Supporting Information

Optimization of Cellulose Nanocrystal Length and Surface Charge Density through Phosphoric Acid Hydrolysis

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Size of Cotton Pulp Prior to CNC Extraction

a)

b)

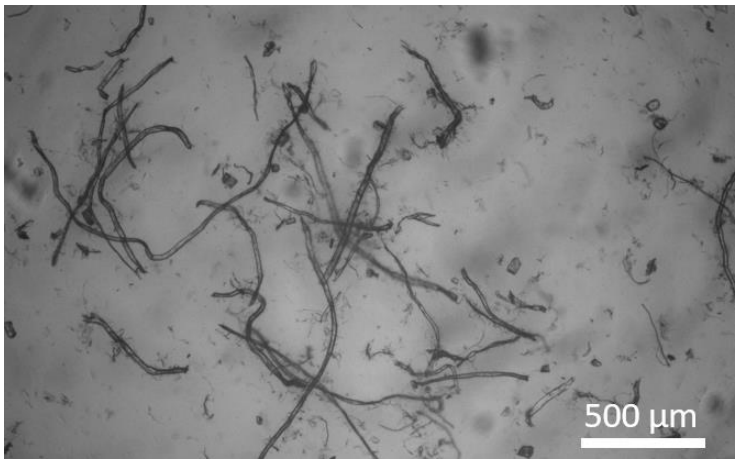
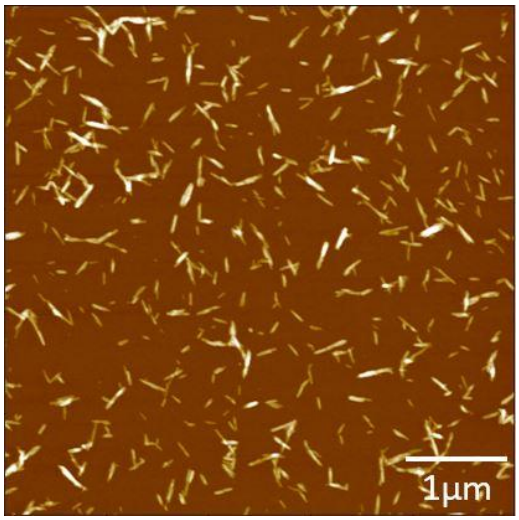
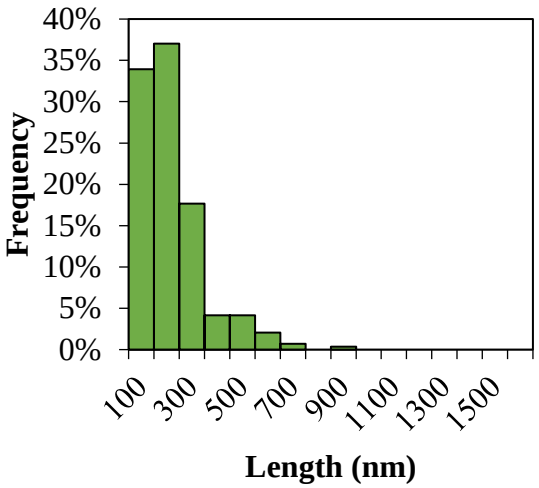


Figure S1: a) Pulp made by blending 2g of Whatman ashless filter aid with 100 mL Milli-Q water and b) fibers in pulp, which have macroscale diameters (4x magnification).

Justification for Choice of Median CNC Length from AFM Analysis:



Average particle length by manually measuring individual S-CNCs: 127±55 nm



Median S-CNC particle length determined using Asylum Research Igor Pro software particle analysis tool: 127 nm

Figure S2: Comparison of CNC length obtained by manually selecting and measuring length vs. using the automated particle sizing software (for sulfuric acid hydrolysed CNCs).

Table S1: Phosphate content, dimensions and calculated surface charge density (assuming CNCs are cylindrical in shape with a density of 1.6 g/mL) of CNCs hydrolysed with phosphoric acid at varying hydrolysis conditions.

