SUPPLEMENTARY MATERIAL

Effect of acetic acid release and pH on lignocellulosic biomass conversion by liquid hot water pretreatment

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Temperature dependency of specific heat capacity and density of pure water

Based on Gmehling, Kleiber et al. (2019), the specific heat capacity of water (in J/(mol K)) can be correlated with temperature by the polynomial formula in equation (S1):

$$C_p = R\left(\frac{A}{\tau} + B + C\tau + D\tau^2 + E\tau^3 + F\tau^4\right), \quad \tau = 1 - \frac{T}{T_c} \tag{S1}$$

Where T_c is the critical temperature (647.096 K), and R is the universal gas constant (8.134471 J/(mol K)). This expression is valid for temperatures between 273 K and 586 K. Values for the parameters are represented in Table S1.

Table S1 – Values of parameters for specific heat capacity correlation.

	A	**B**	**C**	**D**	**E**	**F**
Water	0.255980	12.545950	-31.408960	97.766500	-145.423600	87.018500

Density of liquid water (in kg/m³) is described as function of temperature by Gmehling, Kleiber et al. (2019) in equation (S2), with T in Kelvin and values for the parameters in Table S2:

$$\rho = 18.015 \cdot \sum_{i=1}^{5} A_i(T)^i \tag{1}$$

Table S2 – Values of parameters for water density correlation.

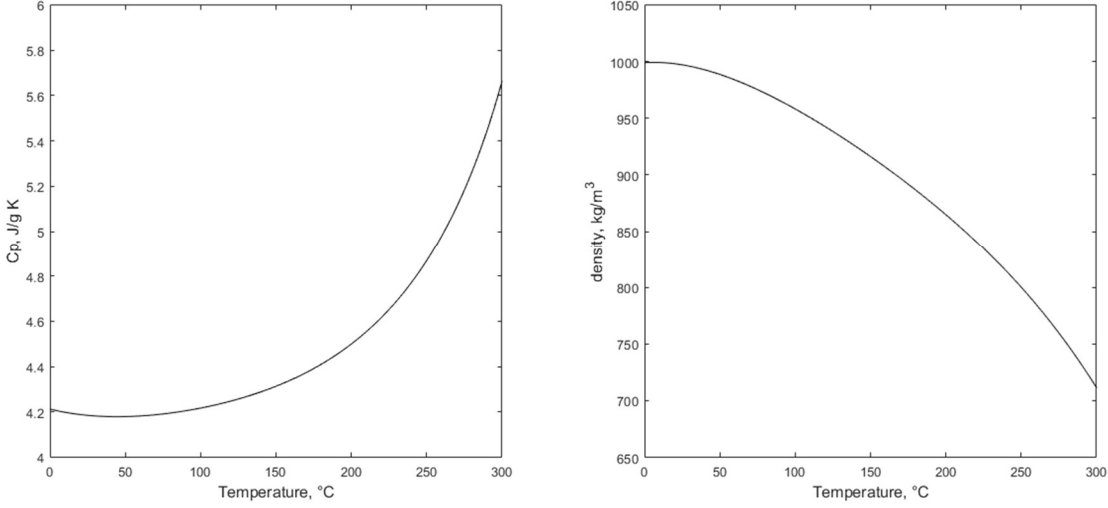|	**A0**	**A1**	**A2**	**A3**	**A4**	**A5**
Water	-13.418392	0.6884103	$-2.44970115\cdot10^{-3}$	$3.7060667\cdot10^{-6}$	$-2.11062995\cdot10^{-9}$	$-1.12273895\cdot10^{-13}$

Figure S1 – Temperature dependency of density and specific heat capacity of pure water (calculated from Gmehling, Kleiber et al. (2019)).

Temperature dependency of dissociation constants

Dissociation constants are temperature dependent, and these dependencies were taken from Fisher and Barnes (1972):

$$\ln(K_w) = \frac{-13445.9}{T} - 22.4773 \cdot \ln(T) + 140.932 \tag{2}$$

$$RT\ln(K_{a,HAc}) = \Delta S_{e,r}^0 \cdot \left[T_r - T - 218 \cdot \left(1 - \exp\left[\exp(-12.741 + 0.01875 \cdot T) - 7.48 \cdot 10^{-4} + \frac{(T-T_r)}{219}\right]\right)\right] - \Delta H_r^0 + T \cdot \Delta S_r^0 + T \cdot a \cdot \left[\ln\left(\frac{T}{T_r}\right) - 1 + \frac{T_r}{T}\right] + \frac{b}{2} \cdot (T - T_r)^2 \tag{3}$$

The parameters used in this expression are reproduced in Table 1. A graphical representation of this temperature dependency is shown in Figure S2.

Table 1. Parameters used to calculate the temperature dependency of the equilibrium constant for acetic acid dissociation in water (Fisher and Barnes (1972)).

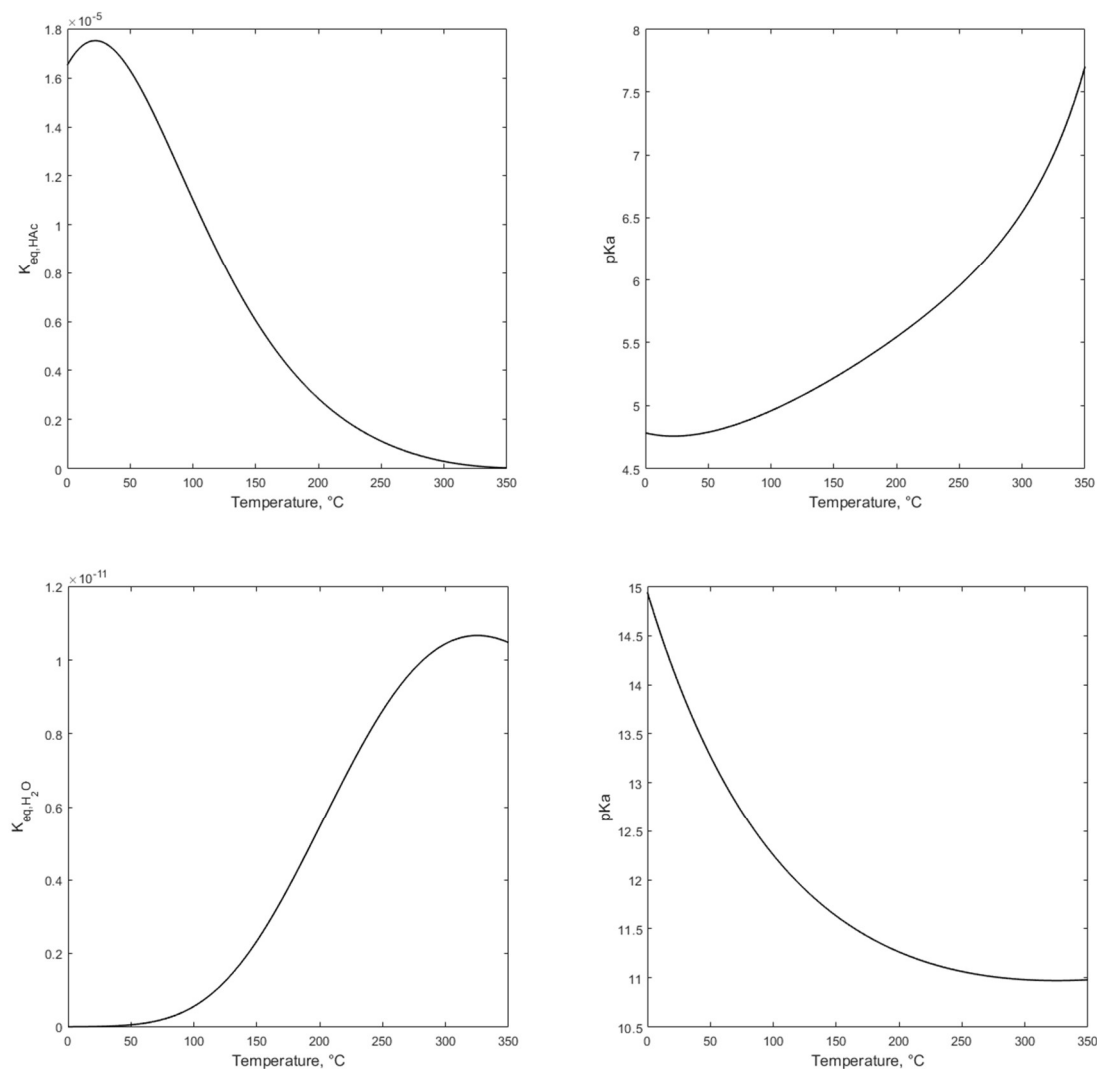| Parameter	Value	Units
$\Delta S_{e,r}^0$	-7.42856	cal/(mol K)
ΔS_r^0	-22.1280	cal/(mol K)
ΔH_r^0	-108.273	cal/mol
Tr	298.15	K
a	-59.9424	-
b	0.112254	-

Figure S2 – Temperature dependency of acetic acid and water dissociation reactions.

Initial concentration of acetyl groups in biomass

The initial concentration of acetyl groups $C_{RAc,o}$ was determined using the molar mass of acetyl groups and the mass fraction water/poplar wood. Therefore, the composition of the selected biomass was required, represented in Table S2.

Table S2 – Composition of poplar biomass. Values expressed in mass percentage, on dry basis (g/ 100 g DM).

