Growth Kinetics of Humins Studied via X-Ray Scattering

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Supplementary Information

Basic Principles of Small Angle X-Ray Scattering (SAXS)

When an X-ray beam shines on a sample, some X-rays are reflected, most transmit through the sample without changing direction, while some are scattered by the sample. There are two types of scattering: elastic scattering occurs when the kinetic energy of the X-ray is conserved before and after being scattered, and inelastic scattering occurs when the kinetic energy of the X-ray changes. The SAXS instrument works with elastic scattering only. The scattering vector, q, is defined as:

$$q = \vec{k}_s - \vec{k}_i$$

where $\vec{k}_s$ is the wave vector describing the scattered direction, and $\vec{k}_i$ is the incident wave vector. The scattering angle, θ, is the angle by which the trajectory of the incident X-ray beam is changed. In elastic scattering, the wavelength of the X-ray, λ, the distance between lattice planes, d, and the angle θ are related by Bragg's Law:

$$\lambda = 2d sin\theta$$

q is in reciprocal space related to the d in the normal space through the relationship: $$q = \frac{2\pi}{d}$$

This is an important relationship that indicates that when we refer to large length scales, we observe them at low q regimes; conversely, we observe small length scales at high q regimes. Combining the above equations, we obtain:

$$q = \frac{4\pi sin\theta}{\lambda}$$

The elastic scattering intensity for a monodisperse system is given by:[1]

$$I(q) = \frac{N}{V}V_p^2(\Delta\rho)^2P(q)S(q)$$

where N is the number of particles, V is the total volume of the system, $\Delta\rho$ is the scattered intensity difference between the suspended particles and the solvent, P(q) is the form factor that includes information on the shape of the particles.

For a spherical particle, the expression of P(q) is given by:[1]

$$P(q) = \frac{3(\sin(qR) - qR\cos(qR))}{(qR)^3}$$

S(q) is the structure factor that accounts for the interaction between particles in concentrated suspensions. When analyzing our dilute system, S(q) was approximated to be equal to 1. [2]

The volume fraction of particles is defined by the total volume of particles over the total solution volume:

$$\varphi = \frac{NV_p}{V}$$

The number of particles per unit volume (N/V) can be calculated from the fitted φ and V_p values.

Incorporating the volume fraction into the expression for the scattered intensity I(q) above, I(q) is rewritten as:

$$I(q) = \varphi V_p(\Delta\rho)^2P(q)S(q)$$

When the system is polydisperse, I(q) becomes:[1]

$$I(q) = \frac{N}{V}V_p^2(\Delta\rho)^2\int_{-\infty}^{\infty} f(r)[r^2j_1(qr)]^2dr$$

where f(r) is the distribution function of sizes, and j_1 is the Bessel function.

For spheroids, the radius of gyration R_g, which is obtained from fitting the I(q) vs. q data, is related to radius of the particle (R) by:[1]

$$R_g = \sqrt{\frac{3}{5}}R$$

The polydispersity PD was calculated as follows:

$$PD = \frac{Standard\ deviation}{Mean\ size}$$

The Porod analysis is used for obtaining the shape of particles:

$$I(q) \sim Sq^{-\alpha} = Sq^{-(6-d)}$$

where α is the Porod (or power law slope) of the particle, and d, which equals 6-α, is the fractal dimension of the particle. For rods, α equals 1. For mass fractals, α is between 2 and 3. For fractal-like shapes with rough surfaces, α is between 3 and 4. For a smooth sphere, α equals 4.
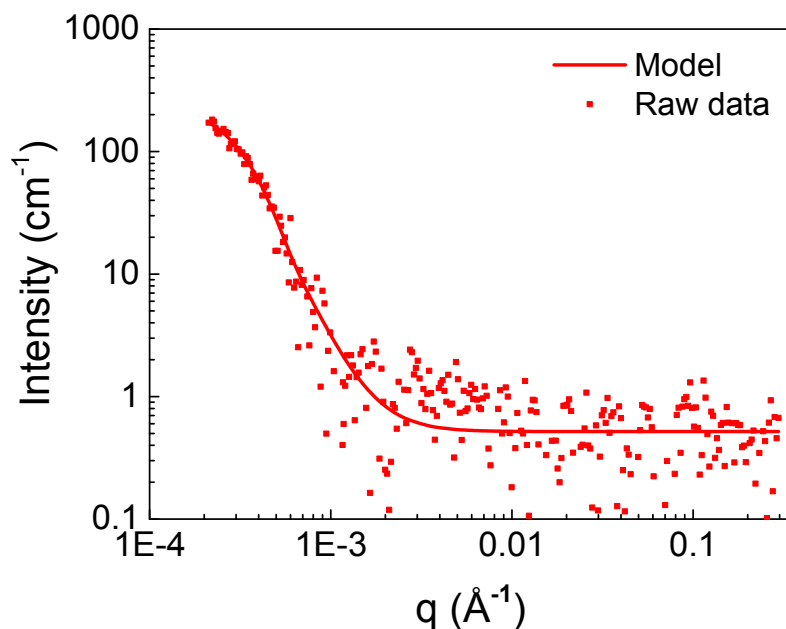
Supplemental Experimental Data

Figure S1. Raw and fitted data in a typical experiment. Data shown here were taken from a 10 wt% pH=0 fructose solution heated at 80 °C at 80 min of reaction time. A Gaussian size distribution model is a good fit for the data.
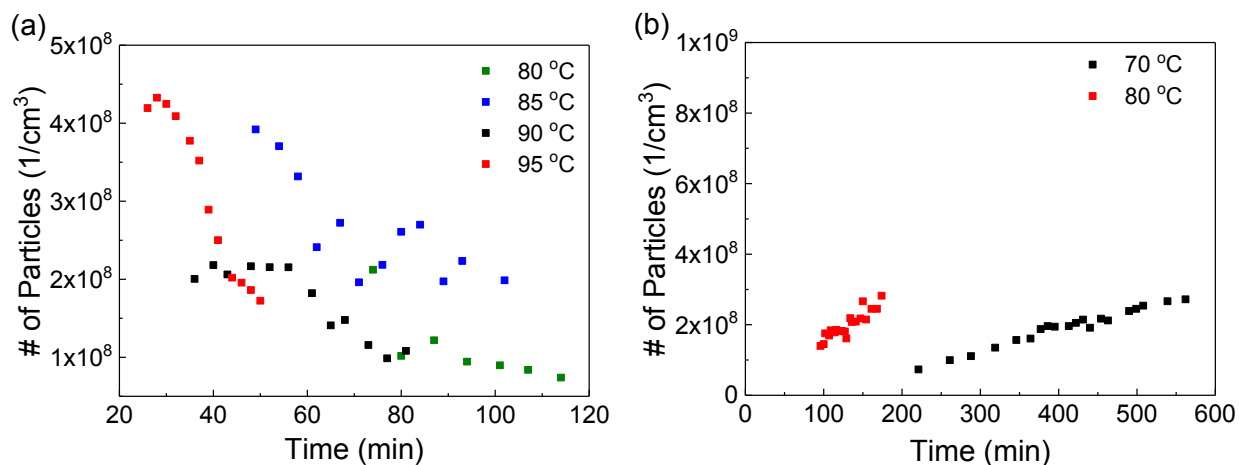

