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Acid-catalyzed Pyrolytic Synthesis of Levoglucosan through Salt-mediated Ring Locking

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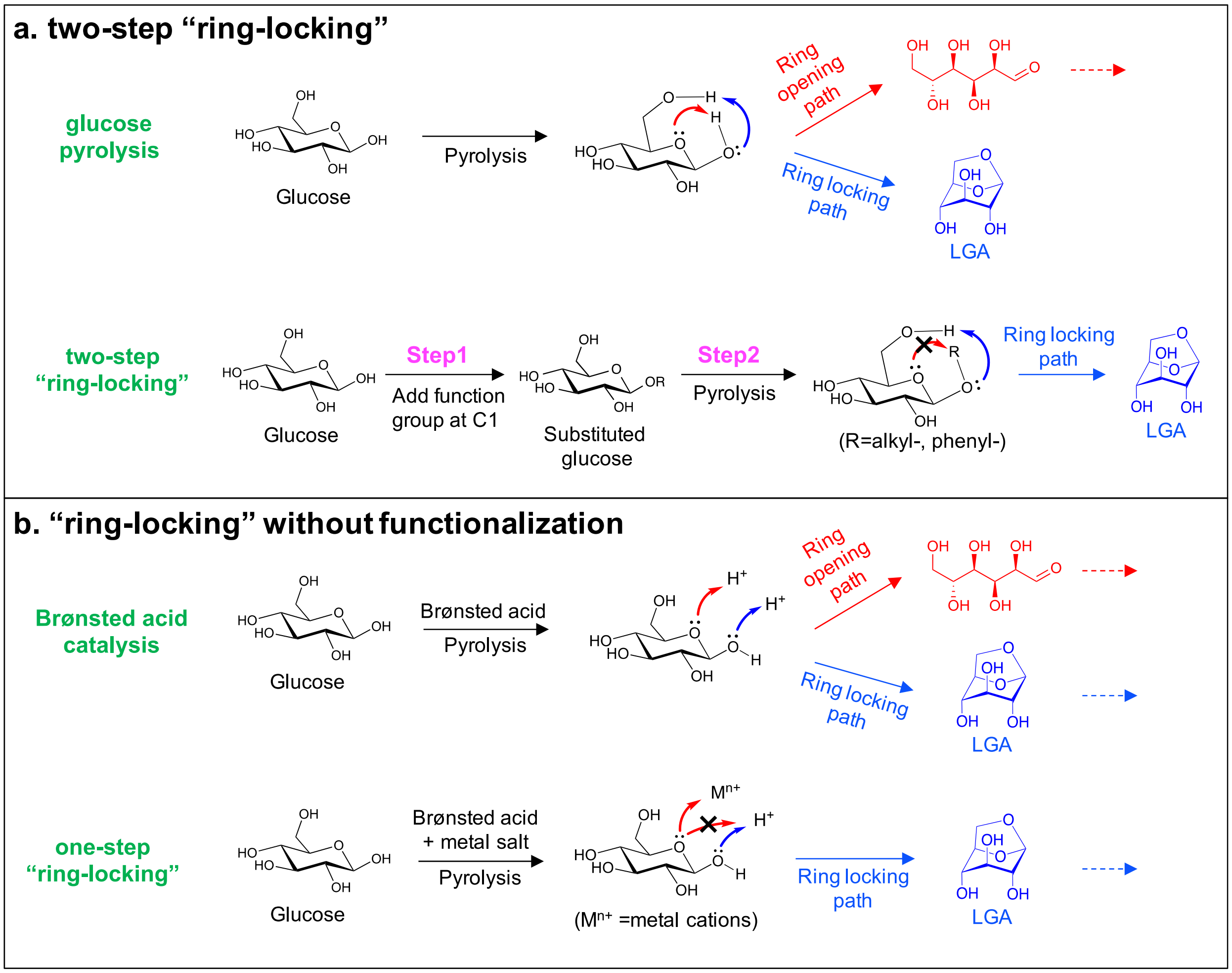
ABSTRACT:

Selectively producing chemicals from cellulosic carbohydrate pyrolysis in large quantities is challenging, especially anhydro-monosaccharides with double-ring, triple-ring, and furan/pyran structures. Formation of these sugar derivatives greatly improves when pyranose ring opening is inhibited during pyrolysis, which is accomplished by chemically replacing the hydroxyl group at the anomeric carbon with an alkoxy group. A simpler ring-locking approach is required for scalable chemicals production, however. In this work, we demonstrate that introducing Na_2SO_4 and H_2SO_4 to glucose pyrolysis significantly increases levoglucosan (LGA) formation, from 6% yield to as high as 40% at 350 °C. With H_2SO_4 as the acid catalyst, Na^+ acts to inhibit ring opening. Glucose pyrolysis with different alkali metal cations (Li^+, Na^+, K^+, Rb^+ and Cs^+) gives different reaction products, which can be explained largely by an ionic electronegativity effect. Weaker electronegativity promotes the formation of ring-opened product such as 5-hydroxymethylfurfural (HMF), and stronger electronegativity increases the formation of sequential dehydration products like levoglucosenone (LGO). Sodium has the optimum ionic electronegativity for preferential association with the ring oxygen. The Na_2SO_4/H_2SO_4 combination improved LGA yields for all carbohydrate substrates tested (up to 70%), including lignocellulose. These findings highlight the potential of using alkali metal salts to produce anhydrosugars in high yield from cellulosic carbohydrate pyrolysis.

