Electronic Supplementary Material (ESI) for Energy & Environmental Science

Supporting Information

Co-pyrolysis Experiments

As mentioned in the main body of the paper, co-pyrolysis experiments were conducted with powder and thin-film mixtures of levoglucosan and fructose to reveal secondary pyrolysis pathways. Powder co-pyrolysis samples were prepared by weighing 0.5-1 mg of levoglucosan and fructose and then mixing them within a cylindrical pyrolysis crucible. Thin-films were prepared by co-precipitating levoglucosan and fructose from aqueous solutions. Figure S1 shows that levoglucosan and fructose thin-films form in the same region of the pyrolysis crucible. Co-pyrolysis samples (powder and thin-film) were pyrolyzed in the Frontier 2020 Micropyrolyzer at 500 °C (typical pyrolysis reaction temperature).[1-3] Volatile products were then swept out of the micropyrolyzer furnace and into an Agilent 7890 GCMS which is kept at sub-ambient temperatures to inhibit product degradation. The multidimensional GCMS was then used to identify and quantify 26 products (including char and permanent gases such as CO and CO_2). Char residue was quantified by injecting oxygen into the micropyrolyzer furnace and quantifying the resulting CO and CO_2.

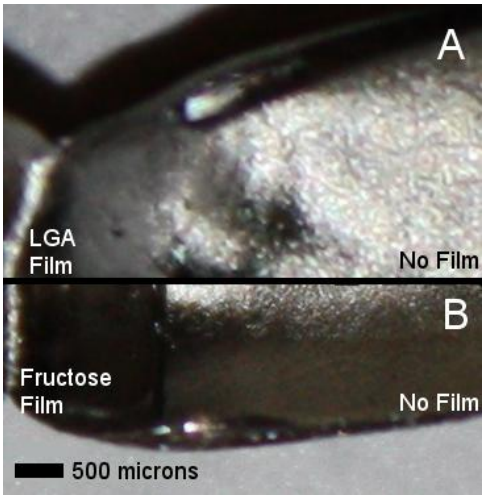
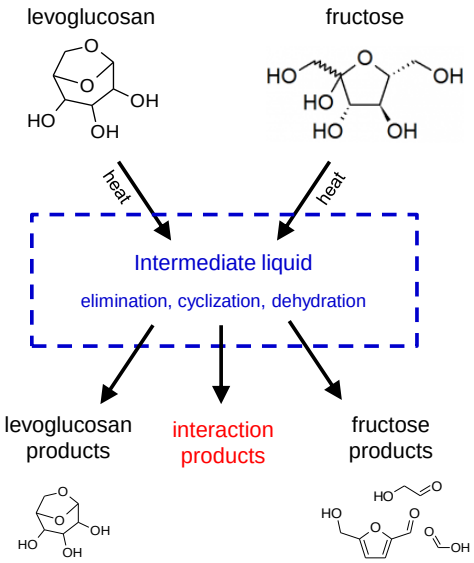


Figure S1. Photos of levoglucosan (A) and fructose (B) thin-films within the pyrolysis crucible. Areas with no reflection indicate the presence of a thin-film (far left) while regions with light reflectance indicate no thin-film (far right).

Fructose was chosen as the co-reactant with levoglucosan because (1) it does not form levoglucosan itself thereby allowing for direct quantification of the anhydrosugar and (2) recent work has shown that simple sugars similar to fructose form an intermediate liquid similar to cellulose.[4] Scheme S1 illustrates the general conversion process for fructose and levoglucosan. Upon heating, the two carbohydrates form

an intermediate liquid wherein many types of condensed-phase reactions occur (e.g., elimination, cyclization and dehydration). The deoxygenated products are then transported from the intermediate liquid to the gas-liquid intermediate and then subsequently volatilize to the gas-phase. Detected products include levoglucosan, fructose-derived oxygenates and interaction products. This work focuses on identifying the reaction pathways for the latter category in order to better understand the stability of cellulose pyrolysis products (e.g., levoglucosan) within the intermediate liquid. Levoglucosan breakdown within the molten phase forms products which have higher energy density (relative to levoglucosan) thereby making the bio-oil product more suitable for fuels production or stationary power generation.



