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Self-heating ignition of materials in storage conditions: from biochar to lithium-ion batteries

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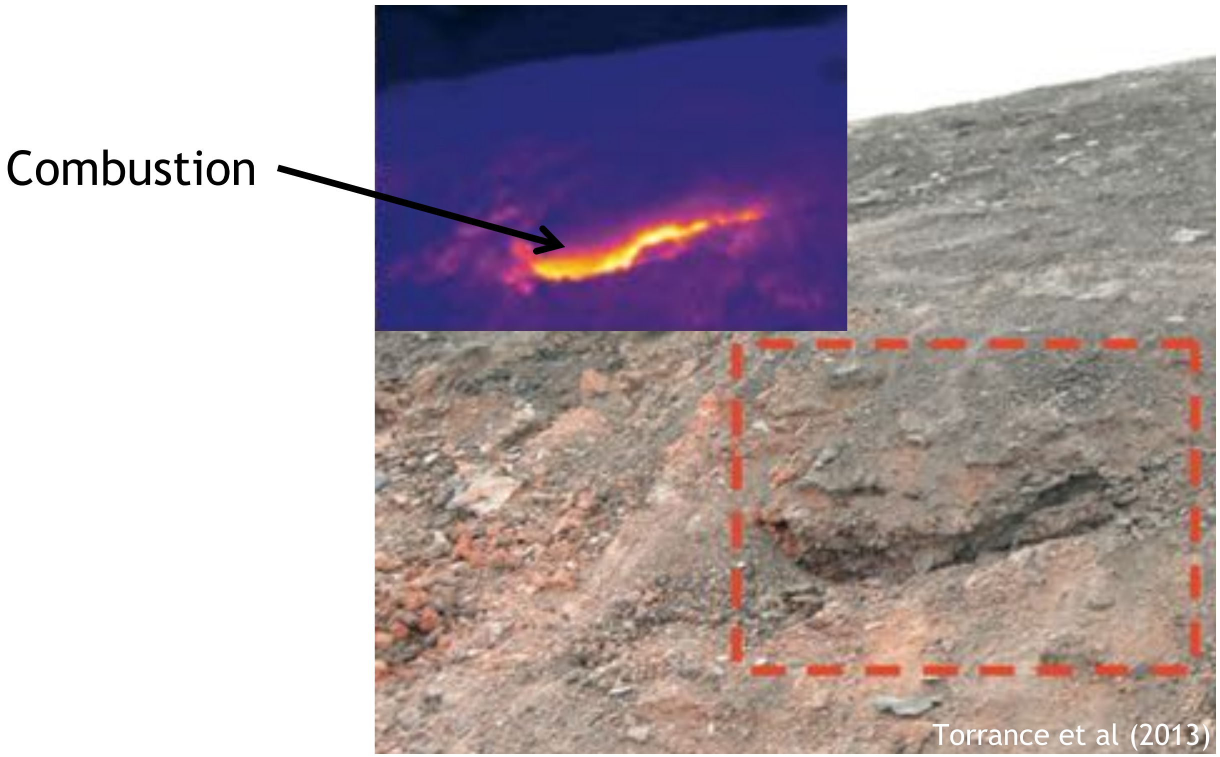
UK FLUIDS NETWORK

Combustion in reactive porous media

Materials where small free spaces (pores, voids) are embedded in the solid where there is a presence of a carbon-rich component.



Permeable to a variety of fluids (air, water or oil) and greatly increases its surface area allowing heterogeneous reactions **with oxygen** to take place.

Storage, transport, use


http://www.thejournal.co.uk/business/business-news/north-east-biomass-specialists-set-4397756

https://thebiomassmonitor.org/2015/01/10/biomass-industry-plays-with-fire-gets-burned-2/

http://www.endswasteandbioenergy.com/article/1412737/explosion-dongs-biomass-plant

In transport, storage and use of biomass and biochar, there are fire risks.

The piles can actually **self-ignite**

Semenov Theory

Consider a system of size L containing a reactive mixture.

Study as a lump model:

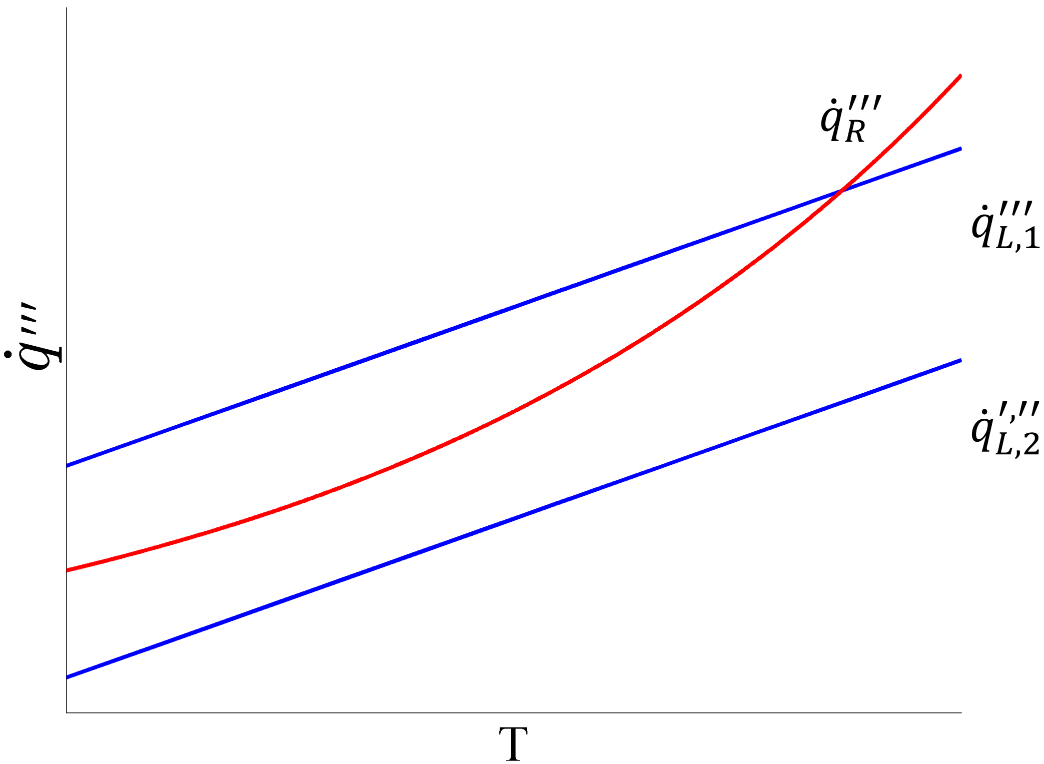
$$\rho c_p \frac{\partial T}{\partial t} = -\dot{q}_L''' + \dot{q}_R'''$$

