Supplemental material to:

The predominant molecular state of bound enzyme determines the strength and type of product inhibition in the hydrolysis of recalcitrant polysaccharides by processive enzymes.

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Equation S1 – Steady-state distribution of enzyme between different complexes for Scheme in Figure 6A

Definition of rate constants is given in Figure 6A of the main article.

First order rate constants are in units of s^{-1}. Second order rate constants k1 and k2 are in units of (ml (mg^{-1} s^{-1})) whereas k3 and k4 are in units of (M^{-1} s^{-1}).

[*S*] – concentration of substrate (mg ml^{-1})

[*I*] – concentration of inhibitor (M)

[E_0] – total concentration of enzyme

$$E = k_{-1}k_{-3}k_{-4}k_{-5} + k_{-1}k_{-3}k_{-4}k_6 + k_{-1}k_{-3}k_{-5}k_{-2} + k_{-1}k_{-3}k_{-2}k_6 + k_{-1}k_{-4}k_{-5}k_2[S] + k_{-1}k_{-4}k_6k_2[S] + k_{-3}k_{-2}k_{-5}k_4[I] + \\ + k_{-3}k_{-2}k_6k_4[I] + k_{-3}k_{-2}k_6k_5$$

$$E*S = k_{-3}k_{-4}k_{-5}k_1[S] + k_6k_{-4}k_{-3}k_1[S] + k_{-2}k_{-5}k_{-3}k_1[S] + k_6k_{-3}k_{-2}k_1[S] + k_1[S]k_{-4}k_{-5}k_2[S] + k_1[S]k_{-4}k_6k_2[S] + \\ + k_{-4}k_{-5}k_2[S]k_3[I] + k_{-4}k_2[S]k_6k_3[I]$$

$$EI = k_{-5}k_{-1}k_{-4}k_3[I] + k_6k_{-1}k_{-4}k_3[I] + k_{-5}k_{-2}k_{-1}k_3[I] + k_6k_{-2}k_{-1}k_3[I] + k_{-2}k_4[I]k_1[S]k_{-5} + k_{-2}k_4[I]k_6k_1[S] + \\ + k_{-2}k_6k_5k_1[S] + k_3[I]k_{-2}k_{-5}k_4[I] + k_3[I]k_{-2}k_6k_4[I] + k_5k_{-2}k_6k_3[I]$$

$$E*SI = k_4[I]k_1[S]k_{-5}k_{-3} + k_4[I]k_6k_1[S]k_{-3} + k_2[S]k_3[I]k_{-1}k_{-5} + k_6k_5k_1[S]k_{-3} + k_2[S]k_6k_3[I]k_{-1} + \\ + k_4[I]k_2[S]k_1[S]k_{-5} + k_4[I]k_2[S]k_6k_1[S] + k_2[S]k_6k_5k_1[S] + k_4[I]k_2[S]k_{-5}k_3[I] + k_4[I]k_2[S]k_6k_3[I] + \\ + k_2[S]k_6k_3[I]k_5$$

$$ES = k_5k_1[S]k_{-4}k_{-3} + k_5k_1[S]k_{-3}k_{-2} + k_5k_1[S]k_{-4}k_2[S] + k_5k_{-4}k_2[S]k_3[I]$$

$$E_0 = E + E*S + EI + E*SI + ES$$

Fractions of enzyme in different forms:

F(E) = E/E_0;

F(E*S) = $E*S/E_0$;

F(EI) = EI/E_0;

F(E*SI) = $E*SI/E_0$;

F(ES) = ES/E_0;

Equation S2 – Steady-state distribution of enzyme between different complexes for Scheme in Figure 6B

Definition of rate constants is given in Figure 6B of the main article.

First order rate constants are in units of s^{-1}. Second order rate constants k1, k2, and k8 are in units of (ml (mg^{-1} s^{-1})) whereas k3 and k4 are in units of (M^{-1} s^{-1}).

[S] – concentration of substrate (mg ml^{-1})

[I] – concentration of inhibitor (M)

[E_0] – total concentration of enzyme

$$E = k_{-1}k_{-3}k_{-8}k_{-4}k_{-5} + k_{-1}k_{-3}k_{-8}k_{-4}k_6 + k_{-1}k_{-3}k_{-8}k_{-5}k_{-2} + k_{-1}k_{-3}k_{-8}k_{-2}k_6 + k_{-1}k_{-8}k_{-4}k_{-5}k_2[S] + k_{-1}k_{-8}k_{-4}k_2[S]k_6 +$$
$$+ k_{-3}k_{-8}k_7k_{-4}k_{-5} + k_{-3}k_{-8}k_{-2}k_4[I]k_{-5} + k_{-3}k_{-8}k_7k_{-4}k_6 + k_{-3}k_{-8}k_{-2}k_4[I]k_6 + k_{-3}k_{-8}k_{-2}k_7k_{-5} + k_{-3}k_{-8}k_{-2}k_6k_5 +$$
$$+ k_{-3}k_{-8}k_{-2}k_7k_6 + k_{-8}k_7k_{-4}k_{-5}k_2[S] + k_{-8}k_7k_{-4}k_2[S]k_6$$