Sample	x_1 (min)	x_2 (°C)	x_3 (wt%)	Phosphate Content (mmol /kg CNC)	Median Particle Length (nm)	Median Particle Height (nm)	Surface Charge Density (e/nm^2)
80-100-70	80	100	70	15±2	475	7.5	0.027±0.004
80-120-70	80	120	70	31±1	284	6.7	0.049±0.002
80-100-75	80	100	75	8±1	312	7.1	0.014±0.002
80-120-75	80	120	75	13±3	238	4.9	0.015±0.004
110-100-72.5	110	100	72.5	13±1	325	7.2	0.022±0.002
120-100-70	120	100	70	10±1	391	6.5	0.016±0.002
120-120-70	120	120	70	44±2	268	7.2	0.075±0.003
120-100-75	120	100	75	18±11	315	6.7	0.03±0.02

X-Ray Diffractometry Profile of 120-120-75

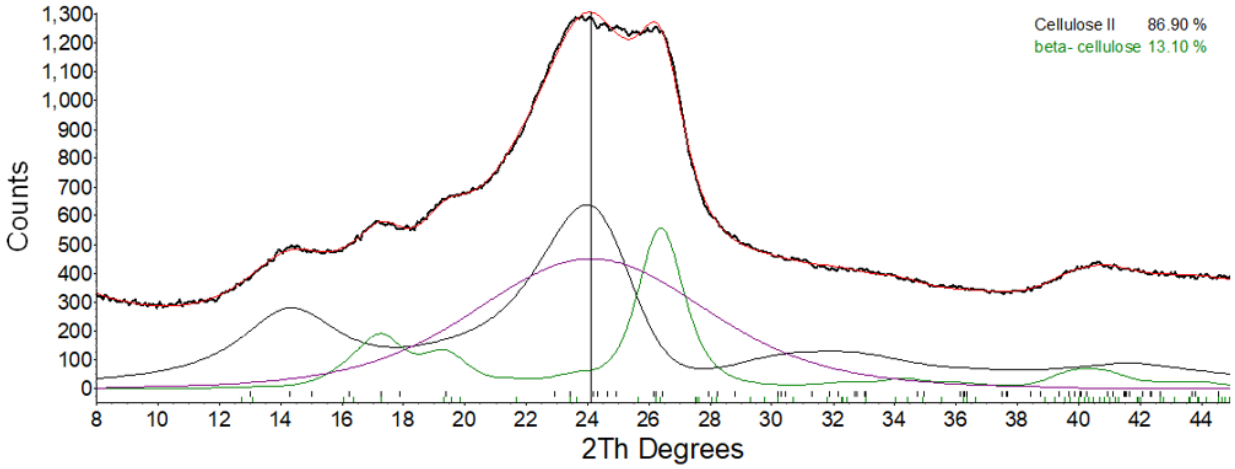


Figure S3: X-Ray Diffractometry profile for ample 120-120-75

Particle Size Distributions for Phosphoric Acid Hydrolysed CNCs Measured by AFM:

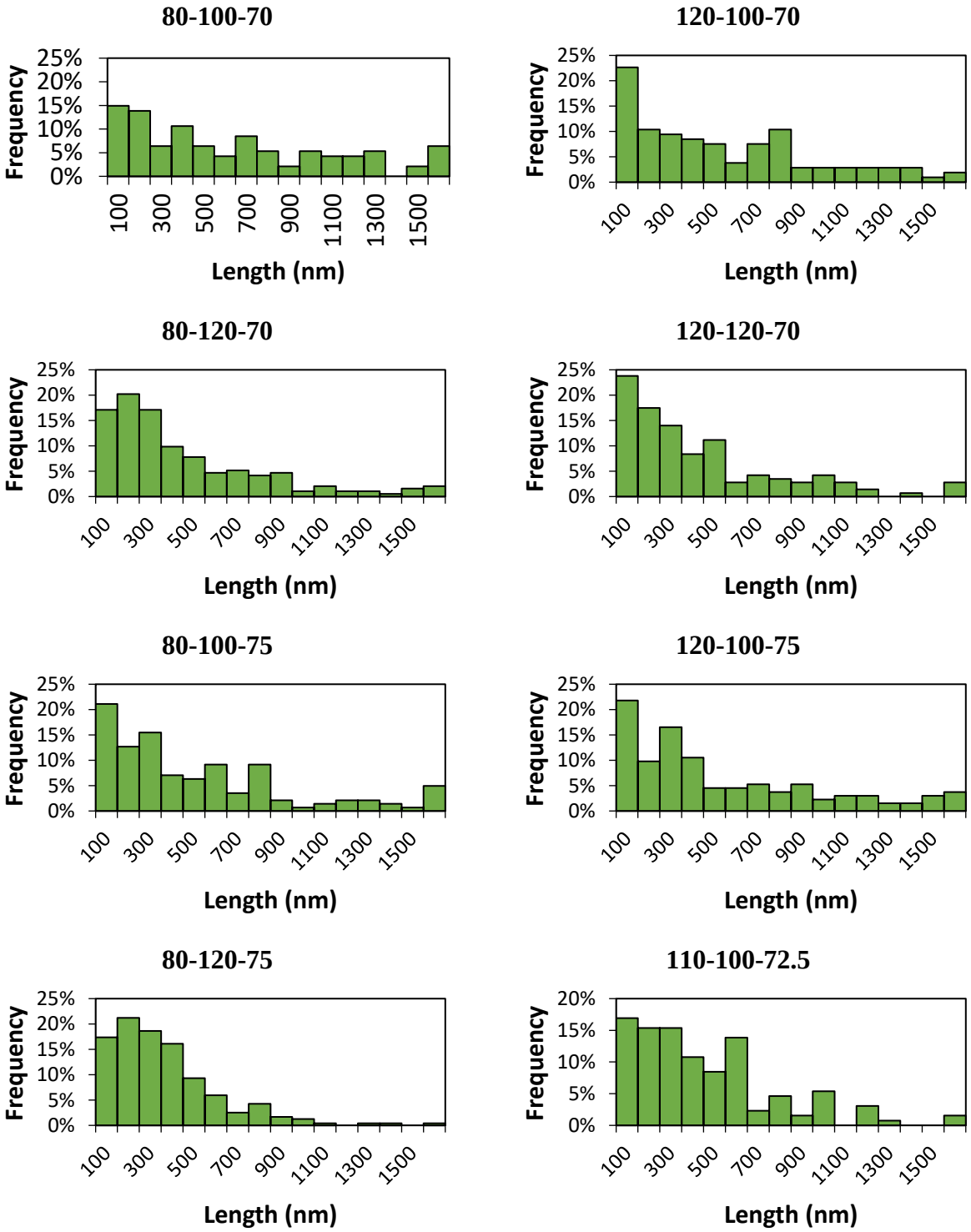


Figure S4: Particle length distributions for CNCs hydrolysed with phosphoric acids with varying hydrolysis times, temperatures and acid concentrations (labelled above each histogram), measured using the automated Asylum Research Igor Pro sizing software on >100 particles from multiple AFM height images (similar to those shown in Figure 1).

Phophate Content Model Output:

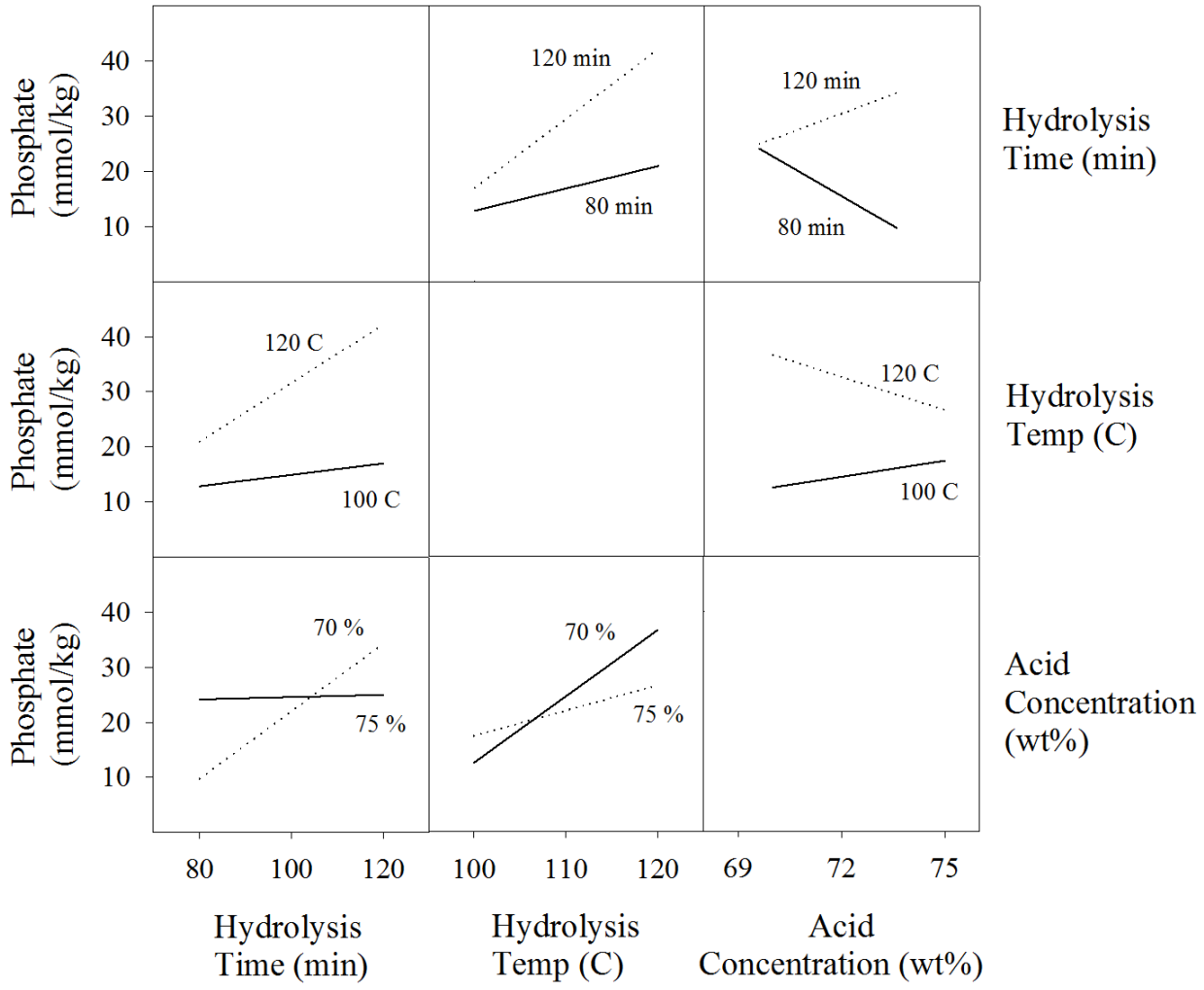


Figure S5: Factor interaction profiles describing the interactions of two hydrolysis parameters and their combined effects on CNC phosphate content.

Effect of pH on CNC Zeta Potential:

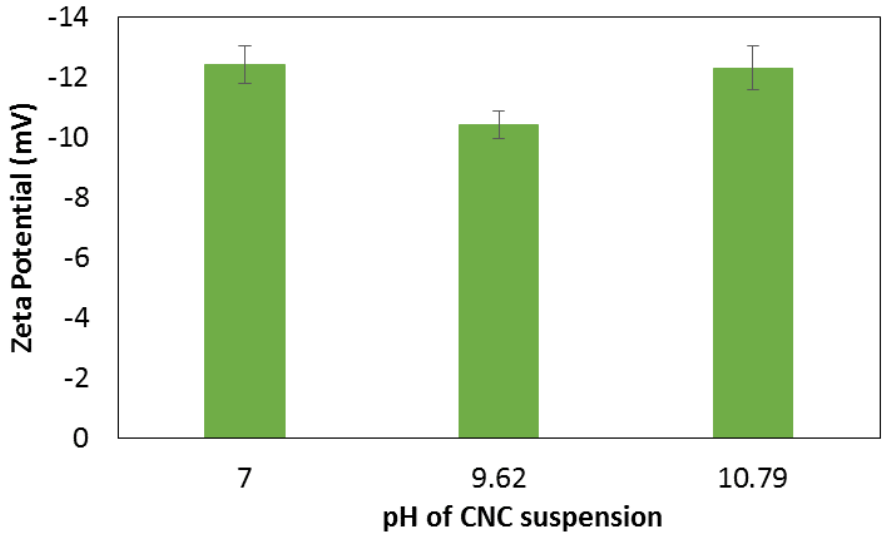


Figure S6: Zeta potential of 120-120-70 CNCs at pH above and below the second pK_a of phosphoric acid (7.2).

Zeta Potential Model Output:

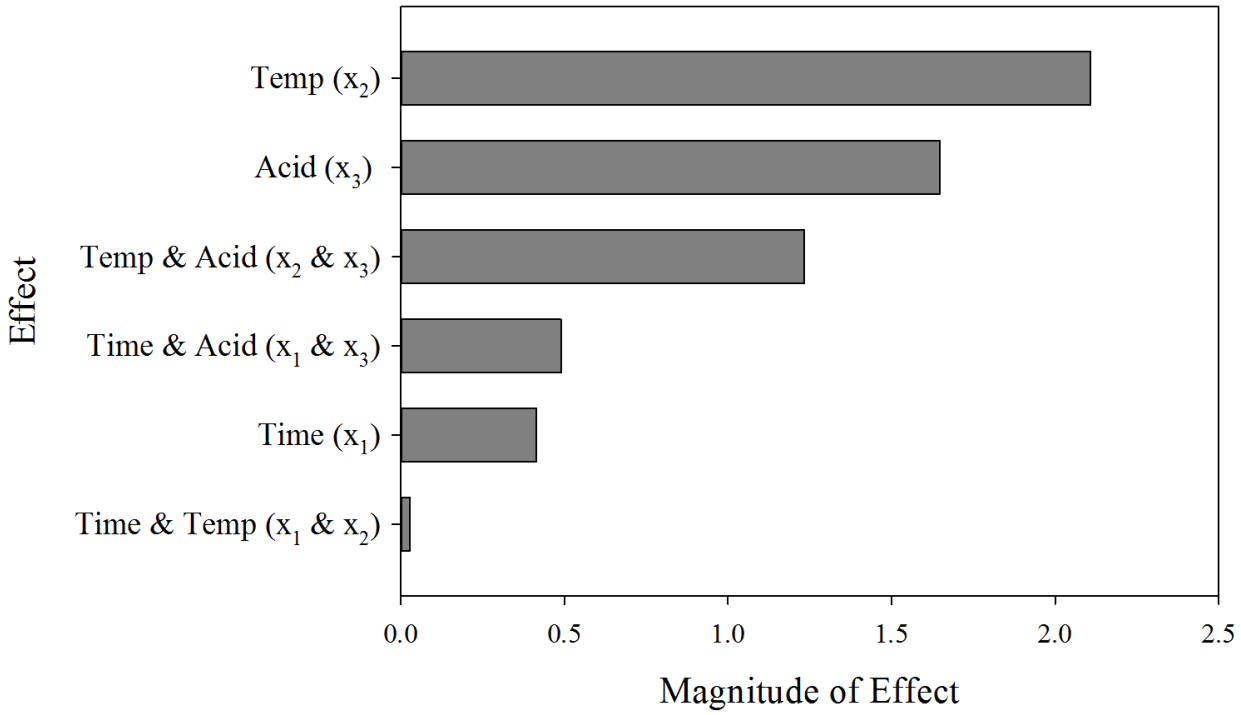


Figure S7: Coefficients for the parameters in a model predicting CNC zeta potential. Dark grey bars indicate negative coefficients.

