Design of a Novel Reactor for *in situ* Measurement of the Dielectric Constant During Hydrothermal Processes

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Motivation

Hydrothermal processes (HTP) break down large biomass molecules into energy-dense products using high temperatures (180-374°C) and pressures (4-22 MPa). HTP studies have previously focused on how the products are affected by varying the process temperature and pressure. However, they may not be the best thermodynamic properties to be used as control levers during HTP. Since changes in temperature and pressure alter another thermodynamic property known as the dielectric constant, we hypothesize that the reactions occurring may be understood better if the dielectric constant is controlled a process parameter.

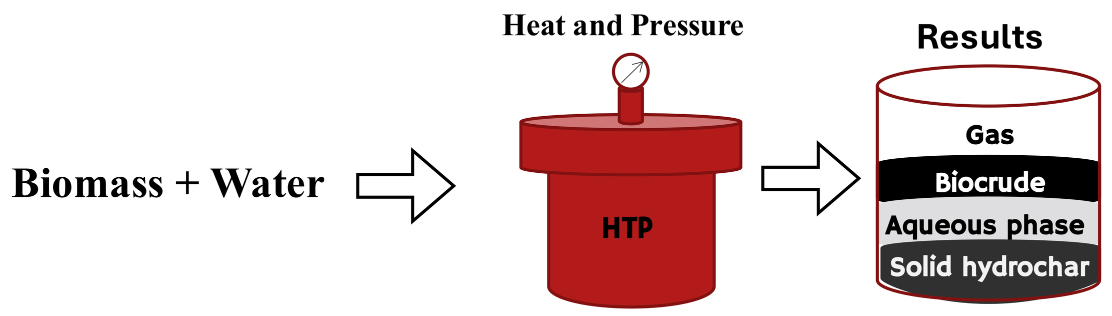

Figure 1: *Graphical summary of a typical Hydrothermal Process*

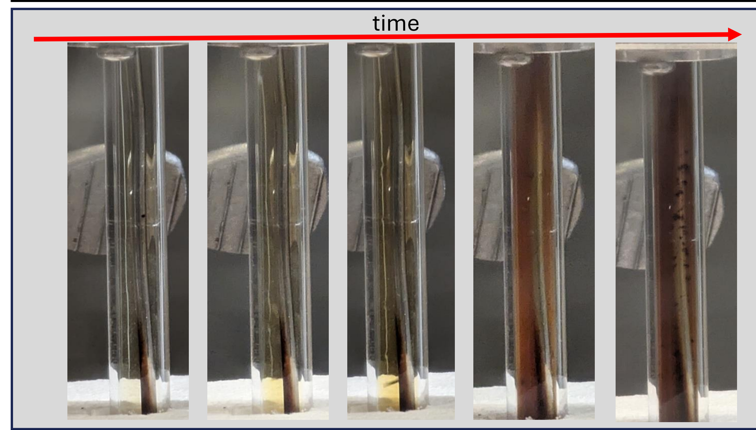

Figure 2: *Transformation of the glucose solution under hydrothermal conditions with time*

The Role of Water in Hydrothermal Reactions

In the subcritical region, water molecules behave as both **reactants** and **catalysts** while the bulk water serves as a **reaction medium**. [2]

Ionic Product (K_w)
Self ionization of water increases along the liquid-vapor equilibrium line up to three orders of magnitude; water is an effective medium for acid and base catalyzed reactions. [2]

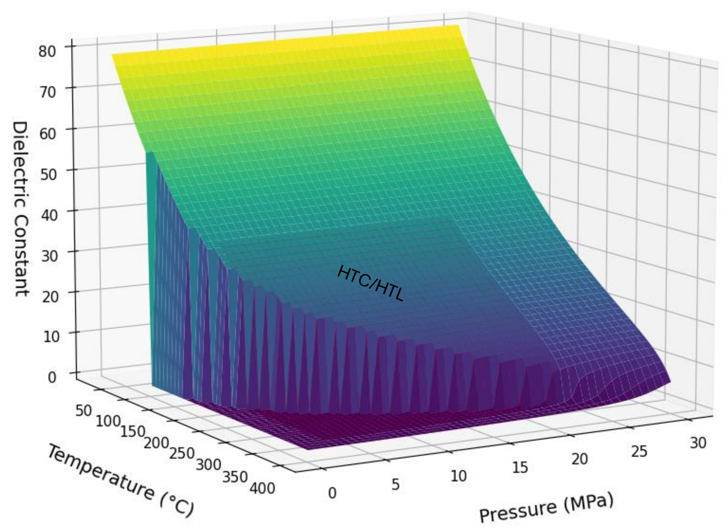

Figure 3: *The change in dielectric constant of pure water as a function of temperature and pressure*

Dielectric Constant (ε_r')
Under hydrothermal reaction conditions, the permanent dipoles of water molecules form activated complexes to attack biomass' chemical bonds. The hydrogen bonding network weakens; diffusion of water molecules is improved, and viscosity decreases.