Self-heating occurs when heat from heterogeneous reactions

$$\dot{q}_R''' = A_0 [F]^a [O]^b \exp\left(-\frac{E_a}{R_u T}\right) \hat{Q}_c$$

surpasses convective cooling

$$\dot{q}_L''' = \frac{hA}{V}(T - T_\infty)$$



$T_{\infty,1} < T_{\infty,2}$

For a critical size L, ignition happens at critical Ta_c

Frank-Kamenetskii Theory

Heat transfer problem being studied is non-steady heat conduction

$$\nabla^2 T + \frac{Q f e^{-\frac{E}{RT}}}{k} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \quad (1)$$

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To solve, Frank-Kamenetskii theory defines dimensionless parameter δ, used to relate geometry of experiment to ambient temperature

$$\delta = \frac{QE\boldsymbol{L^2}fe^{-\frac{E}{RTa}}}{kR\boldsymbol{T_a^2}} \quad (2)$$

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Eq. 1 is solved, and dependence of critical size on ambient temperature is obtained as

$$ln\left[\frac{\delta_c T_{a,c}^2}{{L_c}^2}\right] = \ln\left[\frac{QEf}{Rk}\right] - \frac{E}{R\,T_{a,c}} \quad (3)$$

Assumptions: Arrhenius reactions, material has high enough reaction rate and activation energy so that steady-state condition in time apply

Torrefied biomass and biochar production

Heating **biomass** in a **zero-oxygen** environment to temperatures >250°C

energy-rich gases and liquids, and a solid charcoal, or **char**.

For temperatures <350°C, we call this solid material **torrefied biomass**.
For temperatures >350°C,we call this solid material **biochar**.

Why produce torrefied biomass?

Torrefied biomass is a practical replacement for coal.
Easily integrates into existing coal power plants, enabling plants to generate clean energy without a lengthy or expensive conversion.

Why produce biochar?

Carbon remains sequestered in biochar for centuries, so sustainable biochar production is a powerful tool for carbon sequestration.
Biochar has beneficial effects when added to soils. Its highly porous structure can act like a slow-release 'sponge' for water and useful soil nutrients.