1. Introduction

Biomass pyrolysis is a promising technology for the production of renewable fuels, due to fast conversion rates, simplicity of operation, and feedstock flexibility.[1–4] However, the recent decrease of crude oil prices makes biofuels economically less competitive. Production of a wider product portfolio, especially valuable chemicals, is vital in increasing the profitability from biomass pyrolysis. Anhydrosugars are valuable chemicals primarily prepared from biomass-derived carbohydrate pyrolysis.[5] These molecules are highly needed precursors to synthesize a large number of high value complex chemicals (*e.g.*, drugs, surfactants, polymers) due to their excellent stability, fixed conformation, protected stereoselectivity, and the various reactivities of the hydroxyl groups[6–11]. As a model anhydrosugar, LGA (levoglucosan = 1,6-anhydro-β-D-glucose) is one potential candidate among the sugar-based biorefinery feedstock chemicals by the US Department of Energy[12]. With a bicyclic framework, it is also a chiral building block to antiparasitic agents, antibiotics, and other biologically active compounds[6–10,13]. However, LGA is still a chemical with scarce availability due to the lack of large-scale commercial production. LGA is currently obtained only in small quantities by extensive purification from low-yield carbohydrate pyrolysis[7,13–15]. It is challenging to selectively produce chemicals from carbohydrate pyrolysis because various competing pathways are simultaneously activated and therefore multiple side products are usually produced [16–20].

To address this problem, we previously developed a two-step "ring-locking" strategy to produce high-purity LGA from glucose pyrolysis, by using an alkoxy or phenoxy functional group to replace the hydroxyl group at the anomeric carbon of glucose prior to thermal treatment[21] (Scheme 1a). For example, glucose can be converted into methyl glucosides in methanolic media. This substitution effectively hinders the intramolecular H-bonding with the ring oxygen site. The ring-opening pathway, which leads to other products, is inhibited, but the dehydration pathway to the LGA is not, thus leading to near-quantitative LGA formation. While this two-step approach was very effective for enhancing LGA selectivity, a simpler process that eliminates this alcohol treatment step would be more desirable for ease in scale-up.



Scheme 1. Ring-locking enhances LGA production from glucose pyrolysis by inhibiting intramolecular H-bonding at the ring oxygen. This involves either a (a) two-step[21] or (b) one-step process, as studied in this work.

We hypothesized that a combination of a salt inhibitor and an acid catalyst can simulate the ring-locking effect. Biomass pyrolysis yields more LGA when it is treated with Brønsted acids[22,23]. However, protons (H^+) also activates other pathways[24–26], because carbohydrates have multiple oxygen sites susceptible to protonation. The ring oxygen and the hydroxyl group at the anomeric carbon, in particular, are favorable binding sites for H^+ [26] (Scheme 1b). Protonation at a ring oxygen leads to unwanted ring-opening reactions, and protonation of the anomeric oxygen leads to the desired LGA formation. We rationalized that cations may compete with protons for the ring oxygen site and inhibit the sugar ring from opening during acid-catalyzed pyrolysis (Scheme 1b). There are reported observations that alkali metal cations slow down the acid-catalyzed glucose mutarotation[27,28] in water, and that alkali metal cations form weak complexes with sugars in solution[29,30].

In this study, we demonstrate that the combination of Na_2SO_4 with H_2SO_4 greatly enhances the product yields of anhydrosugars from glucose pyrolysis. We studied the effect of different group I metal sulfates, and identified ionic electronegativity to explain the trends in the formation of LGA and other anhydrosugars like LGO, 1,6-anhydroglucofuranose (AGF), and 5-hydroxymethylfurfural (HMF). To infer the role of Na_2SO_4 as an inhibitor to ring-opening during pyrolysis, we studied the effect of Na_2SO_4 on glucose mutarotation in solution. Relative amounts of H_2SO_4 and Na_2SO_4 were systematically studied to affirm the catalytic nature of H_2SO_4 and the inhibitory nature of Na_2SO_4. The applicability of the Na_2SO_4-H_2SO_4 system on more complex carbohydrate substrates were further assessed.

2. Experimental

2.1 Materials

β-D-glucose (>80.0%, with α-D-glucose as balance) was purchased from TCI America. Levoglucosan (99%, 1,6-Anhydro-β-D-glucose), sigmacell cellulose (type 20, 20 μm), phenyl-β-glucoside (97%), cellobiose (≥99%), α-cyclodextrin (≥98%) and α-D-glucose (96%) were purchased from Sigma Aldrich. Other compounds were purchased for column calibrations: 5-hydroxymethylfurfural (>99%), furfural (99%), DL-glyceraldehyde (>90% GC), glycolaldehyde dimer, and levulinic acid (98%). Corn stover (received from KiOR) was washed to remove the mineral contaminants prior to pyrolysis: 1 g of the substrate was stirred in 20 mL of HNO_3 (0.1 N) for 5 min, filtered, and the solid residue was rinsed with 60 mL DI water.[31] Sulfuric acid solution (0.1 N) was purchased from Fisher Chemical. Lithium sulfate monohydrate (99%), potassium sulfate (99%), rubidium sulfate (99.8%) and cesium sulfate (99.99%) were purchased from Sigma Aldrich. Sodium sulfate anhydrous (99%) was purchased from EMD Chemicals.

2.2 Thin-film for pyrolysis experiments

Following the method described in our previous paper[21], four different thin-film compositions were prepared: sugar-only, sugar-acid, sugar-acid-salt, and sugar-salt. The carbohydrate precursor (with and without the additives) was dissolved in deionized water (18.2 MΩ, Barnstead Nano-pure Diamond System). 4 μL of the solution (8 mg/mL) was transferred into an open-end cylinder quartz tube (1.9 mm diameter, 25 mm length) using a microliter syringe (Hamilton 700 series, 10 μL). The water was removed in a vacuum oven (0.7 atm) at 37 °C for 3 h.

A larger sample size was used for cellulose and corn stover, because these two substrates are not water soluble and the sample preparation procedure was necessarily different. A known amount of the sample was dispersed into DI water, and a known amount of suspension was transferred into quartz tube. The loaded tube was dried in a vacuum oven 0.7 atm), and sample weight was determined by difference using a microbalance (Citizen CM 11 scale, with linearity of ± 5 μg and repeatability of ± 3 μg,).