Figure S2. Number of particles per volume of solution as a function of time for (a) 10 wt % initial fructose solution at various temperatures indicated and (b) 50 wt % initial fructose at solution 70 and 80 °C. Reaction pH=0.
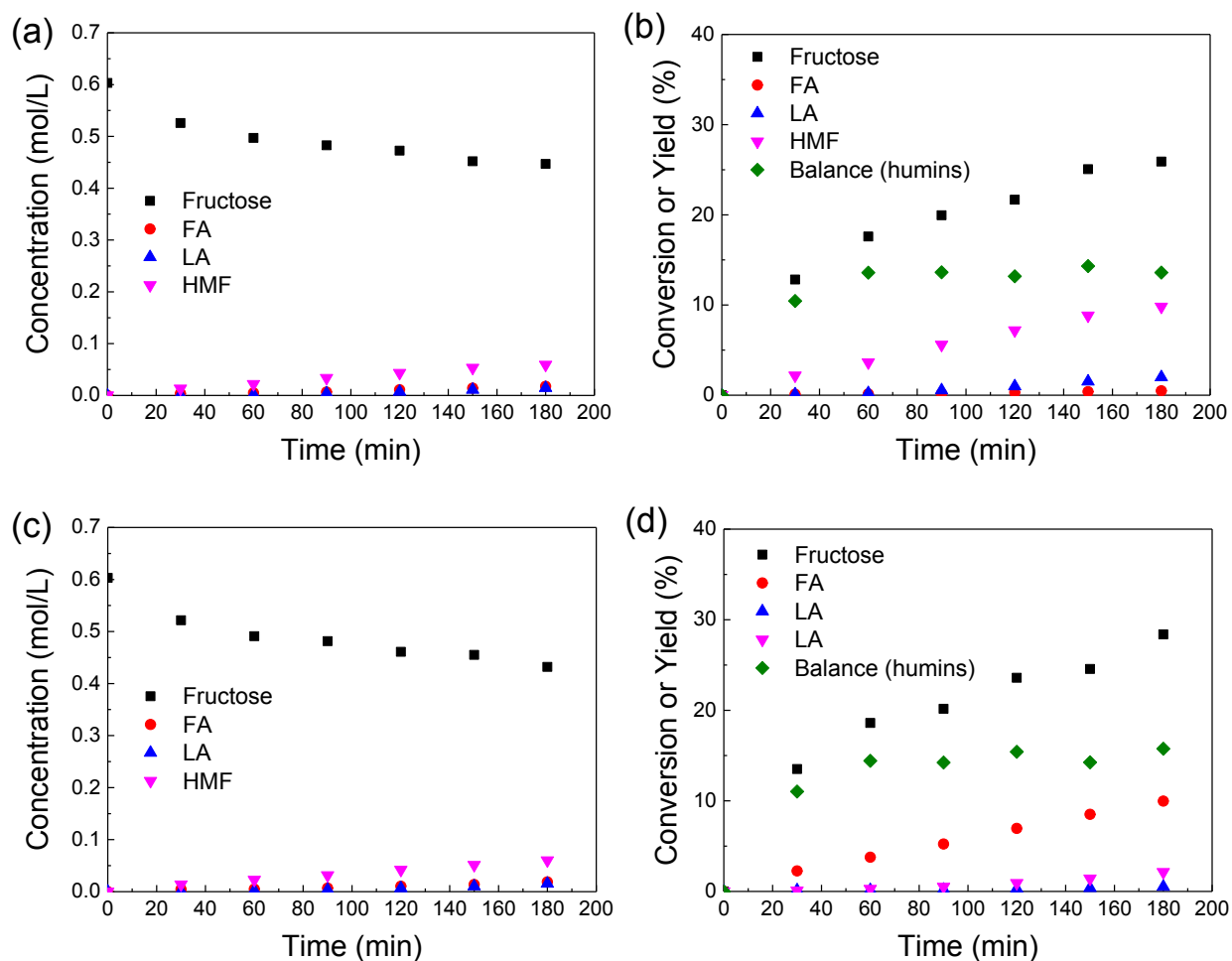
Figure S3. (a) Fructose and FA, LA, HMF concentrations and (b) calculated fructose conversion and product yields as functions of time without stirring. (c) Fructose and FA, LA, HMF concentrations and (d) calculated fructose conversion and product yields as functions of time with stirring at 700 rpm. Reaction conditions: 10 wt% fructose, pH=0, 80 °C.
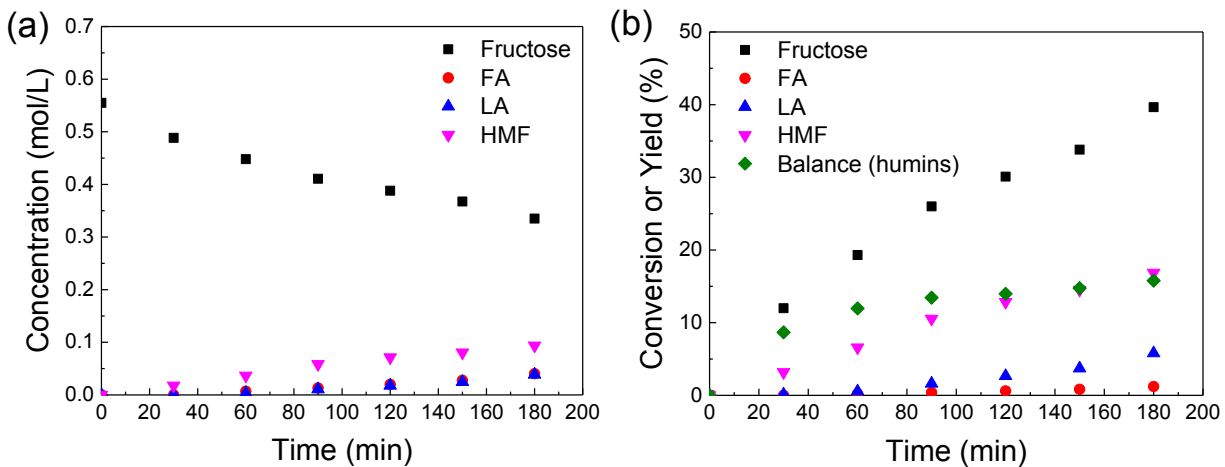
Figure S4. (a) Fructose and FA, LA, HMF concentrations and (b) calculated fructose conversion and product yields as functions of time. Reaction conditions: 10 wt% fructose, pH=0, 85 °C, no stirring.
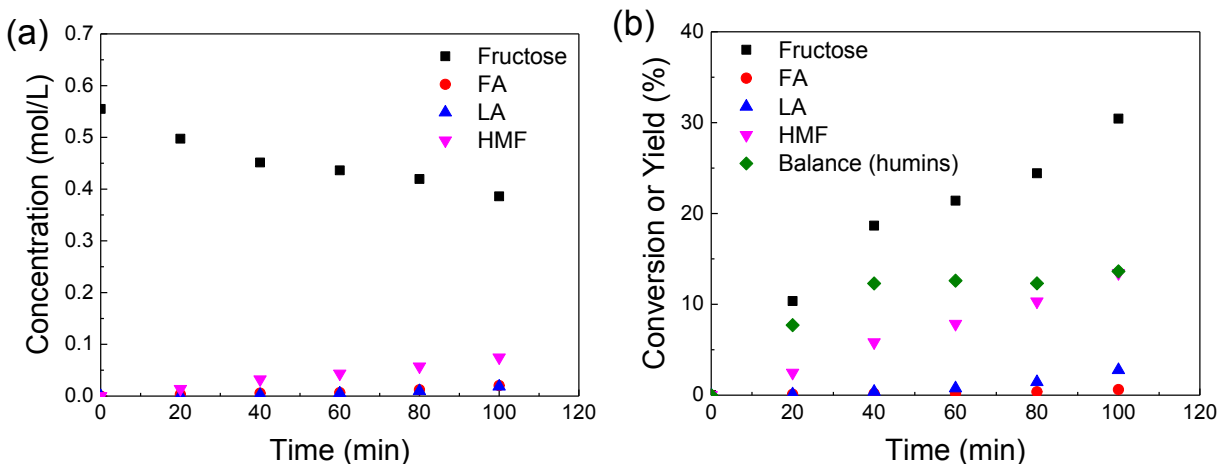