Scheme S1. Schematic of co-pyrolysis of levoglucosan and fructose. Upon heating, levoglucosan and fructose form an intermediate liquid mixture wherein elimination, cyclization and deoxygenation reactions occur to produce volatile products.

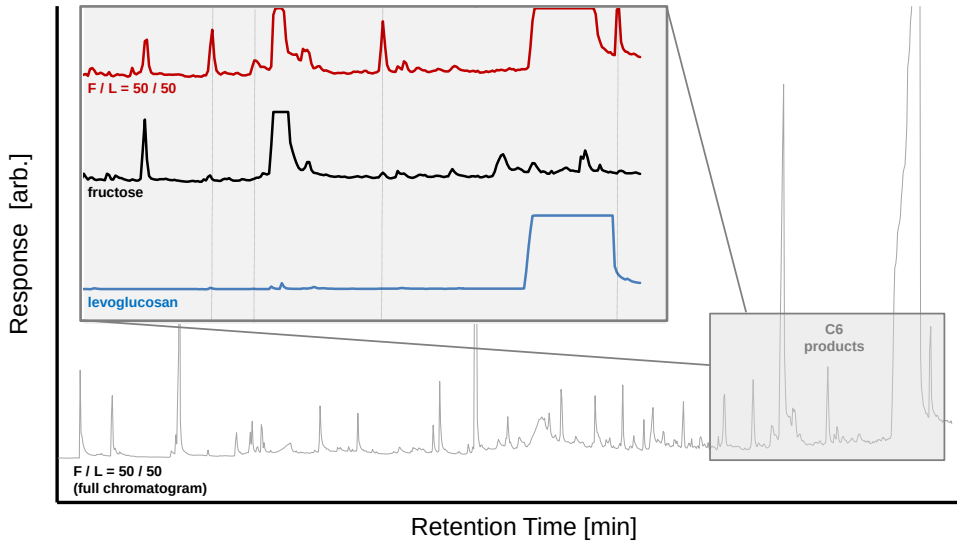


Figure S2. Chromatograms from co-pyrolysis experiments. The 6-carbon region of the chromatogram is shown in the inset to highlight products generated in co-pyrolysis but not for fructose-only and levoglucosan-only pyrolysis.

Effect of Co-pyrolysis on Fructose

The objective of the main part of the paper was to first determine the stability of levoglucosan within the (fructose-derived) intermediate liquid and then identify secondary products, co-reactants and reaction pathways. Of additional consequence is the counter effect of LGA on FCT pyrolysis and this is the objective of this supplementary information section. Table S1 shows the fraction of each product during isotopic co-pyrolysis of ^{13}C-fructose (all carbons labeled) and unlabeled (^{12}C) levoglucosan (50/50 mixture). The relatively low γ_i values for FCT-derived products (shown in red in Table S1) show that the effect of co-pyrolysis on FCT pyrolysis chemistry is either negligible or not as clear as LGA (γ_i values for LGA-derived products, indicated in blue, are much larger). These results hint that the co-reactant affect may be unidirectional (or pseudo-catalytic) in that fructose facilitates LGA break down but LGA has a relatively minor influence on FCT.

Table S1. Summary of isotopic co-pyrolysis experiments. Products that are primarily (i.e., greater than 75%) LGA-derived are shown in red while FCT-derived products are shown in blue. Permanent gases (CO, CO_2) and char are not included since mass spectrometry was not available to analyze these products.

Compound	Fructose / Levoglucosan 50 / 50		
	FCT [% ^{13}C]	LGA [% ^{12}C]	γ_i [-]
Anhydrosugars			
Levoglucosan	1	99	0.8
1,6 anhydroglucofuranose*	4	96	∞
dianhydroglucopyranose*	8	92	∞
Pyrans			
ADGH*	5	95	∞
DHDHMP*	77	23	1.2
DHMP*	18	82	7.6
Furans			
hydroxymethylfurfural	90	10	0.8
Furfural	81	19	0.6
5-methyl furfural	74	26	1.2
2-furanmethanol	76	24	2.0
2,5 dimethyl Furan	58	42	1.7
2-methyl furan	59	41	1.1
Furan	34	66	1.6
DMHF*	28	72	2.2
Light Oxygenates			
methyl glyoxal	81	19	2.0
glycolaldehyde	NA	NA	2.8
formaldehyde	NA	NA	0.7
hydroxyacetone	77	23	2.9
acetic acid	68	32	1.8
2,3 butanedione	54	46	2.2
glyoxal	95	5	1.7
Permanent Gases			
carbon monoxide	NA	NA	1.1
carbon dioxide	NA	NA	1.2
Other			
HMCP*	35	65	2.7
1,2-cyclopentanedione*	58	42	1.7