2.3 Pyroprobe coupled with GC-MS/FID system

Thin-film pyrolysis experiments were conducted using a Model 5150 pyroprobe analytical pyrolyzer (CDS Analytical Inc.) coupled to an Agilent 7890 GC with FID and 5977MSD detectors through a transfer line for online sampling and operated as described previously.[21] We noted the boiling point of LGA is 385 °C,[32] higher than the pyrolysis temperature of 350 °C. To identify any systematic errors resulting from potential condensation or decomposition of LGA in the system, we evaporated a known amount of LGA (mounted as a thin-film samples) and carried out the pyrolysis procedure at 350 °C. We found complete LGA mass balance, and concluded there was no LGA loss in our analytical system from either its condensation or decomposition. Other products were calibrated by injecting standard solutions into the GC/MS/FID system.

2.4 Pyrolysis data evaluation

Product yield values are reported in terms of molar carbon yield, where the moles of carbon in the product are divided by the moles of glucose carbons. For example, the carbon yield of LGA ($C_6H_{10}O_5$) (Y_{LGA}) for glucose is calculated as:

$$Y_{LGA} = \frac{moles\ of\ carbon\ in\ detected\ LGA}{initial\ moles\ of\ carbon\ in\ glucose\ unit} \times 100\% = \frac{6 \times (moles\ of\ detected\ LGA)}{6 \times initial\ moles\ of\ glucose\ unit} \times 100\% \qquad (1)$$

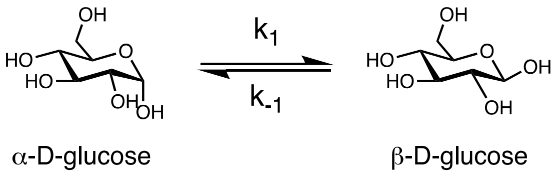
The carbon yields of other products were calculated in a similar way. All experiments were run in triplicate with average error of ± 7%.

2.5 Optical rotation

Optical rotations were measured on a SCHMIDT+HAENSCH polarimeter (Polartronic M) with a 5-cm cell. The as-purchased α-D-glucose (0.08g, 0.8g, 2.4 g) was dissolved in DI water to make

10 mL of solution at three different concentrations (0.04 M, 0.44 M, and 1.33 M). The solubility limit of glucose is ~5 M, but the highest concentration used here was 1.33 M because solutions at higher concentrations were too viscous to handle readily. The experiments were conducted at 20 °C using a wavelength of 589 nm. Time (t) was recorded as soon as glucose was introduced into DI water. The α_0 value was obtained by plotting α_t *vs* t, where α_t is the observed optical rotation of the solution at time t. The value of α_∞ (~12.6°) was measured at 24 h.

Glucose mutarotation reaction rates are assessed by experimentally determining the sum of the forward and back reaction rate constants ($k_{obs} = k_1 + k_{-1}$) of the reaction $A \rightleftharpoons B$, where A is α-D-glucose; B is β-D-glucose; k_1 is the rate constant for conversion of A into B; and k_{-1} is the rate constant for conversion of B into A (Scheme 2). The α and β forms interconvert through reversible cleavage of the bond between the ring oxygen and hemiacetal carbon.



Scheme 2. The mutarotation reaction between the two D-glucose isomers.

The rate law in differential form is expressed as

$$d[A]/dt = -\,k_1[A] + k_{-1}[B] \qquad (2)$$

where *[A]* is the concentration of A (α-D-glucose), *[B]* is the concentration of B (β-D-glucose).

At equilibrium

$$(d[A]/dt)_\infty = 0 = -k_1[A]_\infty + k_{-1}[B]_\infty \qquad (3)$$

where the subscript ∞ denotes at equilibrium.

Integration of equation (2) results in the following equation:

$$([A]_t - [A]_\infty)/([A]_0 - [A]_\infty) = \exp\,[-(k_1 + k_{-1})t] \qquad (4)$$

or

$$2.303 \times \log\{([A]_t - [A]_\infty)/([A]_0 - [A]_\infty)\} = -((k_1 + k_{-1})t = -\,k_{obs}t \qquad (5)$$

where k_{obs} represents how fast the system reaches equilibrium.

At a fixed path length (l) and total glucose concentration (units of g/100mL), the observed optical rotation (α_t) is directly proportional to the concentration of A ($[A]_t$):

$$\alpha_t = [\alpha_\lambda^T] \cdot [A]_t \cdot l \tag{6}$$

where $[\alpha_\lambda^T]$ is specific rotation, λ is wavelength, and T is temperature.

Equation (5) can be rewritten as

$$2.303 \log \{(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)\} = -k_{obs}t \tag{7}$$

From a plot of $\log \{(\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)\}$ as a function of t, k_{obs} (= k_1 + k_{-1}) can be determined from the slope (equal to $k_{obs}/2.303$). The units of k_{obs} are ks^{-1}.

2.6 Computation method

Quantum theoretical calculations of glucose were performed using Gaussian 09 program package[33] with density functional theory (DFT) B3LYP method and 6-31G(d,p) basis set. The calculation specified temperature at 873K (600 °C) in gas phase. The optimized molecular structures and electrostatic potential (MEP) map of glucose were visualized using GaussView 05 software.

3. Results and Discussion

3.1 Glucose pyrolysis with H_2SO_4-Na_2SO_4 combination

We first studied the effect of sufficient sodium sulfate (25 mol% relative to glucose) on the sulfuric-acid-catalyzed glucose pyrolysis (Fig. 1). Literature[23] indicates that sulfuric acid led to higher LGA yield in carbohydrate pyrolysis, compared with other mineral acids (such as HCl, HNO_3 and H_3PO_4). These other mineral acids have a limited effect likely because they have lower boiling points/decomposition temperatures, and would volatilize/decompose during pyrolysis.