Figure S5. (a) Fructose and FA, LA, HMF concentrations and (b) calculated fructose conversion and product yields as functions of time. Reaction conditions: 10 wt% fructose, pH=0, 90 °C, no stirring.
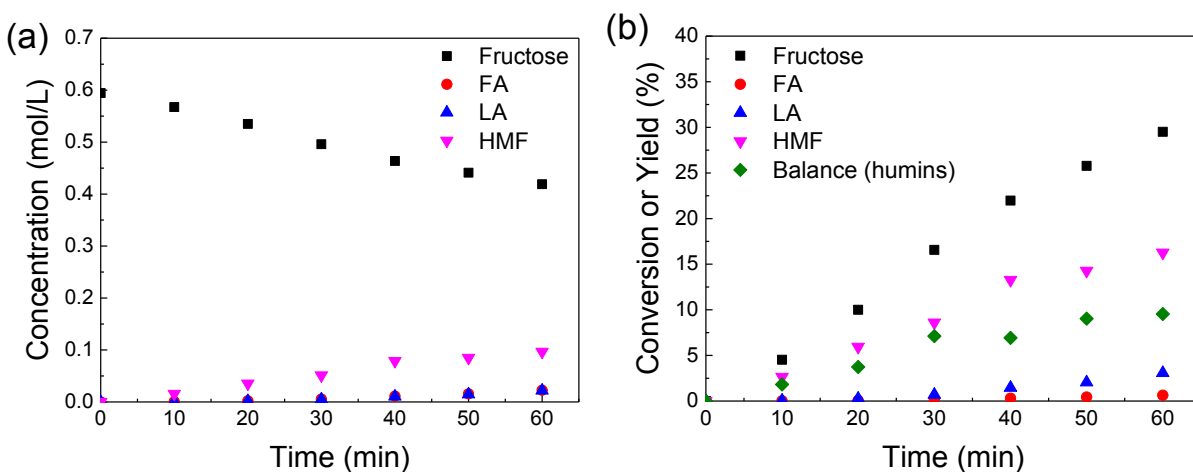

