SUPPORTING INFORMATION

for

Modeling the chemical conversion of organic compounds in sodium borohydride reduction reactions

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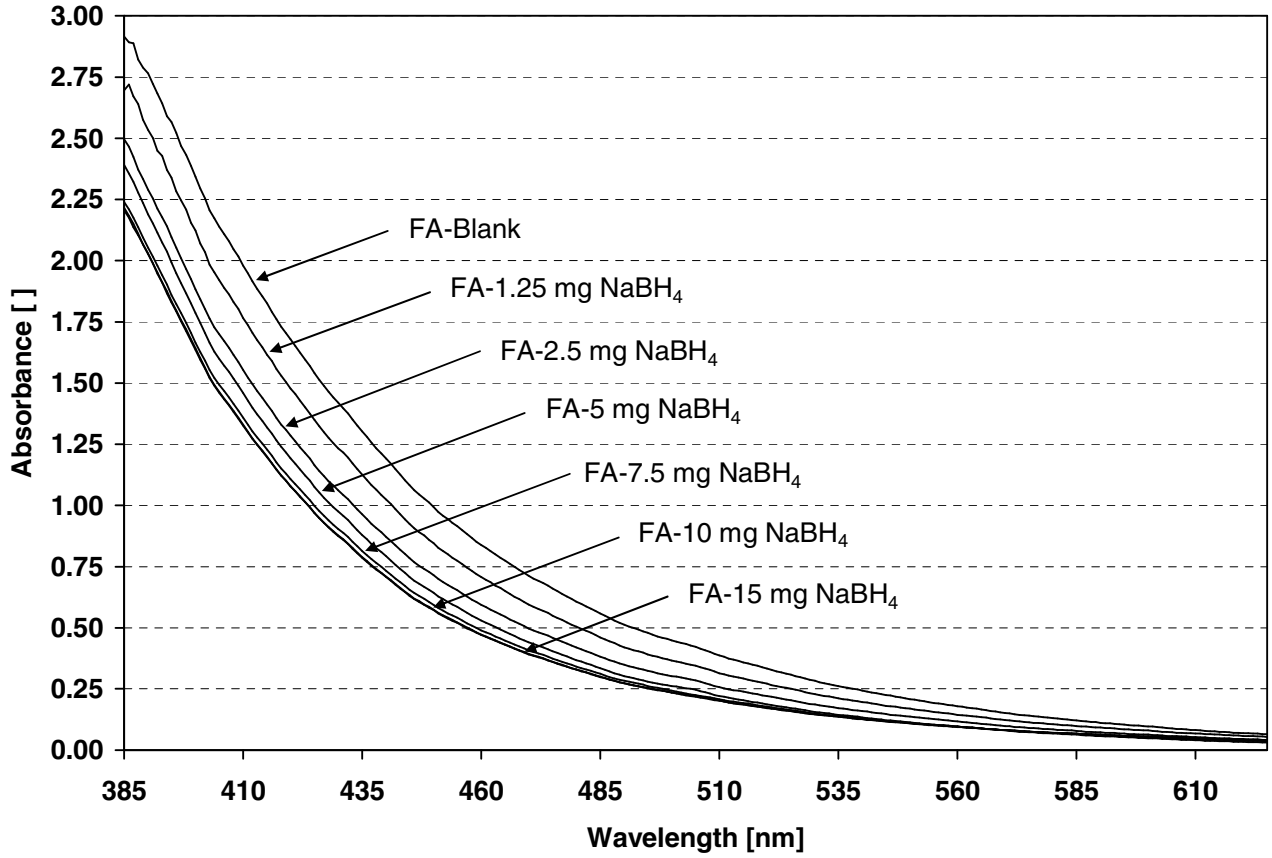

Figure S1. Spectral data of fulvic acid solution absorbance after complete reduction with various amounts of sodium borohydride in 10 ml reaction volume. The wavelength of 465 nm was selected for the comparison of $NaBH_4$ reduction efficiencies in the model development.

Mathematical derivations for chemical efficiency model #2: variable reactive group concentration

Note that all model parameters of chemical model #2 are defined in the same manner as for chemical model #1, unless stated otherwise in the following (see manuscript for details).

In chemical model #2, we allowed for the additional fitting of the FA-reactive group concentration using the following equation:

$$\left[FA\right]_{Tot} = \alpha_0 \left[FA-Ket\right]_{Tot} \quad (1)$$

$\left[FA\right]_{Tot}$ .....total concentration of FA-reactive groups [mol L^{-1}]

$\left[FA-Ket\right]_{Tot}$ .....total concentration of FA-ketone groups [mol L^{-1}]

α_0 .....coefficient and fitting parameter [ ]

This fitting can lead to three possible results for α_0. First, if α_0 = 1, the concentration of FA-reactive groups is equal to the total concentration of FA-ketones. Second, if $\alpha_0 < 1$, the FA-reactive group concentration is less, which implies that not all FA-ketone groups are accessible during the reduction with $NaBH_4$. Third, with $\alpha_0 > 1$, the concentration of FA-reactive groups is greater, and additional FA-functional groups may indeed be relevant for the reaction.

Using a slightly modified nomenclature, chemical model #2 describes the simplified reduction reaction of FA-reactive groups and the correlated mass action expression as

$$FA_{Ox} + NaBH_{4,\mathrm{Red}} \leftrightarrow FA_{\mathrm{Red}} + NaBH_{4,Ox} \quad (2)$$

and

$$K = \frac{\left[FA_{\mathrm{Red}}\right]\left[NaBH_{4,Ox}\right]}{\left[FA_{Ox}\right]\left[NaBH_{4,\mathrm{Red}}\right]} \quad (3)$$

with

$[FA_{Ox}]$, $[FA_{Red}]$ ..... concentration of oxidized/reduced FA-reactive groups [mol L^{-1}]

$[NaBH_{4,Ox}]$, $[NaBH_{4,Red}]$ ..... concentration of oxidized/reduced form of $NaBH_4$ [mol L^{-1}]

Further, the mass balance equation for FA-reactive groups is now defined as

$$[FA]_{Tot} = \alpha_0 [FA - Ket]_{Tot} = [FA_{Ox}] + [FA_{Red}] \tag{4}$$

with

$$[FA_{Ox}] = \alpha_0 [FA - Ket]_{Tot} - [FA_{Red}] \tag{5}$$

and the chemical conversion of reducible FA reactive groups (x_{FA}) is expressed in terms of

$$x_{FA} = \frac{[FA_{Red}]}{[FA]_{Tot}} = \frac{[FA_{Red}]}{\alpha_0 [FA - Ket]_{Tot}} \tag{6}$$

Then we follow the same step-wise mathematical derivation as for chemical model #1, and include the simplifying parameters β_0, β_1 and γ_1 defined in the manuscript, as well as

$$\alpha = \frac{1}{\alpha_0} \tag{7}$$

This results in the following expression for the light absorbance (*ABS*), which is used to fit the absorbance curve for chemical model #2:

$$ABS = \beta_0 - \beta_1 \left\{ \alpha x + 1 - \sqrt{(\alpha x + 1)^2 - \alpha \gamma_1 x} \right\} \tag{8}$$