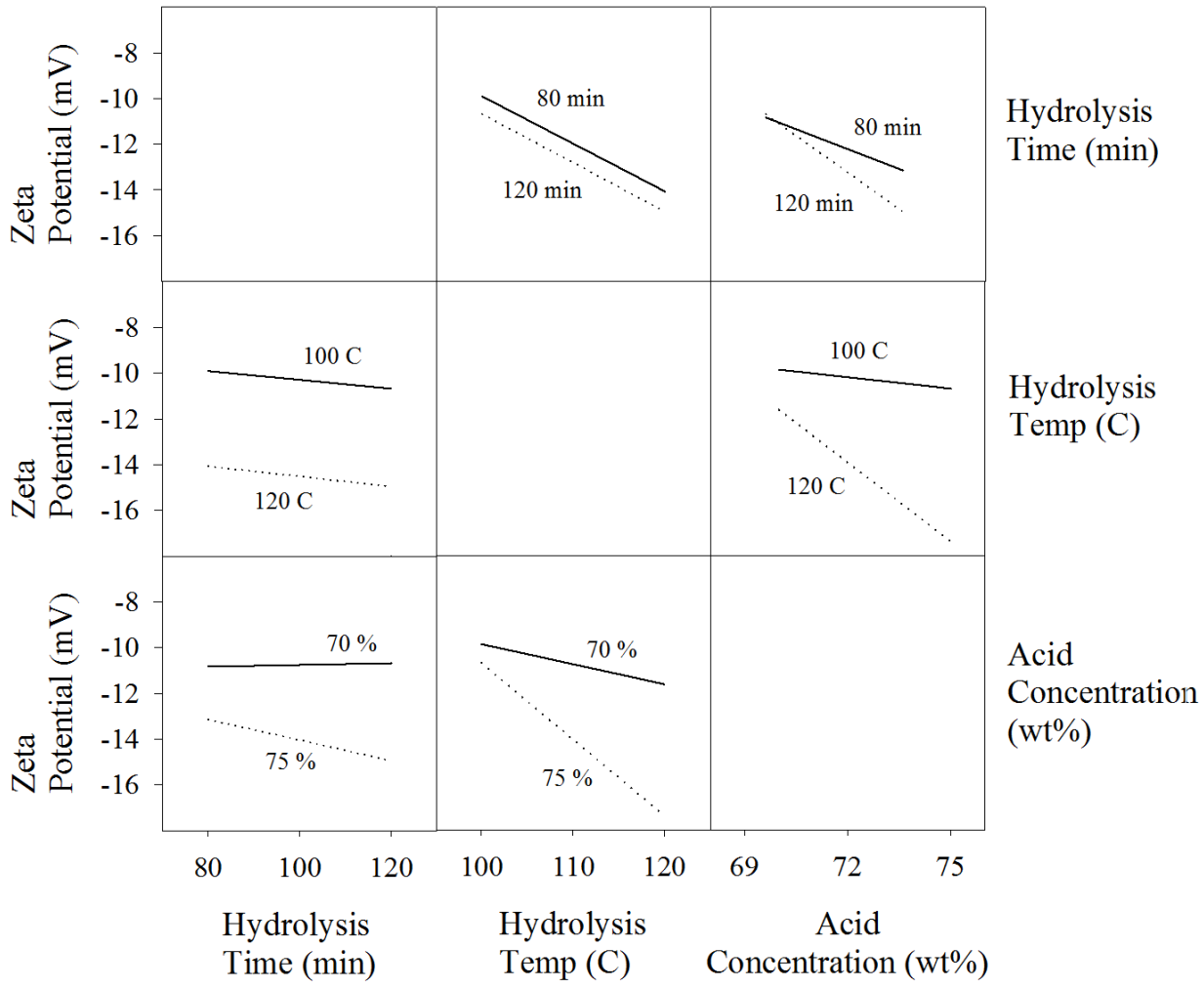


Figure S8: Factor interaction profiles describing the interactions of two hydrolysis parameters and their combined effects on CNC zeta potential.