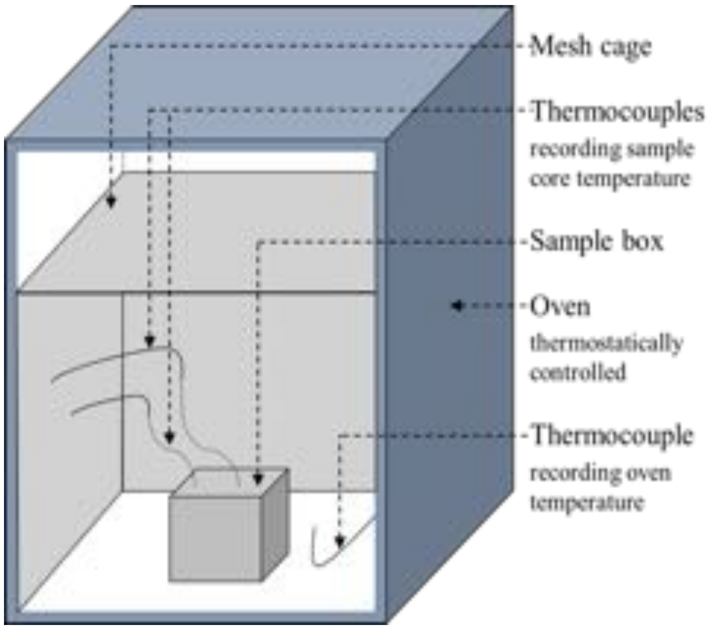
Different biomass and biochar used

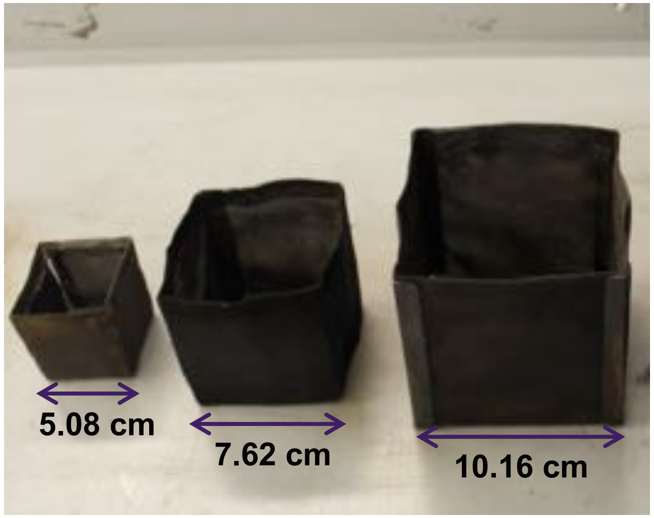
Rice husk

Wheat pellets

Softwood pellets

Experimental setup

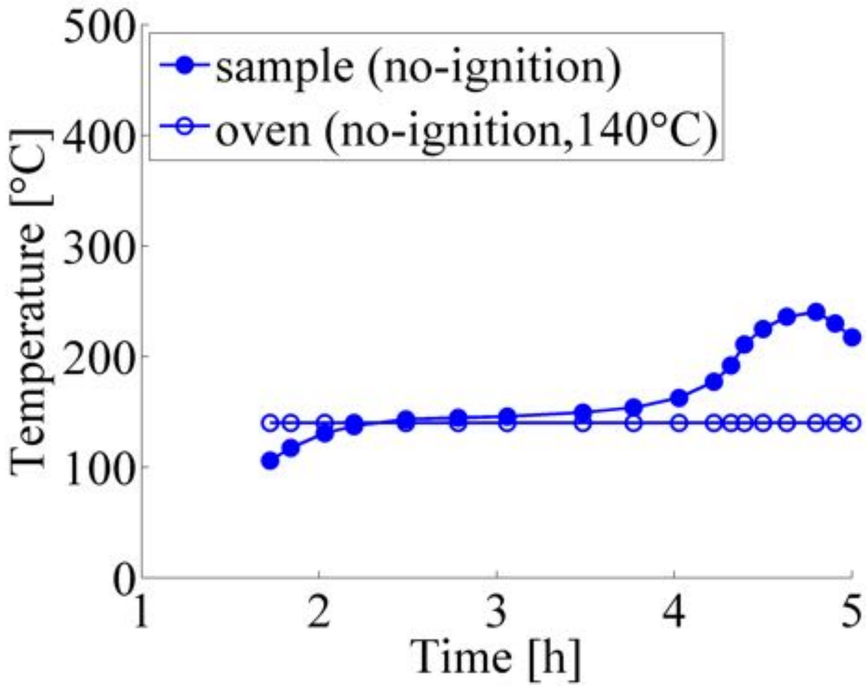




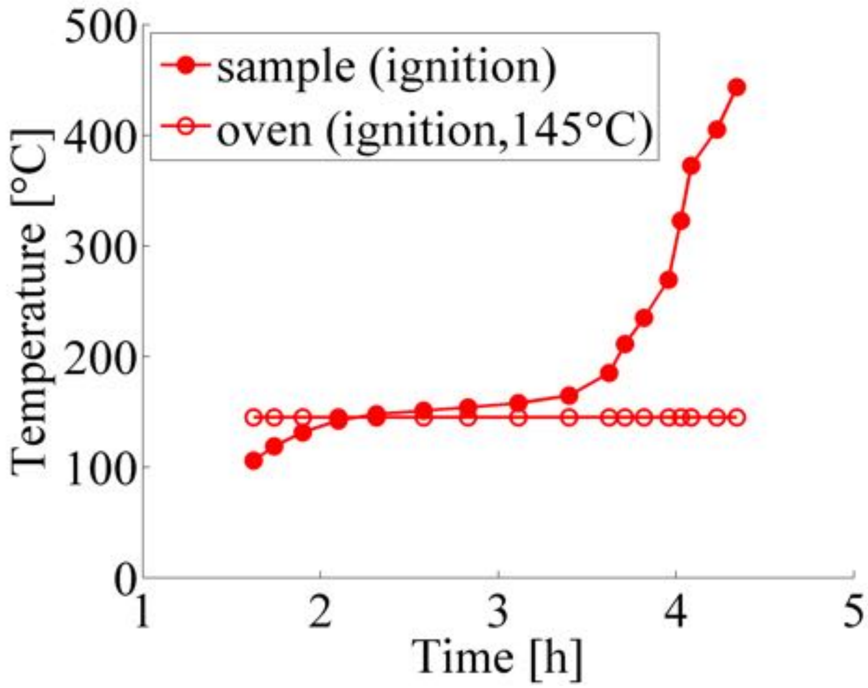
Very extensive experimental campaign, **173 experiments**, 1036 hours of oven heating time

Baskets made of 0.5 mm wide wire mesh used to obtain the experimental data for the largest possible temperature range we can study in a laboratory setting.

Typical ignition curves in self-heating experiments

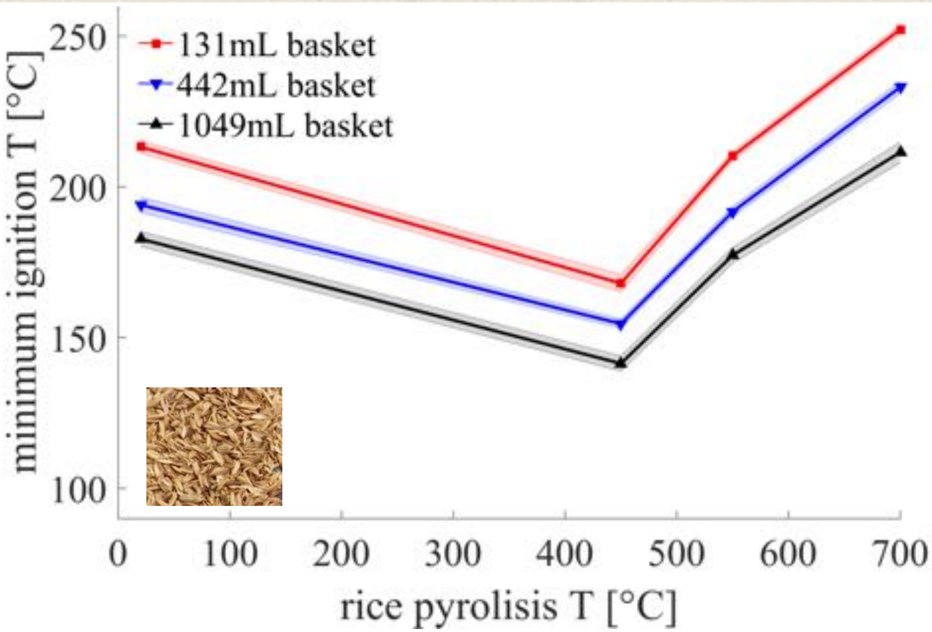


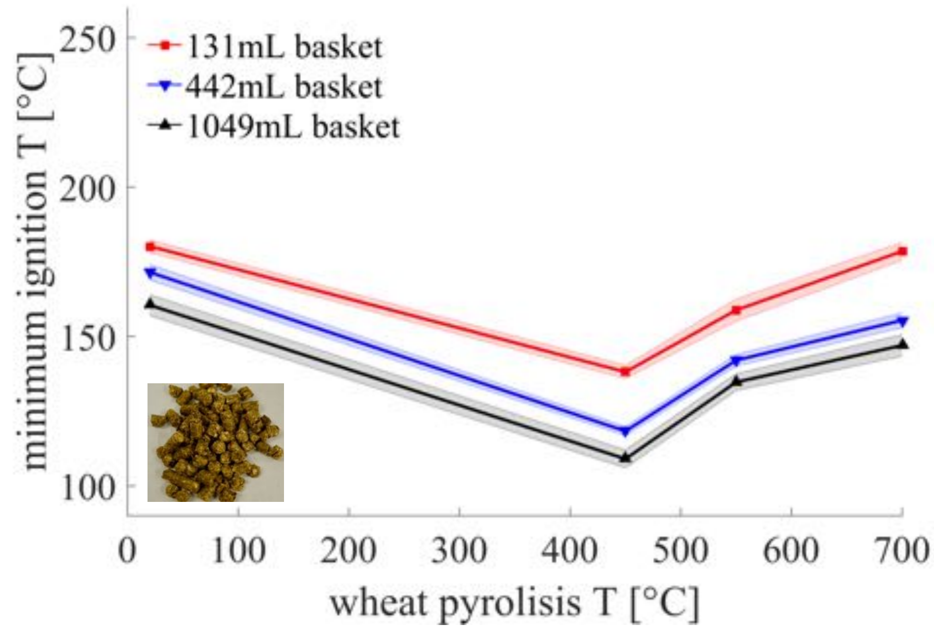
No ignition



Ignition

Comparison of Ignition Temperatures





For rice, feedstock self-ignites at lower temperatures than biochar produced at 700ºC

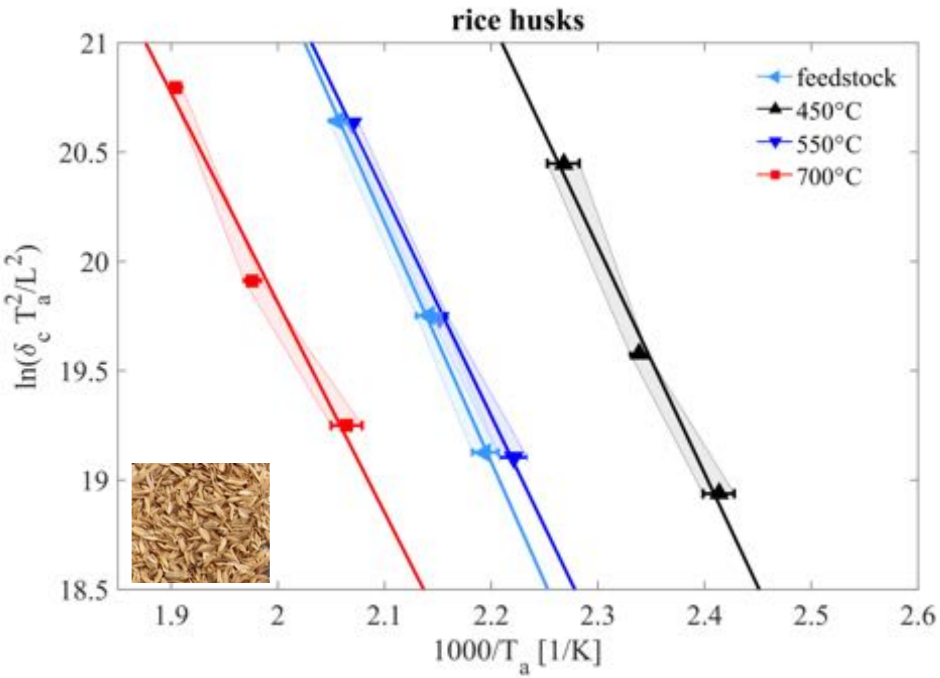
For wheat, feedstock self-ignites at higher temperatures than any of the biochar tested