Figure S6. (a) Fructose and FA, LA, HMF concentrations and (b) calculated fructose conversion and product yields as functions of time. Reaction conditions: 10 wt% fructose, pH=0, 95 °C, no stirring.
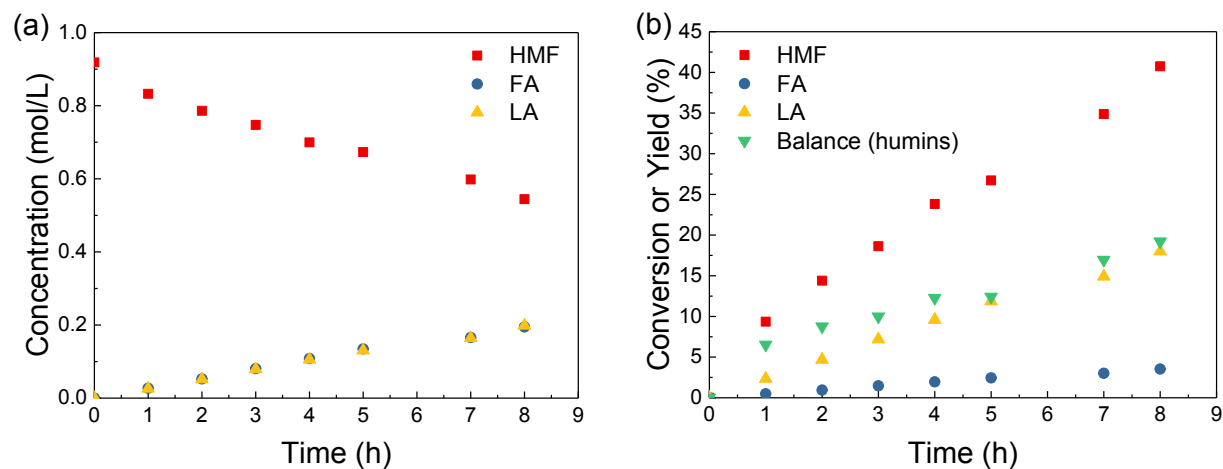
Figure S7. (a) HMF, FA, and LA concentrations and (b) calculated HMF conversion and product yields as a function of time. Reaction conditions: 10 wt% HMF, pH=0, 70 °C, no stirring.

References

1.   D. S. Sivia, *Elementary Scattering Theory: for X-ray and Neutron Users*, Oxford University Press, 2011.
2.   B. Hammouda, "the SANS Toolbox". NIST Center for Neutron Research, 2008. https://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf