Supplementary Information

Materials Characterization

Table S1 shows adsorbed volatiles and non-volatile impurities in glucose, cellodextrin and cellulose starting materials. Glucose and cellobiose were purchased from Sigma-Aldrich chemical company, larger cellodextrins (DP=3-6) were purchased from Santa Cruz Biotechnologies and cellulose was purchased from Alfa Aesar. Viscosity tests, conducted by Doble Engineering, found our cellulose sample to have a degree of polymerization of 133.

Table S1. Adsorbed volatile content and non-volatile impurities for starting materials used in thin-film experiments. Values for glucose, cellohexaose, and cellulose were reported in previous work[1].

	Adsorbed Volatiles [%]	Non-volatile Impurities (name) [%]
Glucose	0.3	--
Cellobiose	--	--
Cellotriose	--	--
Cellotetraose	--	1.5 (glucose) 1.1 (cellotriose)
Cellopentaose	--	1.8 (glucose) 1.3 (cellohexaose)
Cellohexaose	9.9	3.9 (cellopentaose) 2.8 (celloheptaose)* 1.5 (celloctaose)*
Cellulose	5.5	N/A

* Compounds not confirmed via retention time since pure standards are unavailable.

End-Group / Interior Monomer Model Evaluation: Supplemental

In the main body of the paper, the reducing end-group/interior model was evaluated against experimental data for four products of β-1,4-glucan pyrolysis (LGA, HMF, furfural and DAGP). In the supplemental section we show additional results in Figure S1 which support the conclusion presented in the main paper that some but not all product yields can be described by a simple end-group/interior monomer model which uses glucose and cellulose product distributions as inputs. Figure S1 shows that for certain products (i.e., ADGH and AGF) the end-group/interior monomer model cannot predict experimental cellodextrin pyrolysis yields while for others (i.e., furanone and CPD) the model is sufficient. These supplemental results support the conclusion in the main body that the chain length effect, while significant, is not simple to explain.

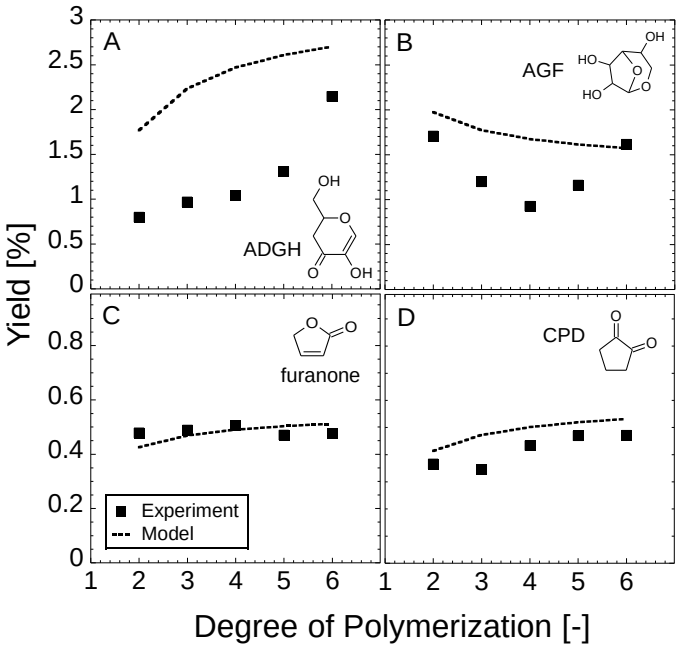

Figure S1. Predictability of product yields from cellodextrin pyrolysis using a simple end-group/interior monomer model. Predicted yields from a simple end-group/interior monomer model are compared to actual yields generated from cellodextrin (DP=2-6) pyrolysis for 1,5-anhydro-4-deoxy-D-glycero-hex-1-en-3-ulose[2] (ADGH, panel A), 1,6-anhydroglucofuranose (AGF, panel B), furanone (panel C) and 1,2-cyclopentanedione (CPD, panel D). Model-predicted yields are calculated from the end-group/interior monomer model described in the main body of the paper. This model assumes reducing end-groups in cellodextrins generate the same products as glucose whereas interior monomers and non-reducing end-groups are analogous to the cellulose product distribution (see Scheme 1 in main body for information on end group types).

To interpret the complex trends in product yields as the DP is increased, we test several simple models which combine product distributions of cellulose with small carbohydrates (i.e., glucose, cellobiose, and cellotriose) to predict yields from pyrolysis of larger cellodextrins (i.e., cellotetraose, cellopentaose, and cellohexaose).

Model I, treats reducing-end groups as glucose, interior monomers and non-reducing end groups as cellulose and is presented in the main body of the paper:

$$Y_p^i = \frac{(n-1)Y_{cel}^i + Y_{gc}^i}{n} \quad (1)$$

Model II treats reducing-end groups and non-reducing end groups as glucose and interior monomers as cellulose:

$$Y_p^i = \frac{(n-2)Y_{cel}^i + 2Y_{gc}^i}{n} \quad (2)$$

Model III treats reducing-end groups and 1st interior monomer as cellobiose, and interior monomers and non-reducing end groups as cellulose:

$$Y_p^i = \frac{(n-2)Y_{cel}^i + 2Y_{cellobiose}^i}{n} \quad (3)$$

Model IV treats reducing-end groups, 1st interior monomer, and 2nd interior monomer as cellotriose, interior monomers and non-reducing end groups as cellulose:

$$Y_p^i = \frac{(n-3)Y_{cel}^i + 3Y_{cellotriose}^i}{n} \quad (4)$$

In (1)-(4), Y_p^i is the predicted yield of product i, n is the DP of the cellodextrin of interest, and Y_{cel} is the actual yield of product i from cellulose pyrolysis. Figure S2A-D shows that all of the four simplified models outlined in (1)-(4) cannot accurately predict cellodextrin yield. The functionality of product yield with respect to DP cannot be captured with any of these simplified models.

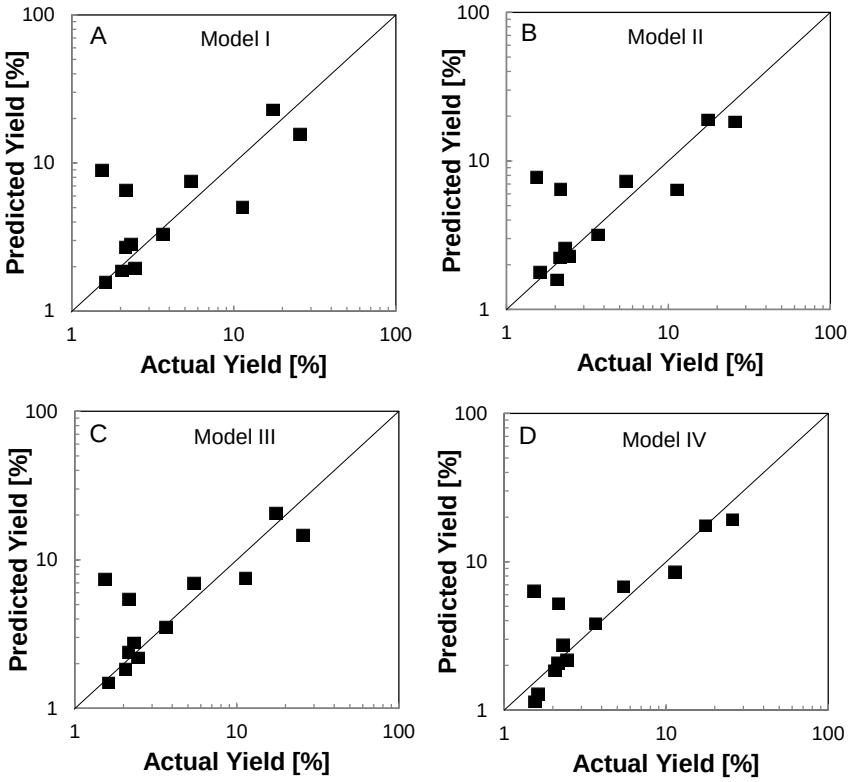

Figure S2. Comparison of predicted and actual yields from cellohexaose pyrolysis.

References

1. M. S. Mettler, S. H. Mushrif, A. D. Paulsen, A. D. Javadekar, D. G. Vlachos and P. J. Dauenhauer, *Energy & Environmental Science*, 2012, **5**, 5414-5424.
2. F. Shafizadeh, T. T. Stevenson, T. G. Cochran and R. H. Furneaux, *Carbohydrate Research*, 1978, **67**, 433-447.