Supporting Information

A Mechanistic Model of Fast Pyrolysis of Glucose-Based

Carbohydrates to Predict Bio-oil Composition

R. Vinu and Linda J. Broadbelt[*]

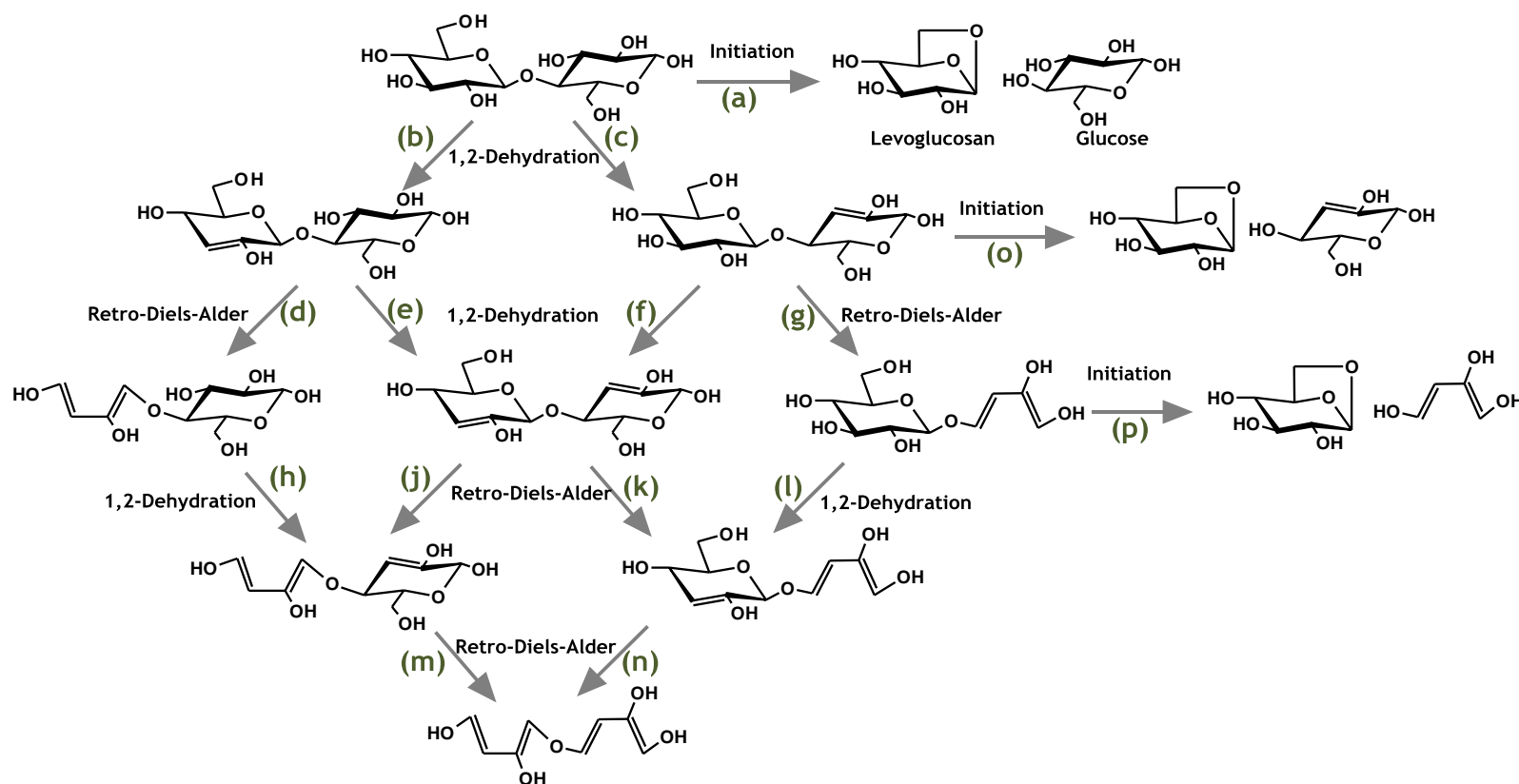*Department of Chemical and Biological Engineering, Northwestern University*

2145 Sheridan Road, Evanston, IL 60208, United States

[*] Corresponding Author. Tel.: +1-847-491-5351; Fax: +1-847-491-3728.

E-mail: broadbelt@northwestern.edu (L. J. Broadbelt)

Scheme SI 1. Mechanism of formation of various dimeric products, anhydrosugars and glucose from cellobiose through dehydration, retro Diels-Alder and glycosidic bond cleavage reactions. 1,2-Dehydration and retro Diels-Alder reactions involve the formation of one molecule of water and glycolaldehyde, respectively. All cellobiose-derived dimers can also react with water to cleave the glycosidic linkage and form the respective monomeric compounds.

SI Appendix A. Continuous Distribution Kinetic Rate Equations for Chain Reactions.

Reactions of the cellulosic chain in Schemes 1 and 2 can be modeled using continuous distribution kinetics which takes into account the chain length dependency of the rates of polymeric species that are undergoing pyrolytic cleavage. Continuous distribution kinetics has been widely used to model polymerization and degradation of synthetic polymers.[63-65] The chain reactions involved in cellulose fast pyrolysis model can be broadly classified as (i) initiation (random chain cleavage), (ii) depropagation and end-chain initiation (specific chain cleavage), and (iii) hydrolysis. Rate equations for the above reaction classes are given below. Detailed derivation of these equations can be found elsewhere.[63,65]

1. Initiation

$$C(x) \xrightarrow{k_{init}(x)} C_{LVG}(x-x') + C'(x') \tag{A.1}$$

Reaction (I) in Scheme 1 falls under this category. This reaction involves the cleavage of glycosidic bond at any random position in the cellulose chain, C, of chain length x, resulting in the formation of a cellulose chain terminated by an LG end, C_{LVG}, of chain length x-x', and another cellulose chain C' of chain length x'. The rate of this reaction is linearly dependent on chain length, $k_{init}(x) = k_{init}*x$.[65] The even distribution of products along all x'≤x is given by the random stoichiometric kernel, $\Omega_{Rand}(x',x) = 1/x$.[65] The rate equations, after applying moments on the initial population balance equation, are given by

$$\frac{dC^{(m)}}{dt} = -k_{init} C^{(m+1)} \tag{A.2}$$

$$\frac{dC_{LVG}^{m}}{dt} = \frac{dC'^{(m)}}{dt} = \frac{k_{init}}{m+1} C^{(m+1)} \tag{A.3}$$

The moments, $C^{(0)}$, $C^{(1)}$ and $C^{(2)}$ denote molar concentration, mass concentration, and second moment, respectively. Number average (M_n) and weight average molecular weight (M_w) of

cellulose are given by $C^{(1)}/C^{(0)}$ and $C^{(2)}/C^{(1)}$, respectively. The Saidel-Katz approximation was utilized to close the moments for the third moment, $C^{(3)}$, as shown in Eq. (A.4).[64]

$$C^{(3)} = 2\frac{C^{(2)}C^{(2)}}{C^{(1)}} - \frac{C^{(2)}C^{(1)}}{C^{(0)}}$$ (A.4)

2. Depropagation and end-chain initiation

$$C(x) \xrightarrow{k_{deprop}} C_{LVG}(x-1) + LVG$$ (A.5)
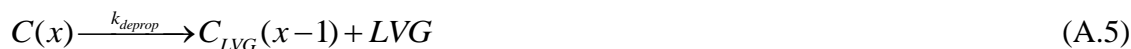
This reaction involves unzipping of monomers (levoglucosan or glucose) from either ends of the cellulose chain according to reactions (II), (III) and (IV) in Scheme 1. As this reaction results in continuous evolution of monomers of unit chain length, the product distribution follows a Dirac delta function given by, $\Omega_{Deprop}(x-1, x) = \delta(x-1)$.[63] The rate equations are as follows.

