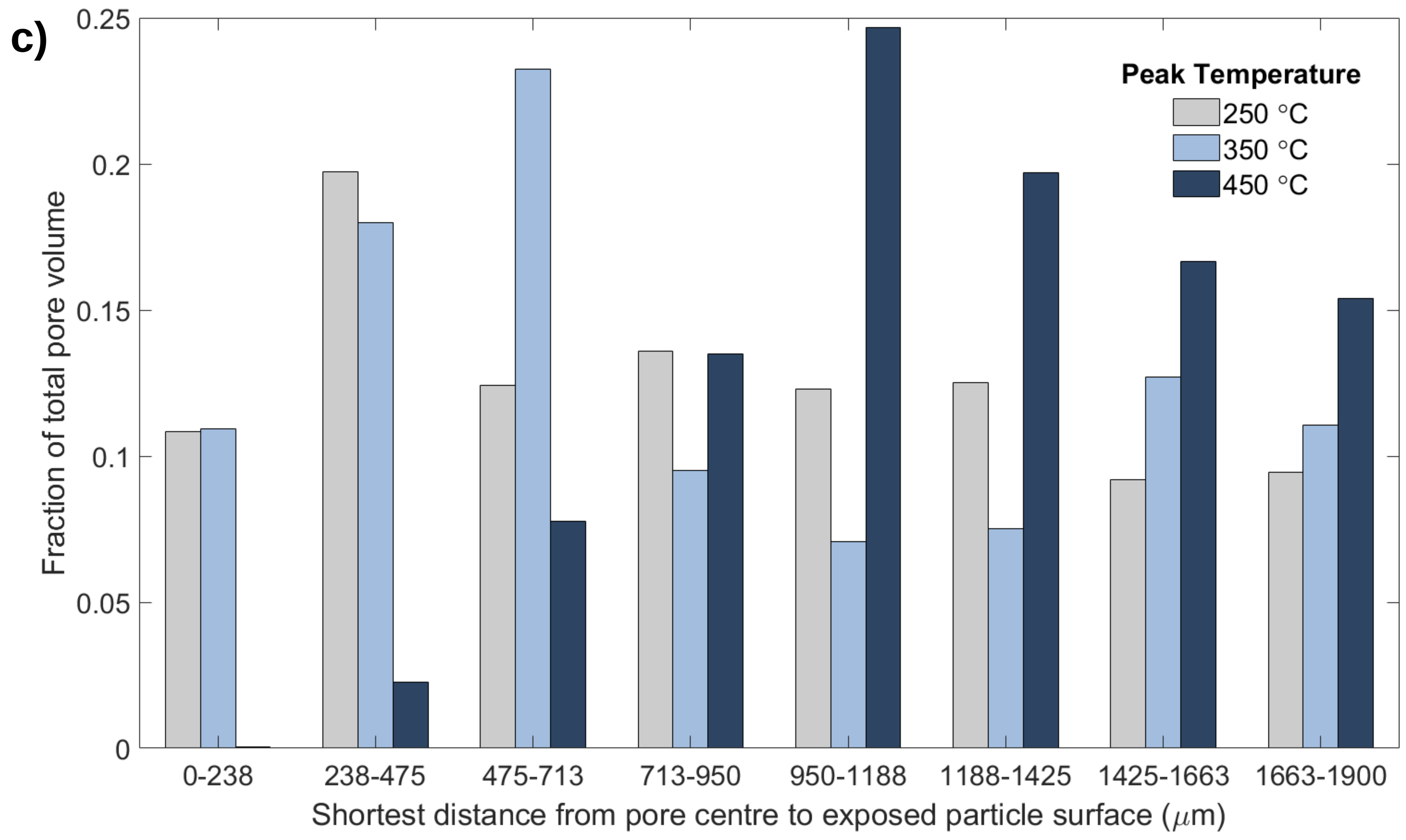


Figure 2. Slices of segmented pore masks for almond shells pyrolysed to (a) 250 °C and (b) 450 °C, and (c) the corresponding distribution of pore volume in terms of distance from the nearest particle surface.

Conclusions

Preliminary results support concurrent internal and external volume loss (see Fig. 1 c-d), but the development of porosity observed thus far does not match any existing models. Current results indicate a band of concentrated pore volume moving from the particle surface to its core over the course of the pyrolysis process. (see Fig. 2 c) The fact that this presents as a moving band, rather than pore volume simply concentrating at the particle surface over time, implies an initial swelling and subsequent shrinking of pores, which can also be subtly observed by eye in the in-situ radiographs.

References

1. Mettler, M. S., Vlachos, D. G. & Dauenhauer, P. J. Top ten fundamental challenges of biomass pyrolysis for biofuels. *Energy Environ. Sci.* **5**, 7797 (2012).
2. Linares, N., Silvestre-Albero, A. M., Serrano, E., Silvestre-Albero, J. & García-Martínez, J. Mesoporous materials for clean energy technologies. *Chem. Soc. Rev.* **43**, 7681–7717 (2014).
3. Titirici, M.-M. et al. Sustainable carbon materials. *Chem. Soc. Rev.* **44**, 250–290 (2015).
4. Di Blasi, C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog. Energy Combust. Sci.* **34**, 47–90 (2008).
5. Gentile, G. *et al.* A computational framework for the pyrolysis of anisotropic biomass particles. *Chem. Eng. J.* **321**, 458–473 (2017).
6. Di Blasi, C. Heat, momentum and mass transport through a shrinking biomass particle exposed to thermal radiation. *Chem. Eng. Sci.* **51**, 1121–1132 (1996).

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