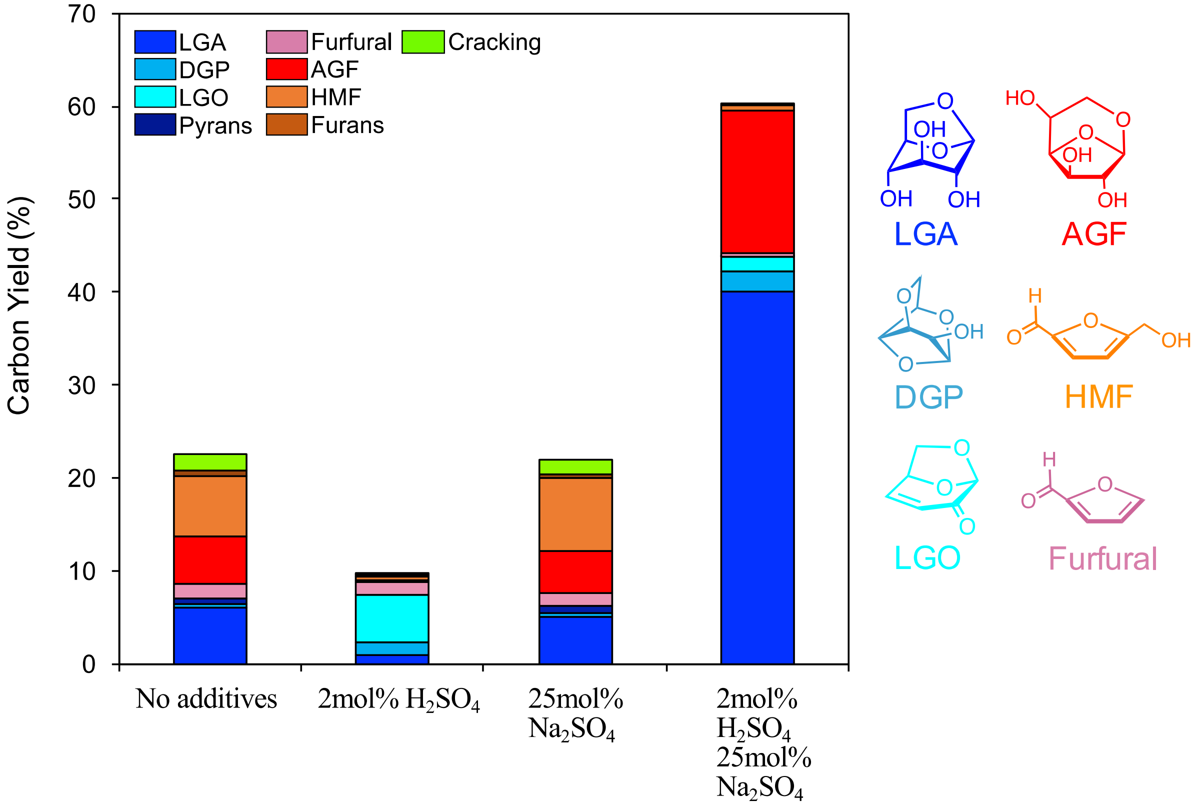


Fig. 1. GC-detectable-product carbon yield from glucose pyrolysis catalyzed by H_2SO_4 alone, or in combination with Na_2SO_4. Char residue accounts for the balance of undetected carbon. Test conditions: glucose mass = 32 μg, H_2SO_4/glucose = 2 mol%, Na_2SO_4/glucose = 25 mol%; pyrolysis temperature = 350 °C, heating time = 60 s. All experiments were run in triplicate. Abbreviations: LGA = levoglucosan; DGP = 1,4:3,6-dianhydroglucose; LGO = levoglucosenone; AGF = 1,6-anhydroglucofuranose; HMF = 5-hydroxymethylfurfural.

Glucose pyrolysis with no additives at 350 °C yielded ~22% gas-phase products in total, with LGA, AGF and HMF as major projects (Fig. 1). When H_2SO_4 was added to the sample, the total carbon yield decreased to ~10%, with a significant decrease in all products except for LGO. LGO yield increased, due to dehydration of LGA. In comparison, it was observed that Na_2SO_4 itself had little catalytic effect on glucose pyrolysis.

Together, the combination of Na_2SO_4 and H_2SO_4 greatly increased the overall product yield from ~22% to ~64%, and especially LGA yield from 6% to 40%. In addition, much less char residue was found in the quartz sample holder. AGF, HMF, furfural and furan derivatives (*e.g.*, 2(5H)-furanone, methyl 2-furoate) were categorized as "ring-opened products" since the species with five-membered ring are typically produced from ring-opening pathways[34], while LGA, LGO, DGP, and pyran derivatives (*i.e.*, pyranone, maltol) with six-membered ring were classified as "ring-locked products". We found that the ring-opened/ring-locked products molar ratio decreased from 1.90 to 0.37, when pyrolysis was carried out in the presence of Na_2SO_4 and H_2SO_4. This relative increase in ring-locked products strongly supports the notion of Na^+ inhibiting the pyranose ring from opening during pyrolysis.

3.2 Products of glucose pyrolysis in the presence of different metal sulfates

Prior studies showed that cations of metal salts interact more closely with carbohydrates than the anions.[20,35–40] We examined the effect of different salts, specifically the sulfates of the group I elements (M = Li, Na, K, Rb, and Cs). Glucose pyrolysis was carried out under the following conditions: (1) without any additives, (2) with H_2SO_4, (3) with a metal sulfate (M_2SO_4), and (4) with the combination of H_2SO_4 and (M_2SO_4). The amount of Na_2SO_4 (25 mol% relative to glucose) and H_2SO_4 (2 mol% relative to glucose) used here is the same as those in Fig. 1. The carbon yields of vapor phase products for these tests are shown in Fig. 2a.