$$\frac{dC^{(m)}}{dt} = -k_{deprop}C^{(m)}$$ (A.6)

$$\frac{dC_{LVG}^{(m)}}{dt} = k_{deprop}\sum_{j=0}^{m}\binom{m}{j}(-1)^{j}C^{(m-j)}$$ (A.7)

$$\frac{d[LVG]}{dt} = k_{deprop}C^{(0)}$$ (A.8)

3. Dehydration or retro-Diels-Alder reaction anywhere in the cellulosic chain

$$C(x) \xrightarrow{k_{Dehyd}/k_{rDA}} C_{mid}(x - x_{H_2O}/x_{GA}) + H_2O/\text{Glycolaldehyde (GA)}$$ (A.9)

Dehydration and subsequent retro Diels-Alder reaction in the dehydrated unit of the cellulose chain result in the formation of glycolaldehyde (reactions (i) and (ii) in Scheme 2). The rate equations for this class of reactions are the same as that of depropagation, except that these reactions mostly take place anywhere in the middle of the cellulose chain and involve a product whose molecular weight is less than that of the monomer. Hence, the ratio of molecular weight
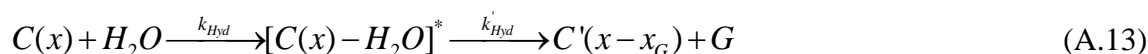
of the evolved product with respect to the monomer (x_{H2O} or x_{GA}) is included in the rate expressions.

$$\frac{dC^{(m)}}{dt} = -k_{Dehyd} C^{(m)} \tag{A.10}$$

$$\frac{dC^{(m)}_{mid}}{dt} = k_{Dehyd} \sum_{j=0}^{m} \binom{m}{j} (-x_{H_2O})^j C^{(m-j)} \tag{A.11}$$

$$\frac{d[H_2O]}{dt} = k_{Dehyd} C^{(0)} \tag{A.12}$$

4. Hydrolysis of cellulosic chain to form glucose (G) from chain end

$$C(x) + H_2O \xrightarrow{k_{Hyd}} [C(x) - H_2O]^* \xrightarrow{k'_{Hyd}} C'(x - x_G) + G \tag{A.13}$$

Hydrolysis at either ends of the cellulose chain results in the formation of glucose according to reaction (V) in Scheme 1. Moment solutions do not exist for bimolecular reactions involving the formation of two products. Hence, in deriving the rate equations for reaction (A.13), we need to assume an intermediate short-lived species $[C(x)–H_2O]^*$ for which the pseudo-steady-state approximation (PSSA) can be applied. The rate coefficient k'_{Hyd} was only utilized for derivation purposes, and the final rate equations in terms of final species concentrations and k_{Hyd} are given by the following.
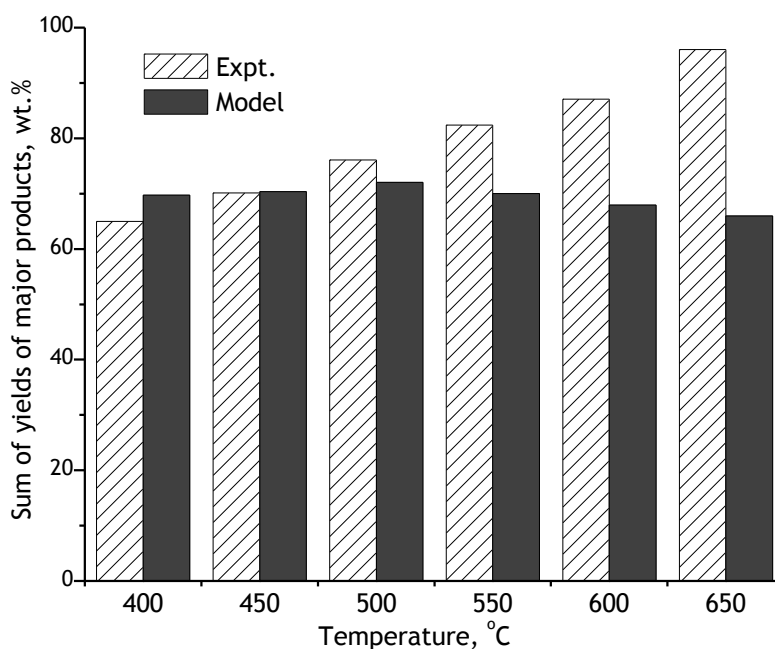
$$\frac{dC^{(m)}}{dt} = -k_{Hyd} C^{(m)} [H_2O] \tag{A.14}$$

$$-\frac{d[H_2O]}{dt} = \frac{d[G]}{dt} = k_{Hyd} C^{(0)} [H_2O] \tag{A.15}$$

$$\frac{dC'^{(m)}}{dt} = k_{Hyd} \sum_{j=0}^{m} \binom{m}{j} (-x_G)^j \sum_{p=0}^{q} \binom{q}{p} (x_{H_2O})^p C^{(q-p)} [H_2O] \tag{A.16}$$

Table SI 1. Size of fast pyrolysis model in terms of the number of species and reactions for cellulose, maltohexaose, cellobiose and glucose.

| Carbohydrate	No. of species	No. of reactions
Cellulose/Maltohexaose	52	99
Cellobiose	49	65
Glucose	40	41

Figure SI 1. Comparison of total yield of the major products (levoglucosan + glycolaldehyde + formic acid + HMF + furfural) obtained from the model with experiments at different temperatures.
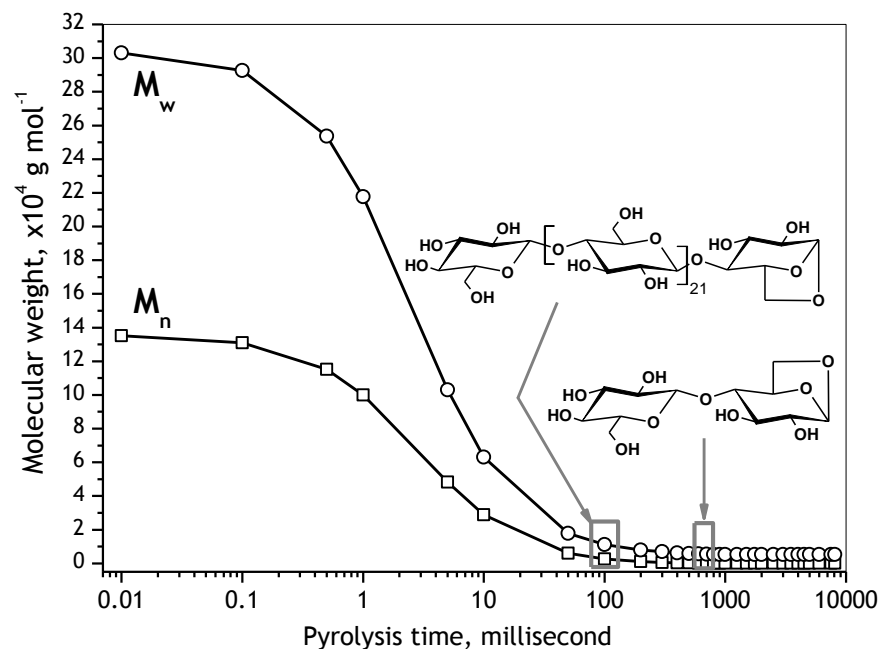
Figure SI 2. Model time evolution of number average (M_n) and weight average (M_w) molecular weights of cellulose at 500 ^oC. The predominant species during 100 ms and 600 – 700 ms are shown in the figure.
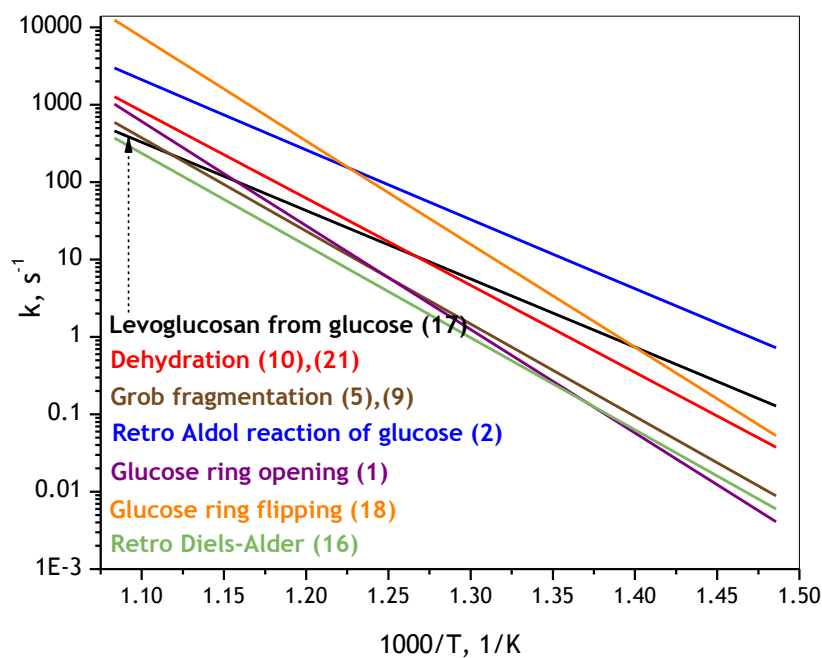
Figure SI 3. Variation of rate coefficients with temperature for selected reactions that compete with dehydration of glucose to form levoglucosan. The reaction indices refer to Scheme 3.
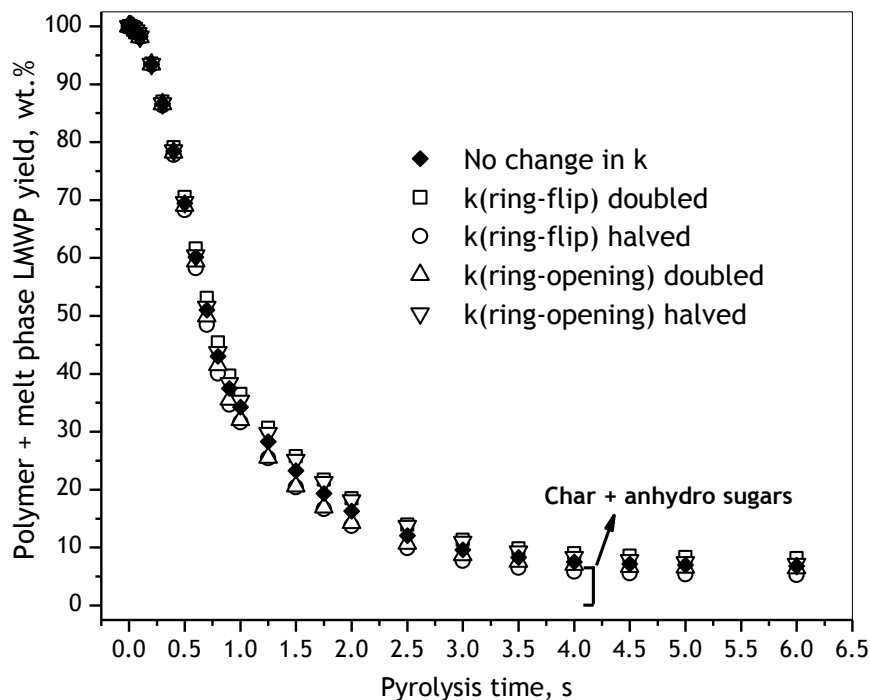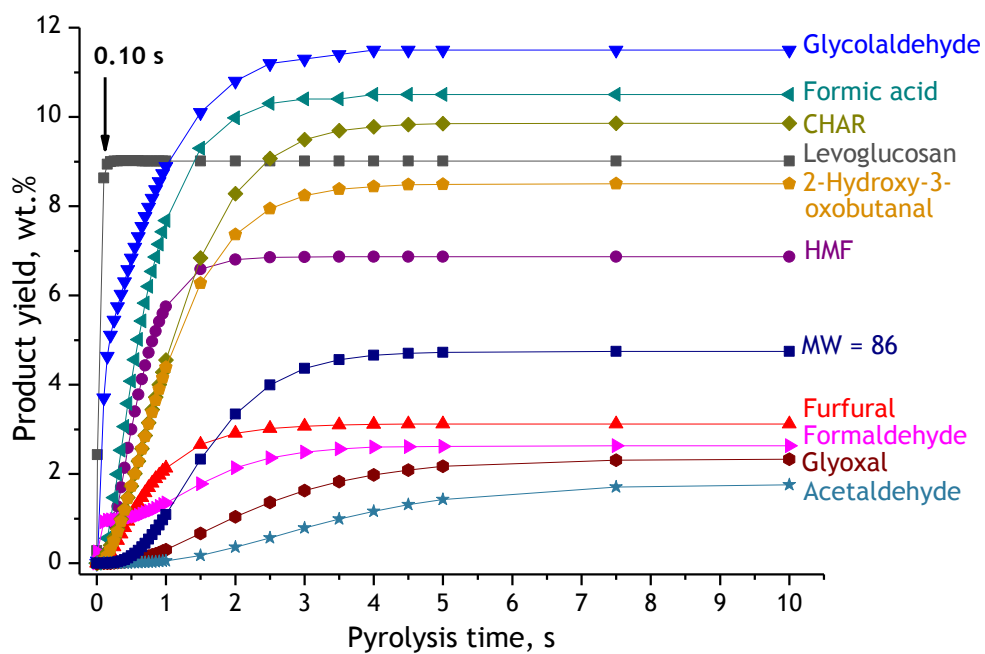
Figure SI 4. Sensitivity of model time evolution of the remaining solid fraction (polymer + melt phase) after reaction for various values of rate constants of ring opening and ring flipping at 500 °C.
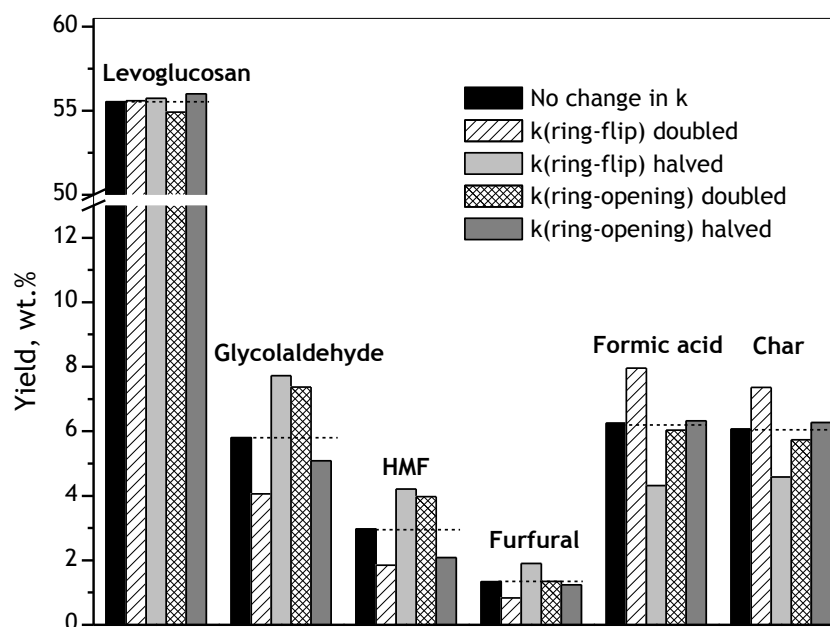
Figure SI 5. Sensitivity of model yields of the major products for various values of rate constants of ring opening and ring flipping at 500 °C.

Figure SI 6. Model time evolution of various fast pyrolysis products from glucose at 500 $^{\circ}$C.