The permanent dipole moment and hydrogen bonds influence the polarizability of water, which is measured via the dielectric constant. As ε_r' is lowered, water becomes more miscible with hydrophobic organic compounds. [3]

Overall: As T ↑ P ↑ → ε_r' ↓ and pK_w ↓

Research Goals

- The significance of dielectric constant in hydrothermal processes has been inferred in the literature through the changes in thermodynamic and transport properties of pure water. An ongoing debate still exists on whether ionic product or dielectric constant is the principal trigger for the hydrothermal reactions.
- The lack of in situ dielectric constant data presents us with an opportunity to measure it and study the roles which it plays during these hydrothermal processes.
- **Goal 1:** Design and construct a hydrothermal reactor that can measure, *in situ* and in real time, the dielectric constant of the reacting medium.
- **Goal 2:** Validate reactor and *in situ* dielectric constant measurements for known solvents and mixtures across HTP-relevant conditions

Method: Design of the Apparatus

High temperature and pressure dielectric constant measurements using the Cavity Perturbation Method

- Cavity perturbation method: non-intrusive, non-contact approach that can handle conductive, reacting biomass samples at high temperature.
- The method uses a cylindrical resonant cavity which is an aluminium shell excited by an external electromagnetic wave (EMW) source. A vector network analyzer supplies EMWs in the microwave range (1±0.05 GHz) and detects the transmitted waves from which the resonant frequency is obtained. The sample causes a shift in the resonant frequency; perturbation assumptions allow us to compute the complex permittivity from the frequency shift.
- The reusable, custom-made quartz batch reactor is microwave transparent and withstands hydrothermal pressures and temperatures.
- Internal temperatures and pressures are continuously monitored. Dual-zone ceramic heaters change the reaction temperature.

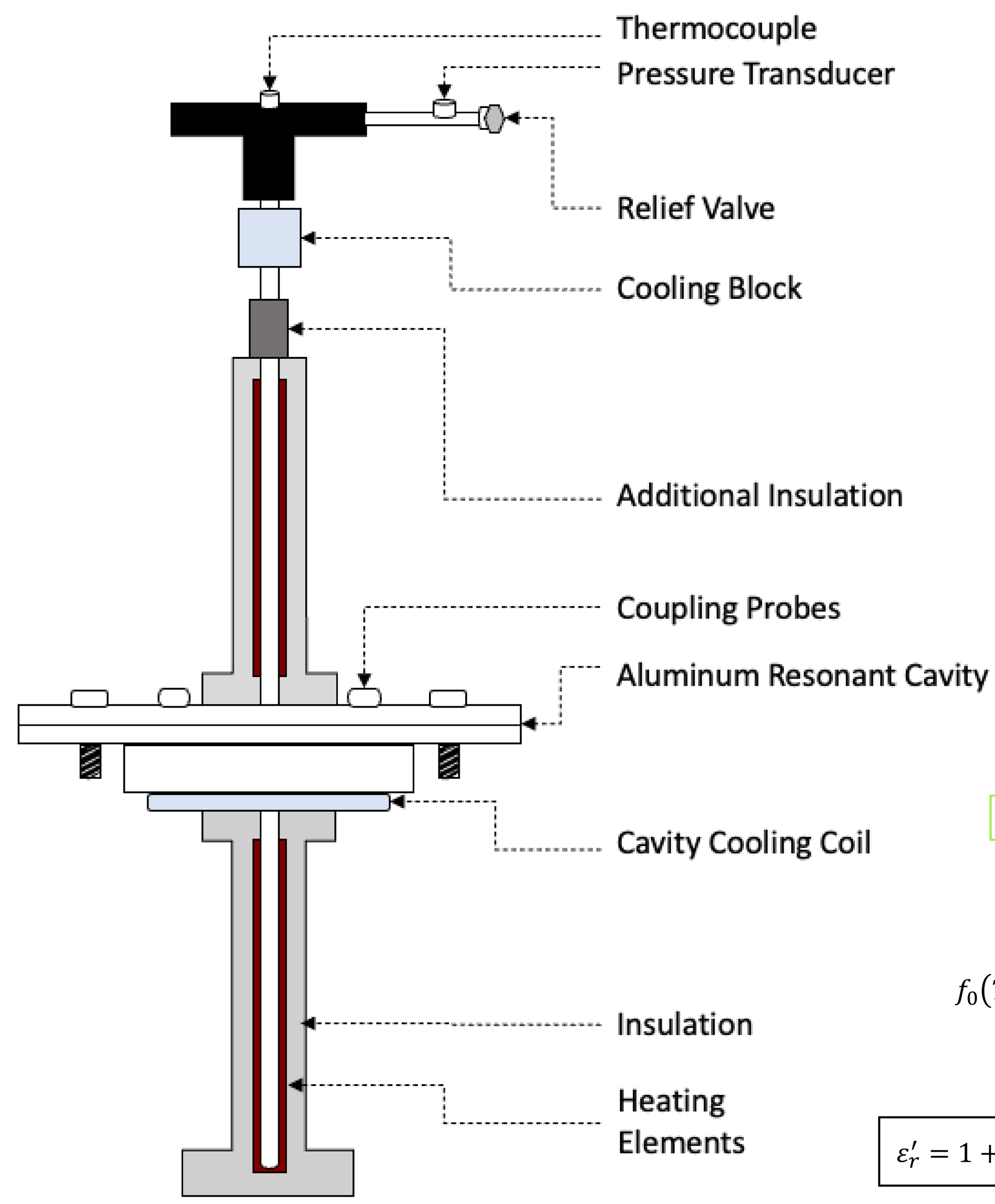

Figure 4: *Schematic diagram of the apparatus*

Governing Equations

▪Perturbation theory requires 3 assumptions: (1) The sample is in uniform field. (2) The cavity is cylindrical. (3) Stored energy in the sample is minimal. [1]

▪The fundamental mode with one electric field maxima at the axis parallel to the sample and the reactor diameter of 4 mm meet the requirements (Figure 6)

▪The empirical formula is obtained by applying the perturbation assumptions to the eigenvalues of the Helmholtz Equation:

$$\nabla^2 \vec{E} + (j\omega\mu\sigma - \omega^2\varepsilon\mu)\vec{E} = 0 \quad (1)$$

$$f_0(TM_{mnp}) = \frac{c_{air}}{2\pi}\sqrt{\left(\frac{t'_{mn}}{a}\right)^2 + \left(\frac{p\pi}{h}\right)^2} \quad (2)$$

$$\varepsilon_r' = 1 + 2C\frac{(f_1 - f_2)}{f_1} \qquad \varepsilon_r'' = C \times \left(\frac{1}{Q_2} - \frac{1}{Q_1}\right) \quad (3)$$

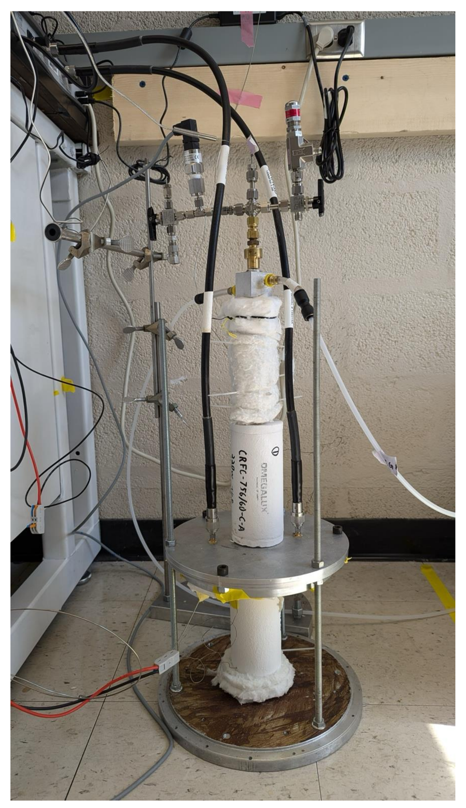

Figure 5: *Experimental set-up of the apparatus*

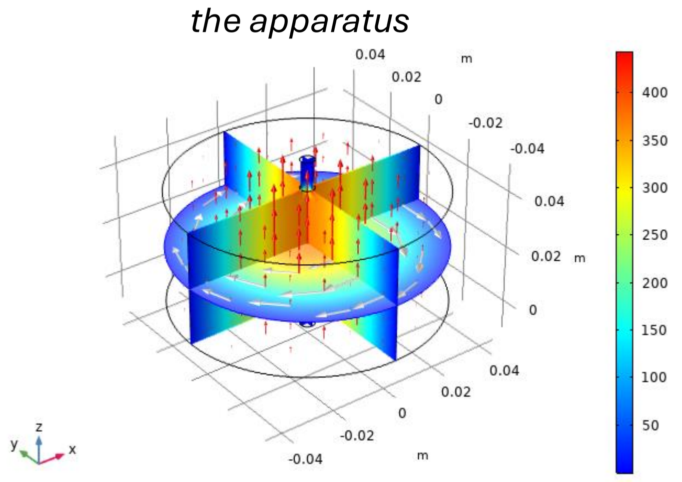

Figure 6: *Electric field distribution inside the cavity with one electric maxima at the center*

Calibration and Validation of Reactor Design

- The apparatus was calibrated using pure water and performance validated with other organic solvents such acetone.
- Hydrothermal carbonization of a 5% glucose solution performed. The dielectric constant of the glucose solution approaches towards that of pure water as the mixture enters the carbonization region.

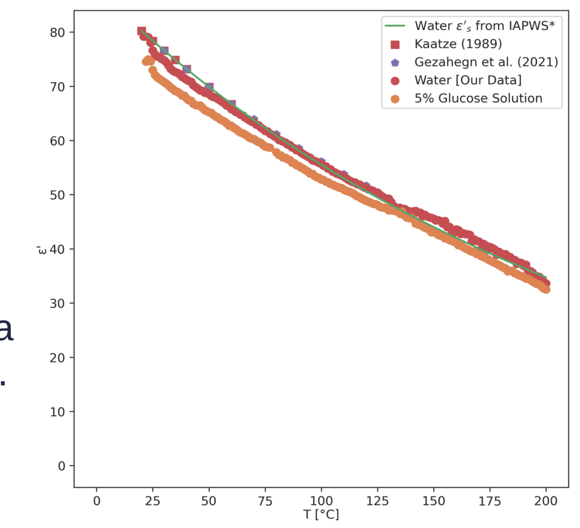

Figure 7: *The change in the dielectric constant of 5% glucose solution compared to that of pure water*

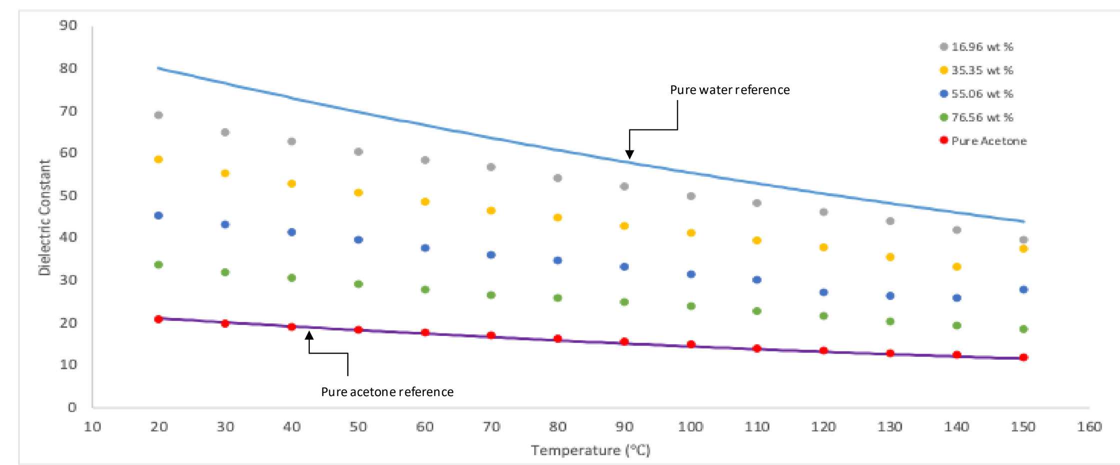

Figure 8: *Dielectric constant vs Temperature plots for different compositions of acetone-water binary mixtures*

Applications in Green Chemistry

- A more effective process design from the improved understanding in the fundamentals of biomass interaction with water – the universal solvent.
- Process end-points observed via the dielectric constant readings will reduce both energy and time requirements during hydrothermal processes.
- The introduction of dielectric constant as a process parameter can lead to a more efficient method in tuning the selectivity of the HTL end products.
- The applicability of dielectric constant can be expanded to the downstream upgrading of HTL products such as in liquid-liquid extraction.

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