Compared to our "base cases" (no additives or with H_2SO_4 only), the combination of H_2SO_4 and a M_2SO_4 had strong but different impacts on the yields of LGA and other products. The yields of LGA and AGF followed a volcano shape as the atomic number of the group I metal ions increased from Li^+ to Cs^+; the highest yield of LGA and total products occurred with Na^+. The metal ions (Cs^+, Rb^+ and K^+) of higher atomic number led to higher HMF formation (a ring-opened product). Metal ions (Li^+ and Na^+) of lower atomic number increased the yield of LGO (which is a dehydration product derived from LGA). Without H_2SO_4, group I metal sulfates themselves did not change the pyrolysis product yields much, though Rb^+ and Cs^+ led to slightly more HMF and less LGA and AGF.

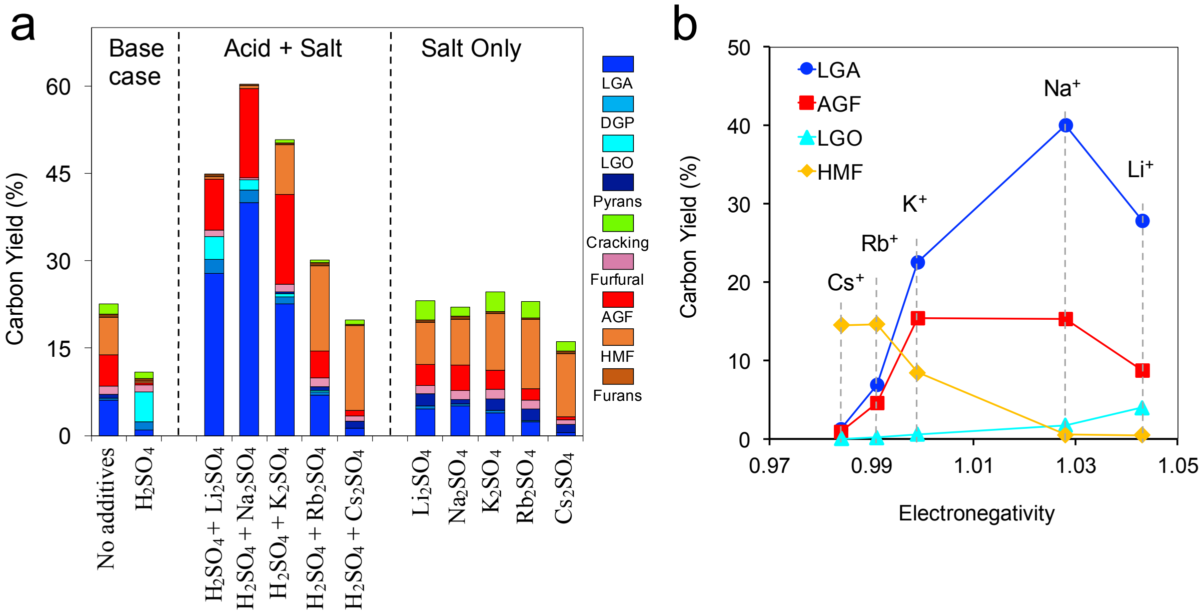


Fig. 2. (a) Glucose pyrolysis catalyzed by H_2SO_4 alone, or in combination with a metal sulfate M_2SO_4. (b) Correlation between the yields of the four major products and electronegativity values[41] of the monovalent metal cation M^+. Test conditions: glucose mass = 32 μg, H_2SO_4/glucose = 2 mol%, metal sulfate/glucose = 25 mol%; pyrolysis temperature = 350 °C, heating time = 60 s.

The wide range of product yields from the H_2SO_4/M_2SO_4 combinations suggests significant interaction of the cations with carbohydrates that select for different reaction pathways during pyrolysis.[38,42,43] We ascribe the strength of such interaction to the ability of the metal ion to attract electrons, which is characterized by a high electronegativity (EN) value. Accounting for electron affinity, ionization radius, and coordination numbers, EN values of the cations are generally higher than EN values of the zero-valent form (Table S1).[41]

As shown in Fig. 2b, metal ions with low EN's (Cs^+ and Rb^+) resulted in the formation of the ring-opened product HMF (~15%), and those with higher EN's led to high yields of ring-locked products of LGA (~35%), and minor amounts of HMF (<1%) and LGO (<1%). At the highest EN (Li^+), LGA and LGO yields decreased and increased, respectively. Unlike HMF, we noticed that the yield of AGF (the ring-opened product) followed LGA yields. This is consistent with a previous report[44] that there are two pathways that contribute to AGF formation: one involves LGA isomerization[45] and the other involves glucose ring opening[34]. If we consider Na^+ as having the optimum EN for LGA production, then a higher-EN metal cation promotes Lewis-acid-catalyzed dehydration reactions (which converts LGA into LGO) and a lower-EN metal cation does not prevent the glucose ring from opening (which leads to HMF formation).

In considering the electron density of the sugar oxygens, we understand qualitatively how EN has an important effect on the association of the metal cation with the oxygens. Glucose exists in two forms at equilibrium, a cyclic pyranose hemiacetal (>99%) and a linear aldehyde (<1%). The cyclic form has five hydroxyl oxygens and one ether oxygen (ring oxygen), and the linear form has five hydroxyl oxygens and one carbonyl oxygen. The electron density of the various oxygens follows as hydroxyl oxygen < ring (ether) oxygen < carbonyl oxygen (Fig. 3). Metal ions with intermediate EN (*e.g.*, Na^+) associate with the ring oxygen site, inhibiting H^+ from attacking this site and initiating ring-opening (Fig. 3a).