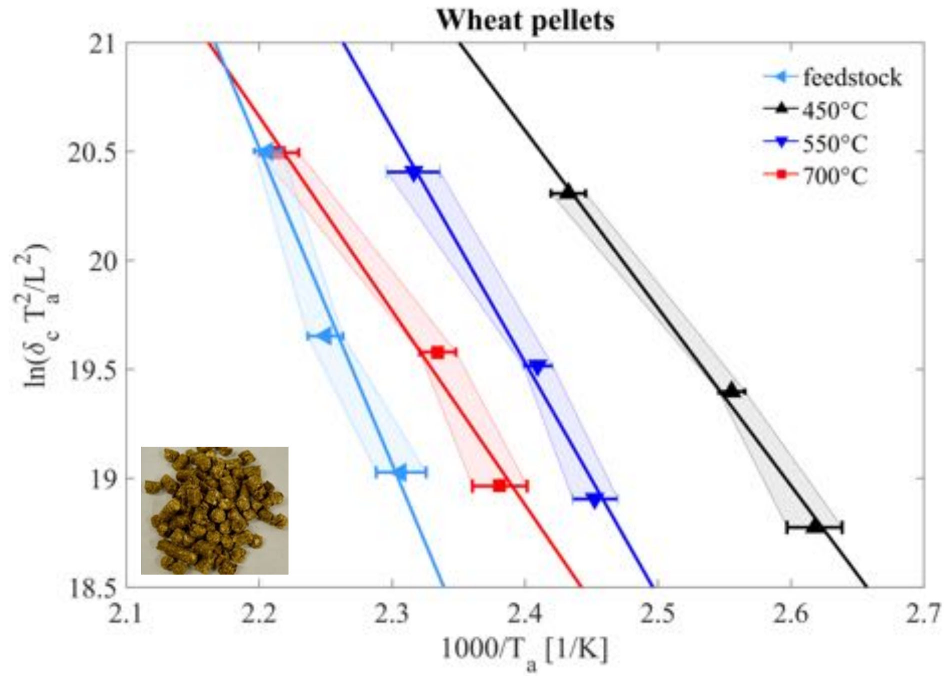
How do we obtain thermal parameters and reactivity?

$$ln\left[\frac{\delta_c T_{a,c}^2}{{L_c}^2}\right] = \ln\left[\frac{QEf}{Rk}\right] - \frac{E}{R\ T_{a,c}}$$

F. Restuccia, O. Masek, R.M. Hadden, G. Rein. *Quantifying self-heating ignition of biochar as a function of feedstock and the pyrolysis reactor temperatur*e, Fuel Vol 236, 2019, pp 201-213. https://doi.org/10.1016/j.fuel.2018.08.141

Frank-Kamenetskii plot





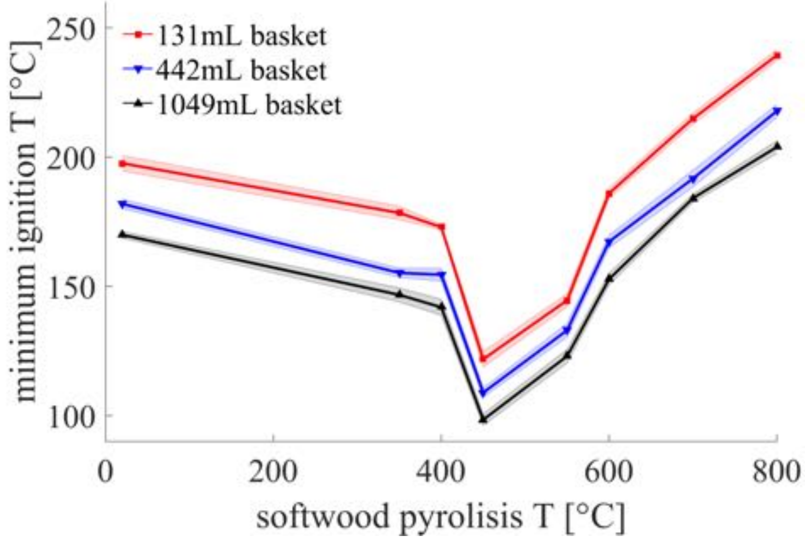
	ln(QEf/ Rk)	E (kJ/mol)	R^2
wheat feedstock	52.45	120.68	0.972
wheat 450°C	40.16	67.76	0.994
wheat 550°C	45.28	89.20	0.989
wheat 700°C	40.27	74.09	0.982
rice feedstock	43.21	91.20	0.999
rice 450°C	43.91	86.18	0.989
rice 550°C	41.57	84.17	0.998
rice 700°C	39.00	79.75	0.980

Biochar produced at 450ºC is most prone to self-heating ignition for both materials

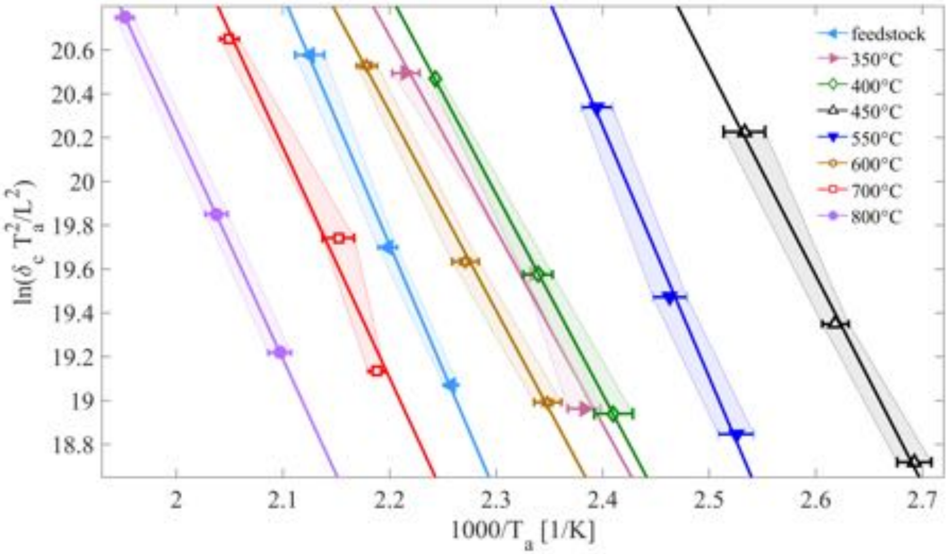
For rice, feedstock and Biochar produced at 550ºC present very similar self-heating ignition behaviour