	This work	Literature*
Glucan	41.34	42.73
Xylan	18.22	16.20
Acetyl group	4.25	4.25
Lignin	Not determined	26.14

The rest of the calculation is described as follow:

$$M_{Acetyl} = 43.045 \; \frac{g}{mol} \qquad\qquad x_{water}^{wood} = 0.108 \; \frac{kg \; water}{kg \; wood}$$

$$Poplar \; Biomass = 0.0425 \; \frac{kg \; acetyl \; groups}{kg \; dry \; wood}$$

$$Acetyl \; content = \frac{0.0425 \cdot 1000}{43.045} = 0.9873 \frac{mol}{kg \; dry \; wood} = 0.8807 \frac{mol}{kg \; wood}$$

The reaction mixture has a 1:9 biomass/water mass ratio. Therefore, using the density of pure water at room temperature, the initial concentration of acetyl groups $C_{OAC,o}$ is calculated as:

$$C_{RAc,0} = 0.8807 \frac{mol}{kg \; wood} \times 0.100 \frac{kg \; wood}{kg \; reaction \; mixture} \times 1000 \frac{kg \; reaction \; mixture}{m^3 \; reaction \; mixture}$$

$$= \mathbf{87.7} \; \frac{\boldsymbol{mol}}{\boldsymbol{m^3}}$$

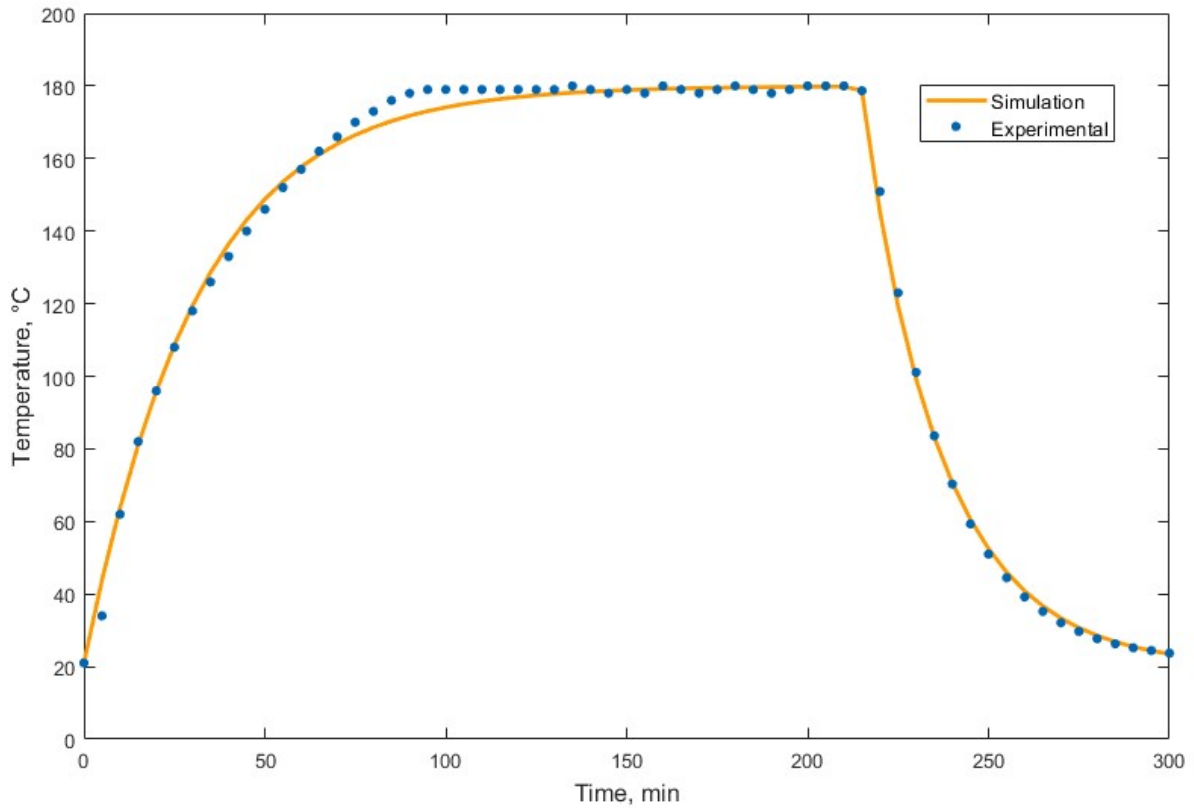## Alternative temperature profile fitting

Figure S3 – Temperature profile from experimental and simulated LHW pretreatment process of poplar at 180 °C for 120 min, using expression in equation S7.

References

Fisher, J. R. and H. L. Barnes (1972). "Ion-product constant of water to 350. deg." The Journal of Physical Chemistry **76**(1): 90-99.

Gmehling, J., M. Kleiber, B. Kolbe and J. Rarey (2019). Chemical thermodynamics for process simulation, John Wiley & Sons.

Mante, O. D., S. P. Babu and T. E. Amidon (2014). "A comprehensive study on relating cell-wall components of lignocellulosic biomass to oxygenated species formed during pyrolysis." Journal of Analytical and Applied Pyrolysis **108**: 56-67.