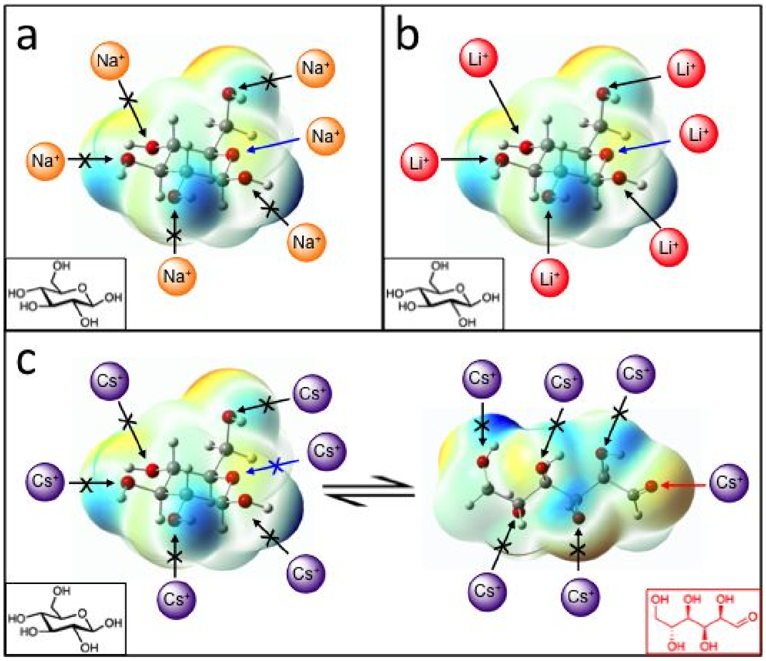


Fig. 3. Possible interactions between glucose and metal ions: (a) Na^+, (b) Li^+, and (c) Cs^+. The blue arrow represents the desired association of the metal cation with the ring oxygen, and the red arrow represents the undesired association of the metal cation with the carbonyl oxygen.

Metal ions with a higher EN (*e.g.*, Li^+) could associate with the ring oxygen as well as the hydroxyl oxygens and promote Lewis-acid-catalyzed bond cleavage (Fig. 3b)[38,43]. Metal ions with lower EN's (*e.g.*, Cs^+ and Rb^+) would weakly associate with the hydroxyl oxygen and the ring oxygen, allowing H^+ to attack the ring oxygen. They further associate with the carbonyl oxygen, which could stabilize the linear form of glucose after ring-opening and promote acid-catalyzed HMF formation (Fig. 3c).

3.3 Corroborating evidence for Na_2SO_4 as a ring-opening inhibitor

To corroborate the idea that Na^+ competes with H^+ for the ring oxygen and inhibits ring-opening reactions, we studied the aqueous-phase glucose mutarotation reaction in the presence of Na_2SO_4 and H_2SO_4. Glucose mutarotation involves the interconversion between the α and β cyclic anomers through the ring-opening of glucose. We hypothesized that fast mutarotation rates are due to rapid ring-opening in water, therefore correlating to rapid ring-opening (and decreased LGA formation) during pyrolysis.

Acid solutions promote glucose mutarotation by protonating the ring oxygen atom resulting in ring opening and conversion to the linear form of glucose. At a lower glucose concentration (0.04 M), the observed glucose mutarotation rate constant increased from 0.27 ks^{-1} to ~0.29 ks^{-1} when adding H_2SO_4 (2.5 mol%) (Fig. 4). The co-addition of 25 mol% Na_2SO_4 lowered acid-catalyzed glucose mutarotation rate constants from ~0.29 ks^{-1} to ~0.28 ks^{-1}. This is consistent with idea that Na^+ competes with H^+ for the ring oxygen site, and thus hindering acid-catalyzed glucose mutarotation.

The acid and salt effects were more apparent at higher glucose concentrations. At a glucose concentration of 1.33 M (and the same ratio among glucose, Na_2SO_4 and H_2SO_4), the mutarotation rate constant increased from 0.30 ks^{-1} to 0.75 ks^{-1} with acid and decreased to 0.68 ks^{-1} with Na^+ co-addition. This suggests that the Na^+ inhibition effect on acid-catalyzed ring-opening is strong within the salt/acid/glucose thin films used in the pyrolysis experiments. Na^+ outcompetes H^+ for the ring oxygen, slowing ring-opening and leading to greater LGA selectivity and yield.

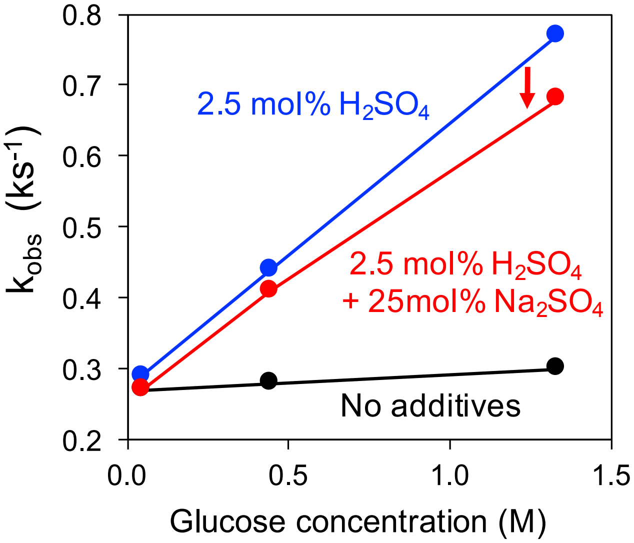


Fig. 4. Glucose optical rotation rate constant k_{obs} as a function of glucose concentration in three cases: (1) no additives, (2) 2.5mol% H_2SO_4, (3) 2.5mol% H_2SO_4 + 25mol% Na_2SO_4. The ratios of H_2SO_4, Na_2SO_4 and glucose are constant.

3.4 H_2SO_4 and Na_2SO_4 loading effect on pyrolysis products

We examined a full range of Na_2SO_4 (0-25 mol%) and H_2SO_4 (0-5.5 mol%) concentrations on product yields, to gain a deeper understanding of the competition between Na^+ and H^+ for the glucose ring oxygen (Fig. 5).

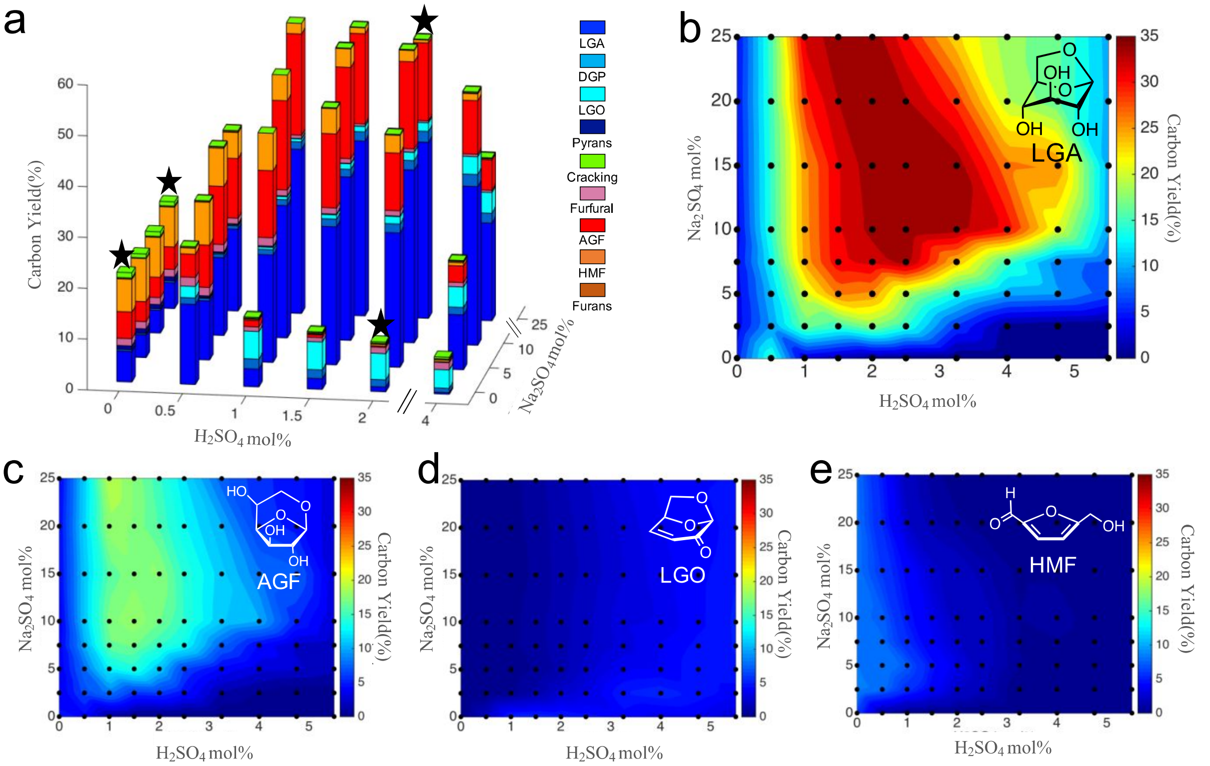


Fig. 5. (a) Carbon yields from glucose pyrolysis as functions of H_2SO_4 (0-5.5 mol% relative to glucose) and Na_2SO_4 content (0-25 mol% relative to glucose). The data of Fig. 1 are marked by black-filled stars. (b)-(e) Response maps showing LGA, AGF, LGO and HMF yields interpolated from 80 experimental data points (marked by black-filled circles). All experiments were repeated more than three times. Test conditions: glucose mass = 32 μg, pyrolysis temperature = 350 °C, heating time = 60 s.

With 0 mol% Na_2SO_4, glucose pyrolysis resulted in yields of LGA, AGF, HMF, and furfural that increased, peaked, and decreased with increasing H_2SO_4 content. The yields of DGP and LGO continued to increase. The product distribution suggests the typical non-selective acid-catalyzed mechanism (*e.g.*, ring-opening and ring-locking pathways). The increased H_2SO_4 loading promoted sequential dehydration, decomposition and condensation reactions. The yield of LGA reached a maximum of 16% when H_2SO_4 was 0.5 mol%.

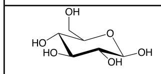
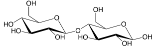
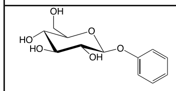
We then considered the influence of added Na_2SO_4 on glucose pyrolysis. At the lower H_2SO_4 loadings (<0.5 mol%), higher Na_2SO_4 content had no noticeable impact on LGA yield (Fig. 5a,b). At higher H_2SO_4 loadings (≥1 mol%), higher Na_2SO_4 content significantly increased LGA yield. As shown in Fig. 5a and Fig. 5b, LGA reached maximum yields at moderate-to-high Na_2SO_4 loadings (>10 mol%) and moderate H_2SO_4 loading (1.5-2.5 mol%). These data indicate that the competition between Na^+ and H^+ is not obvious at lower H_2SO_4 and Na_2SO_4 loadings, but at higher H_2SO_4 and Na_2SO_4 loadings, the Na^+ competes effectively with the H^+ to inhibit ring-opening and therefore increasing LGA yield. These results are consistent with mutarotation results (Fig. 4, S1).

In addition, the yield of AGF (Fig. 5c) followed a similar trend to LGA case, which further supporting the idea that AGF may arise from LGA isomerization. To probe this, we pyrolyzed LGA in the presence of H_2SO_4 and/or Na_2SO_4. LGA was not reactive but it became highly reactive in the presence of H_2SO_4. AGF yield increased from <1% to ~5% when in the co-presence of Na_2SO_4 (Fig. S2, Scheme S1). LGO (which comes from the dehydration of LGA) had higher yield at high acid loading (>3.25 mol%) and lower yield at high Na_2SO_4 (Fig. 5d). HMF was favored at low acid loadings (<1.5 mol%), and moderate Na_2SO_4 loading (Fig. 5e).