F. Restuccia, O. Masek, R.M. Hadden, G. Rein. *Quantifying self-heating ignition of biochar as a function of feedstock and the pyrolysis reactor temperature*, Fuel Vol 236, 2019, pp 201-213. https://doi.org/10.1016/j.fuel.2018.08.141

Quantifying most reactive softwood biochar



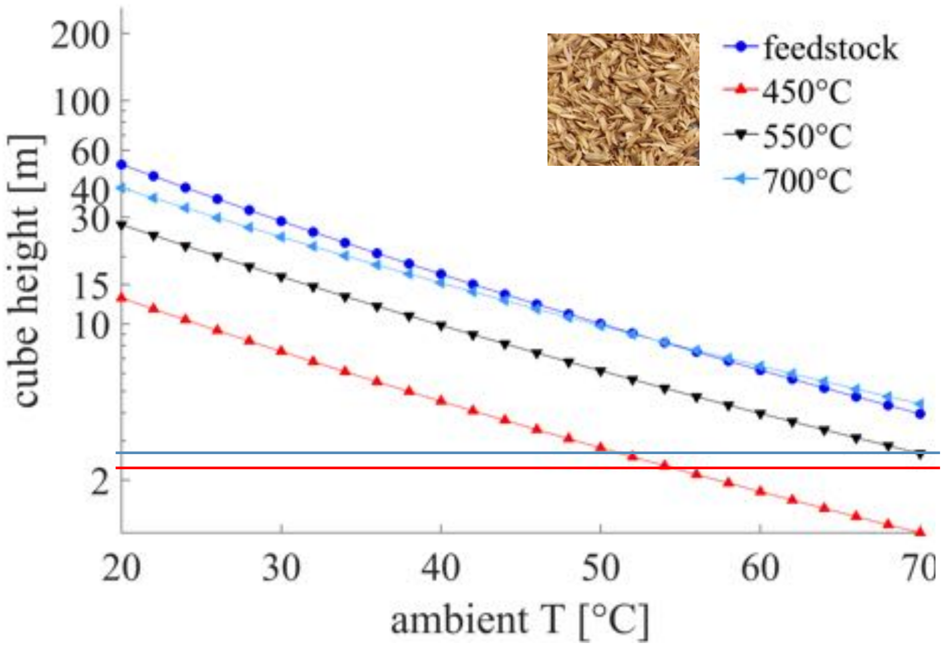
	ln(QEf/ Rk)	E (kJ/mol)	R^2
softwood feedstock	44.72	94.52	0.999
softwood 350°C	40.15	73.65	0.982
softwood 400°C	40.97	76.01	1.000
softwood 450°C	44.20	78.76	0.997
softwood 550°C	47.73	95.18	0.996
softwood 600°C	40.26	75.37	0.998
softwood 700°C	42.24	87.44	0.975
softwood 800°C	41.29	87.51	1.000

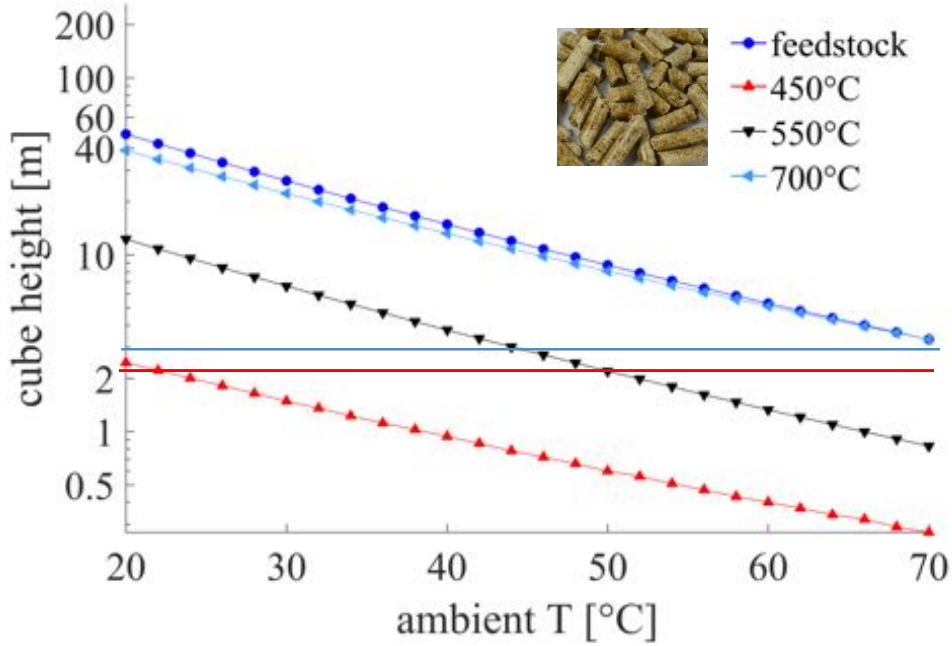


Peak of reactivity for biochar produced at 450°C, reactivity quickly decreases with a drop or increase of production temperature

F. Restuccia, O. Masek, R.M. Hadden, G. Rein. *Quantifying self-heating ignition of biochar as a function of feed-stock and the pyrolysis reactor temperature*, Fuel Vol 236, 2019, pp 201-213. https://doi.org/10.1016/j.fuel.2018.08.141

Upscaling results





Standard domestic storage size
Open top container trailer size

For biochar produced at 450ºC, softwood pellets will ignite even for domestic storage sizes for typical domestic storage sizes for temperatures >20ºC

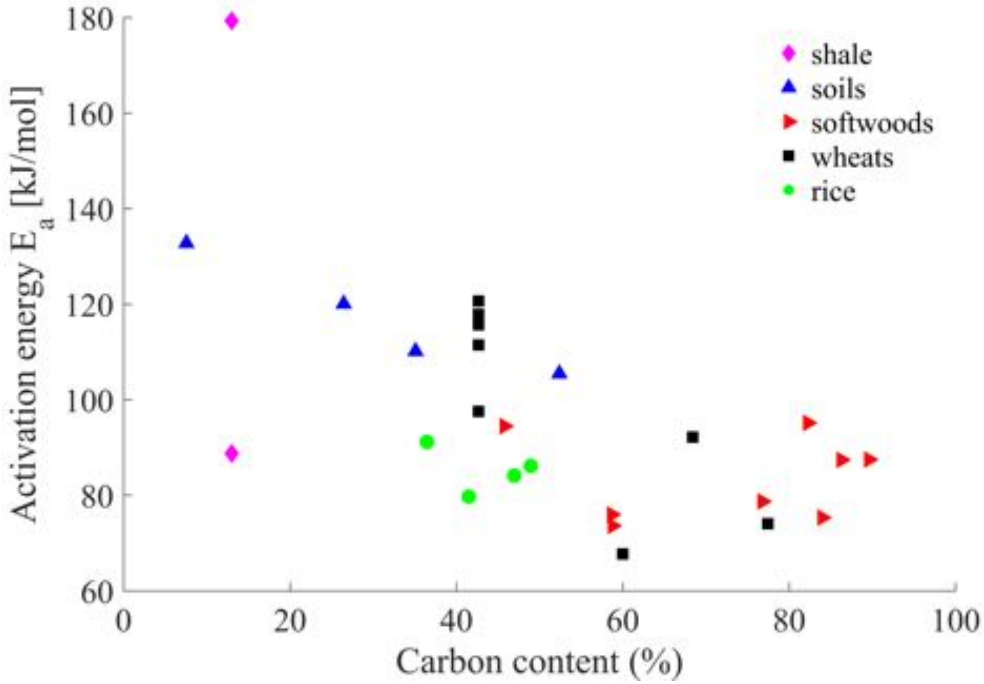
This is not the case for rice, where temperatures above 50ºC would be required

F. Restuccia, O. Masek, R.M. Hadden, G. Rein. *Quantifying self-heating ignition of biochar as a function of feed-stock and the pyrolysis reactor temperature*, Fuel Vol 236, 2019, pp 201-213. https://doi.org/10.1016/j.fuel.2018.08.141

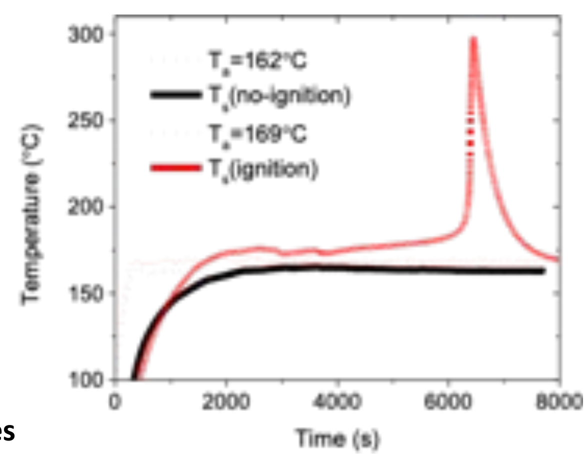
Other materials

Self-heating ignition of

- **Biomass**
- **Biochar**
- **Fine particles**
- **Soils**
- **Shale rock**
- **Lithium-ion batteries**



Restuccia et al, *Combustion and Flame*, 2017
Restuccia et al, *Fire Safety Journal*, 2017
Restuccia et al, *Fuel*, 2019
Restuccia et al, *Fuel, 2019*
Yuan et al, *Fuel*, 2019
Yuan et al, *Combustion and Flame* (in review)
He et al, *Fire Technology* (in review)
Hu et al, *Fire Technology* (in review)



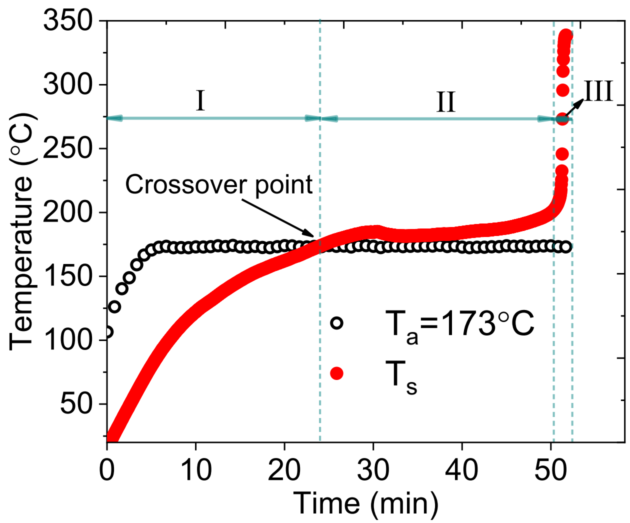
Most recently applied to Li-ion batteries

Li-ion battery fires

Li-ion Battery

Stage I: Heating up

1-cell:

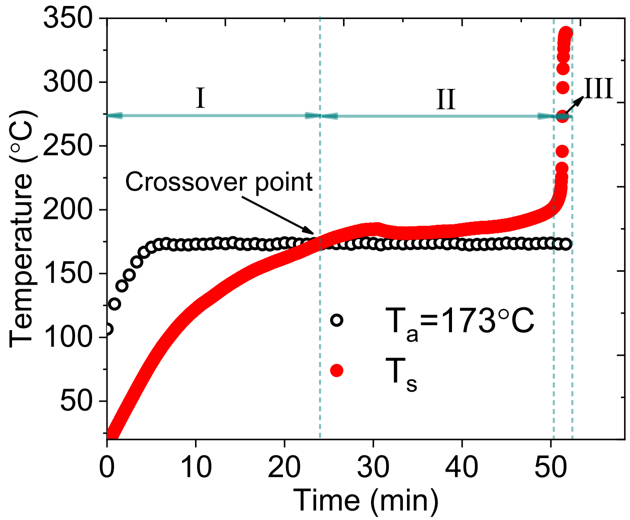


Stage	Criteria	Observation
I. Heating up	T_c increases significantly above its initial temperature.	(1) Slight swelling. (2) Fast T_c increase.

Li-ion Battery

Stage II: Self-heating

1-cell:

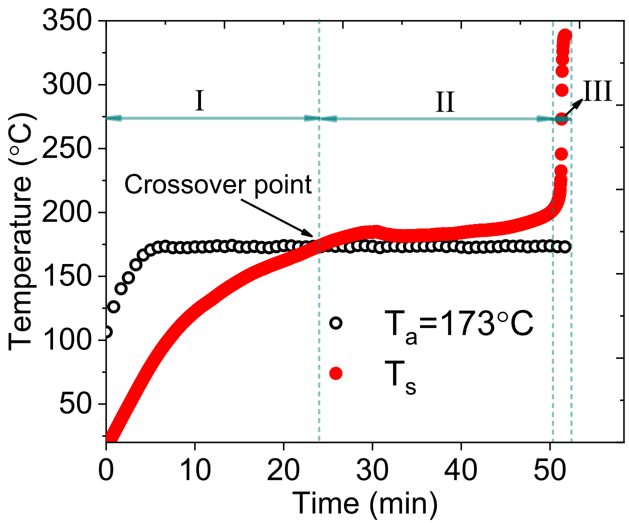


Stage	Criteria	Observation
II. Self-heating	Crossover: $T_c > T_a$	(1) No obvious swelling. (2) Electrolyte leakage. (3) Colour of cathode gradually changes from white to yellow. (4) Crossover: T_c increases over T_a, followed by a slight drop, and very slow increase.

Li-ion Battery

Stage III: Thermal runaway

1-cell:

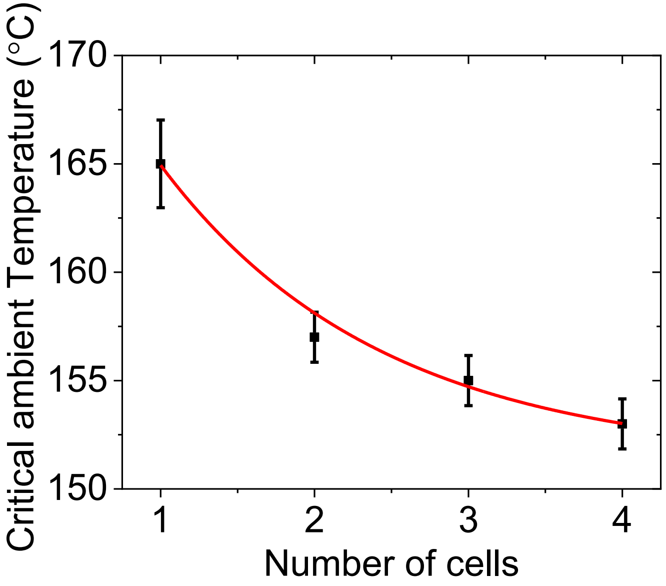


Stage	Criteria	Observation
III. Thermal runaway	T_c increases sharply.	(1) Rapid swelling in 2-3 s. (2) Plastic coating near cathode melting. (3) No further colour change at cathode. (4) T_c fast increase. (5) Venting ($T_a > T_{a,cr}$) and smoke. No flare, no fire and no sparks observed in any of our experiments.

Li-ion Battery- quantity effect

A clear trend is shown, which is the required ambient temperature for cell self-heating ignition decreases as the number of cells increases due to the heat transfer effects.

During storage, massive number of cells will affect this critical ambient temperature.



Conclusions

- We show ignition by spontaneous exothermic reactions at low ambient temperatures for various types of biomass and biochar.
- We compare the spontaneous ignition temperatures for wheat pellets, softwood pellets and rice husks biomass and biochar.
- For these materials, the biochar most prone to ignition is the one produced by pyrolysis at 450°C. It is much more prone to ignition than the feedstock.
- We show self-heating ignition trend for li-ion batteries, and show decreasing temperature for self-heating ignition with increasing number of cells
- Our work contributes to understanding and predicting the onset of accidental fires for transport and storage.

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