$$E*S = k_1[S]k_{-4}k_{-5}k_{-3}k_{-8} + k_1[S]k_{-4}k_{-3}k_{-8}k_6 + k_1[S]k_{-5}k_{-3}k_{-8}k_{-2} + k_1[S]k_{-3}k_{-8}k_{-2}k_6 + k_1[S]k_{-4}k_{-5}k_{-8}k_2[S] +$$
$$+ k_1[S]k_{-4}k_{-8}k_2[S]k_6 + k_{-4}k_{-5}k_2[S]k_3[I]k_{-8} + k_{-4}k_2[S]k_6k_3[I]k_{-8}$$

$$EI = k_3[I]k_{-1}k_{-8}k_{-4}k_{-5} + k_3[I]k_{-1}k_{-8}k_{-4}k_6 + k_3[I]k_{-2}k_{-1}k_{-8}k_{-5} + k_3[I]k_{-2}k_{-1}k_{-8}k_6 + k_{-2}k_4[I]k_1[S]k_{-5}k_{-8} +$$
$$+ k_{-2}k_4[I]k_6k_1[S]k_{-8} + k_{-2}k_6k_5k_1[S]k_{-8} + k_3[I]k_{-8}k_7k_{-4}k_{-5} + k_3[I]k_{-2}k_{-8}k_4[I]k_{-5} + k_3[I]k_{-8}k_7k_{-4}k_6 +$$
$$+ k_3[I]k_{-2}k_{-8}k_4[I]k_6 + k_3[I]k_{-2}k_{-8}k_7k_{-5} + k_3[I]k_{-2}k_{-8}k_6k_5 + k_3[I]k_{-2}k_{-8}k_6k_7$$

$$E*SI = k_4[I]k_1[S]k_{-5}k_{-3}k_{-8} + k_4[I]k_6k_1[S]k_{-3}k_{-8} + k_2[S]k_3[I]k_{-1}k_{-8}k_{-5} + k_6k_5k_1[S]k_{-3}k_{-8} +$$
$$+ k_2[S]k_6k_3[I]k_{-1}k_{-8} + k_4[I]k_2[S]k_1[S]k_{-5}k_{-8} + k_4[I]k_2[S]k_6k_1[S]k_{-8} + k_2[S]k_6k_5k_1[S]k_{-8} +$$
$$+ k_4[I]k_2[S]k_{-5}k_3[I]k_{-8} + k_4[I]k_2[S]k_6k_3[I]k_{-8} + k_2[S]k_3[I]k_{-8}k_7k_{-5} + k_2[S]k_6k_3[I]k_5k_{-8} +$$
$$+ k_2[S]k_6k_3[I]k_{-8}k_7$$

$$ES = k_5k_1[S]k_{-4}k_{-3}k_{-8} + k_5k_1[S]k_{-3}k_{-8}k_{-2} + k_5k_1[S]k_{-4}k_{-8}k_2[S] + k_5k_{-4}k_2[S]k_3[I]k_{-8}$$

$$E*ST = k_8[S]k_{-1}k_{-3}k_{-4}k_{-5} + k_8[S]k_{-1}k_{-3}k_{-4}k_6 + k_8[S]k_{-1}k_{-3}k_{-5}k_{-2} + k_8[S]k_{-1}k_{-3}k_{-2}k_6 + k_7k_1[S]k_{-4}k_{-5}k_{-3} +$$
$$+ k_7k_1[S]k_{-4}k_{-3}k_6 + k_7k_1[S]k_{-5}k_{-3}k_{-2} + k_7k_1[S]k_{-3}k_{-2}k_6 + k_8[S]k_{-1}k_{-4}k_{-5}k_2[S] + k_8[S]k_{-1}k_{-4}k_2[S]k_6 +$$
$$+ k_7k_1[S]k_{-4}k_{-5}k_2[S] + k_7k_1[S]k_{-4}k_2[S]k_6 + k_8[S]k_7k_{-3}k_{-4}k_{-5} + k_8[S]k_{-3}k_{-2}k_4[I]k_{-5} + k_8[S]k_7k_{-3}k_{-4}k_6 +$$
$$+ k_8[S]k_{-3}k_{-2}k_4[I]k_6 + k_8[S]k_7k_{-3}k_{-5}k_{-2} + k_8[S]k_{-3}k_{-2}k_6k_5 + k_8[S]k_7k_{-3}k_{-2}k_6 + k_7k_{-4}k_{-5}k_2[S]k_3[I] +$$
$$+ k_7k_{-4}k_2[S]k_6k_3[I] + k_8[S]k_7k_{-4}k_{-5}k_2[S] + k_8[S]k_7k_{-4}k_2[S]k_6$$

$$E_0 = E + E*S + EI + E*SI + ES + E*ST$$

Fractions of enzyme in different forms:

F(E) = E/E_0;

F(E*S) = $E*S/E_0$;

F(EI) = EI/E_0;

F(E*SI) = $E*SI/E_0$;

F(ES) = ES/E_0;

F(E*ST) = $E*ST/E_0$;