Isotope Labeling Experiments

Figure 3 of the main paper uses isotopically-labeled starting materials in conjunction with mass spectrometry to identify both the origin of carbon atoms within several products, but also to quantify the degree of proton exchange during reaction. Isotopically labeled samples were obtained from the following venders: carbon-labeled (C^{13}) fructose from Cambridge Isotope Laboratory with ≥ 98% chemical purity (CP) and 99% isotopic purity (IP); deuterated fructose (D7, C-H positions only) was obtained from Omicron Biochemicals with CP=99.9% and IP=98%; deuterated glucose (D7, C-H positions only) was obtained from Cambridge Isotope laboratory at CP≥98% and IP=98%; and deuterated glucose (D12, C-H and O-H positions) was obtained from Isotec at CP=99% and IP=97%. All isotopic samples were used as received.

In order to quantify signals from the mass spectrometer (MS), individual peaks representing a given mass-to-charge ratio (m/z) are benchmarked against the sum of all peaks within the parent ion region (PIR),[5-7] which is illustrated from the raw mass spectra shown in Figure S4. PIR is defined by the

molecular weight of the selected product, which is confirmed by comparing analyte and pure standard retention times.

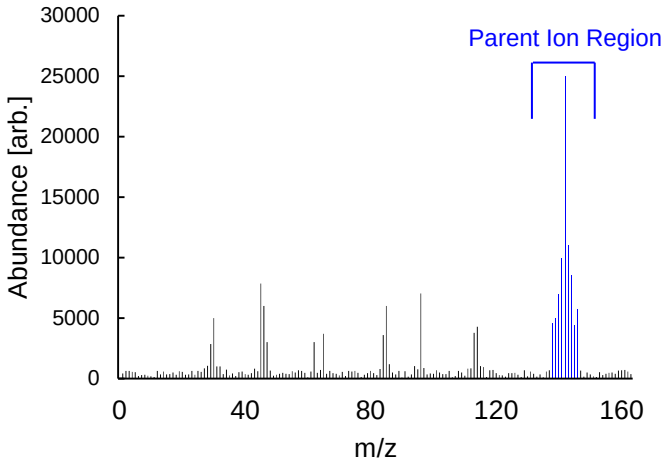


Figure S4. Example mass spectrum with parent ion region (PIR) highlighted in blue.

In the first set of isotopic labeling experiments, carbon-13 fructose was co-pyrolyzed with unlabeled (UL) levoglucosan. Products generated from co-pyrolysis are either fully labeled (all carbons C^{13}) or fully unlabeled (all carbons C^{12}). It is possible that carbon scrambling could occur (where a given product has some C^{12} and C^{13}), but in our experiments this is not observed. In order to determine the fraction of a single product that is labeled (with C^{13}), the relationship given in Paine et al is used.[5]

$$x = \frac{I_m + S_m}{S_{m,0} - S_m} \qquad (1)$$

Where the parameters in (3) are defined as:

x = the mass fraction of the isotopically labeled (with C^{13}) portion of the analyte

m = the molecular weight of the labeled (C^{13}) analyte

m,0 = the molecular weight of the unlabeled analyte

I_m = the normalized intensity of peak m from the labeled/unlabeled mixture

S_m = the normalized intensity of peak m (all carbons C^{13}) from unlabeled reference

$S_{m,0}$ = the normalized intensity of peak m,0 (all carbons C^{12}) from unlabeled reference

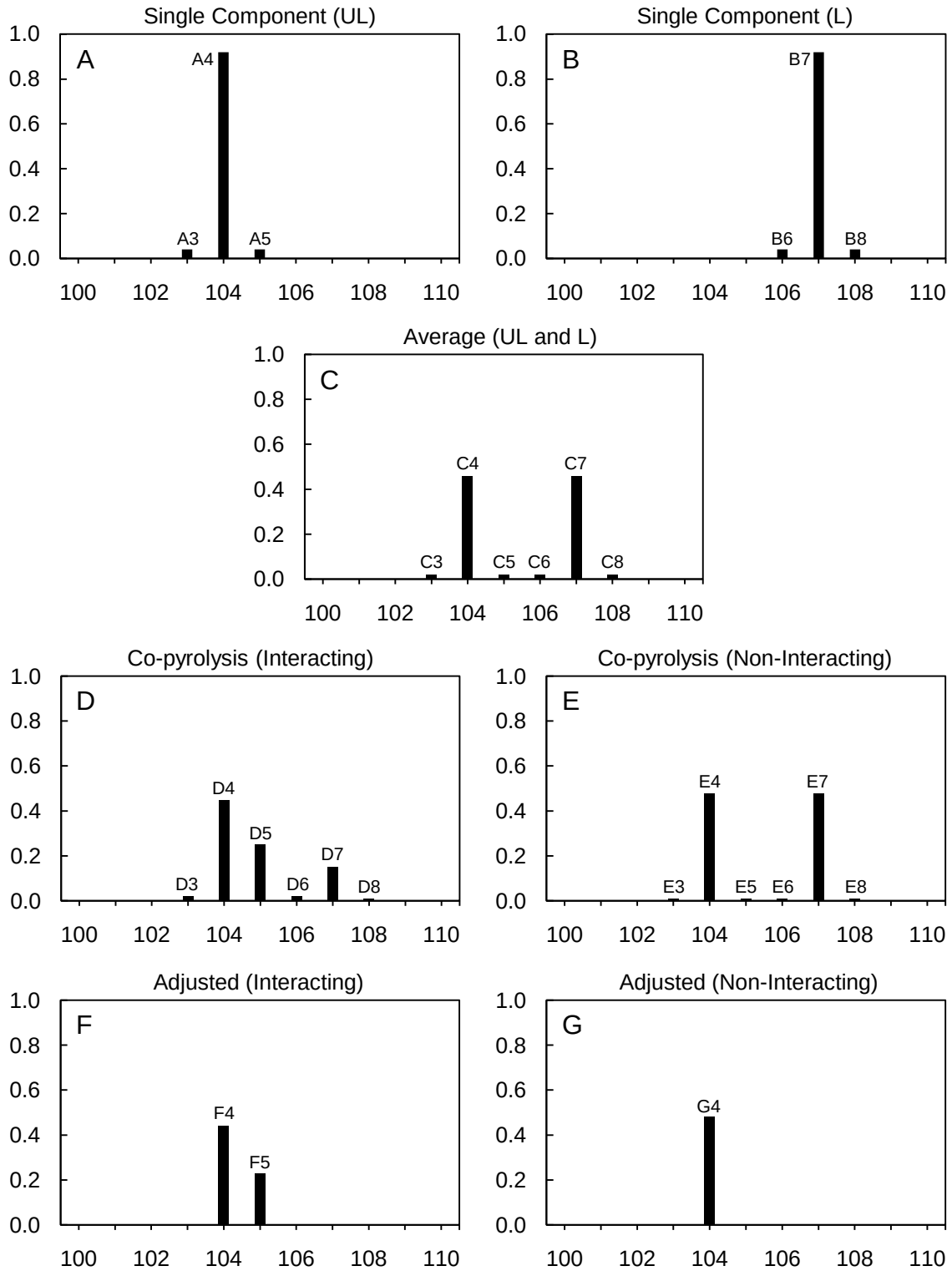


Figure S5. Methodology for calculating hydrogen exchange (interacting) between deuterated (L) glucose and unlabeled (UL) levoglucosan. For all plots (A-G), y-axis is the relative response and the x-axis the mass over charge ratio (m/z). Peak labeles run from A1 to A8 starting with m/z = 101 and ending with m/z = 108. The mass spectra portray an imaginary compound with 3 Hydrogens and a molecular weight of 104.

Hydrogen exchange experiments were conducted with labeled glucose (D12) and unlabeled levoglucosan. During co-pyrolysis, products of interest are produced by both labeled glucose and levoglucosan pyrolysis. For a given analyte, various isotopes exist which are unlabeled (all hydrogens with molecular weight of one), fully deuterated, or partially deuterated. This results in a spectrum of isotopes with multiple peaks in the mass spectrum of the parent ion region (PIR), as can be seen in Figure S5D. A single MS peak m/z=i at a given m/z has contributions not only from the isotope with m/z=i, but also from nearby isotopes (m/z≠i) which also fragment to generate peaks at m/z=i. Contributions to isotope i from nearby isotopes (with m/z≠i) must be subtracted out to get the actual amount of isotope i for a given analyte.

The parent ion in a given mass spectra is encompassed by smaller ions as seen in Figure S5A-B. Upon examination of Figure S5C, we see significant peaks between the deuterated (MW=107) and unlabeled (MW=104, true MW of this analyte) primary ions. In order to determine the percentage of this analyte that is deuterated, we first collect spectra for analytes produced from separate (single component) pyrolysis of unlabeled and labeled (D12) glucose pyrolysis (Figure S5A-B). During co-pyrolysis, single component pyrolysis spectra will contribute to the overall co-pyrolysis spectra. To determine the amount of hydrogen exchange in a co-pyrolysis run, the interactive effects (hydrogen exchange) must be separated from spectra produced from single component pyrolysis (non-interacting). In order to subtract single component effects from the co-pyrolysis spectra, we first average the two single component spectra. We use a weighted average based on the product yield from deuterated and unlabeled glucose pyrolysis. If this is done with the example spectra for the case where deuterated and unlabeled glucose generate the same yield of a given analyte, we obtain the Spectra shown in Figure S5C. The averaged spectrum (defined in the equation below) is used as a reference to analyze hydrogen exchange in co-pyrolysis of deuterated glucose and unlabeled levoglucosan.

$$C4 = \frac{A4 + B4}{2} \qquad (2)$$

Figure S5D shows that several shifted ions form in the parent ion region during isotopic co-pyrolysis. In Figure S5E, a hypothetical spectrum for "non-interacting" co-pyrolysis is shown. This spectrum shows that when no hydrogen exchange occurs, the average (of single component) spectrum illustrated in Figure S5C is generated. Returning to Figure S5D, this spectrum needs to be amended to subtract out contributions to this spectrum from the labeled sample (we want to only study hydrogen exchange in the labeled sample). We must also account for the effects of small ions surrounding the primary ion. In Figure S5A, we see two small peaks (A3 and A5) next to the primary ion A4. An analogous spectrum is produced for the labeled sample shown in Figure S5B. This will be true for any shift of the parent ion.

The minor peaks must then be subtracted from each isotope in Figure S5D-E to produce an "adjusted spectra", shown in Figure S5F-G. This analysis is described using the following equation:

$$S_m^{act} = S_m - \sum_{i=0}^{n} S_{m+i} \frac{S'_{m-i+i}}{S'_{m,0}} \quad (3)$$

Where,

S_m^{act} = the adjusted normalized intensity of peak m

S_m = the normalized intensity of peak m from the co-pyrolysis spectrum

S_{m+i} = the normalized intensity of peak m+i from the co-pyrolysis spectrum

S'_{m-i+1} = the normalized intensity of peak m-i+1 from the averaged reference spectrum

$S'_{m,0}$= the normalized intensity of the primary ion peak from the averaged reference spectrum

i = runs from zero to the total number of hydrogens in the compound

The relative intensity of peak F5 is calculated from the co-pyrolysis spectrum given in Figure S5D in the following way:

$$F5 = D5 - D4\frac{C4}{C4} - D6\frac{C3}{C4} - D7\frac{C2}{C4} \quad (4)$$

Or

$$0.23 = 0.25 - 0.45\frac{0.02}{0.46} - 0.02\frac{0.02}{0.46} - 0.15\frac{0.00}{0.46} \quad (5)$$

The above analysis is repeated for every isotope in the spectrum (i.e., peaks: m, m+1, m+2, etc.). The final adjusted peaks are then be used to determine the percent of labeling (or deuteration). To perform this calculation, peaks F4 and F5 in Figure S5F are normalized by the sum of all labeled peaks, where X is the percent of the analyte that is 1x deuterated.

$$X = 100\%\left(\frac{F5}{F4+F5+F6+F7}\right) \quad (6)$$

References

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