3.5 Application of H_2SO_4-Na_2SO_4 system to complex biomass

Having demonstrated that the co-addition of Na_2SO_4 and H_2SO_4 significantly enhanced LGA yields from glucose pyrolysis, we applied this concept to more complex glucose-containing substrates. The LGA yield from the pyrolysis of cellobiose, phenyl-β-glucoside and α-cyclodextrin all increased with Na_2SO_4/H_2SO_4 co-addition (Table 1). As discussed previously, LGA yield from glucose pyrolysis increased from 6% to 40% with Na_2SO_4/H_2SO_4. The overall ratio of ring-opened products (*e.g.*, AGF and HMF) to ring-locked products (*e.g.*, LGA and LGO) decreased, from 1.90 to 0.37.

Table 1. Product yields from the pyrolysis of different glucose-based substrates without and with Na_2SO_4+H_2SO_4.[a,b,c]

Substrate	*Ratio of glycosidic bonds to glucose units*	LGA		AGF		LGO		HMF		Ratio of ring-opening to ring-locking products	
		w/o	w/	w/o	w/	w/o	w/	w/o	w/	w/o	w/
 β-glucose	0	6%	40%	5%	15%	0%	2%	6%	<1%	1.90	0.37
 Cellobiose	0.5	16%	38%	3%	7%	0%	2%	9%	<1%	0.86	0.29
 Phenyl-β-glucoside	1	28%	70%	0%	7%	0%	4%	0%	0%	0	0.09
α-Cyclodextrin	1	22%	55%	<1%	6%	0%	3%	2%	<1%	0.12	0.13
Cellulose**	~1	10%	40%	0%	3%	0%	<1%	0%	<1%	0	0.11
Corn stover**	~1	4wt%	9wt%	<1wt%	<1wt%	0wt%	1wt%	<1wt%	<1wt%	~0.19	~0.10

[a]Test conditions: H_2SO_4/glucose-unit = 2 mol%, Na_2SO_4/glucose-unit = 25 mol%

[b]For β-glucose, phenyl-β-glucoside and α-cyclodextrin: sugar = 32 μg, Na_2SO_4 = 6.3 μg, H_2SO_4 = 0.4 μg; pyrolysis temperature = 350 °C

[c]For cellulose and corn stover: substrate = 200-300 μg, Na_2SO_4 = 78.9 μg, H_2SO_4 = 4.4 μg; pyrolysis temperature = 600 °C

Cellobiose contains two glucose units linked with one *1-β-4'*-glycosidic bond. This bond is located at the anomeric carbon of one unit, and the other glucose ring has a hydroxyl group at its anomeric carbon. We can consider this compound and β-glucose to have a glycosidic-bond/glucose-unit ratio of 0.5 and 0, respectively. Cellobiose pyrolysis generated more LGA (yield of 16%) and less ring-opened products compared to glucose pyrolysis. This observation is similar to previous reports[31,44] and is consistent with the ring-locking concept[21] that glycosidic bond hinders the ring-opening of one of the glucose units and enhance LGA production. With Na_2SO_4/H_2SO_4 co-addition, the LGA yield increased to 38% and the ring-opened/ring-locked product ratio decreased from 0.86 to 0.29. The Na^+ successfully hinders ring-opening of the other glucose unit.

Phenyl-β-glucoside has a phenoxy group at the anomeric carbon; we can consider this sugar compound to have a glycosidic-bond/glucose-unit ratio of 1. Its pyrolysis generated even more LGA (yield of 28%) and no ring-opened products, compared to glucose and cellobiose pyrolysis. The results show a positive correlation between LGA yield and glycosidic-bond/glucose-unit ratio. With Na_2SO_4/H_2SO_4 co-addition, the LGA yield increased to 70%. The ring-opened/ring-locked product ratio increased slightly from zero to 0.09, due to AGF formed from Na^+-associated LGA.

The oligosaccharide α-cyclodextrin contains six glucose units linked into ring structure via glycosidic bonds between an anomeric carbon and carbon-4 of adjacent units. Its pyrolysis generated more LGA and less ring-opened products compared to glucose pyrolysis, as expected for a compound with a higher glycosidic-bond/glucose-unit ratio. With Na_2SO_4/H_2SO_4 co-addition, the LGA yield increased from 22% to 55%. The ring-opened/ring-locked product ratio did not change significantly. Even though α-cylodextrin and phenyl-β-glucoside had the same glycosidic-bond/glucose-unit ratio of 1, their pyrolysis products were not the same. We attribute these differences to the glucose units of α-cyclodextrin having the glycosidic bond in the α position instead of the β position. A functional group at the anomeric carbon inhibits ring-opening more effectively in the β position.[21]

Finally, we explored the impact of Na_2SO_4/H_2SO_4 co-addition on cellulose and corn stover pyrolysis. These substrates have glycosidic-bond/glucose-unit ratios of ~1, but their cellulose content is crystalline in structure, impacting their pyrolysis chemistry. We performed pyrolysis at 600 °C, as no reaction occurred at 350 °C. We observed that LGA yield increased for both substrates with Na_2SO_4/H_2SO_4 co-addition. In the cellulose case, LGA yield increased from 10% to 40%. Product yields were difficult to quantify in the corn stover case. This biomass material contains lignin and hemicellulose, and its pyrolysis is known to yield a plethora of compounds like acetyl furan, 1-hydroxy-2-butanone, methyl glyoxal, 2-(4-methoxyphenyl)ethanol, 4-hydroxy-3-methoxyphenyl acetone and others.[1,46] We estimated LGA yield (normalized to mass of the cellulose content) increased from 4 to 9 wt% when Na_2SO_4/H_2SO_4 was co-added.

4. Conclusions

In this work, we identified that the combination of Na_2SO_4 and an acid (*e.g.*, H_2SO_4) significantly enhanced the yield of levoglucosan as a result of ring-locking. Group I metal sulfates (Li, Na, K, Rb and Cs) were selected as the potential salt inhibitors in this study, among which Na_2SO_4 gave the highest LGA yield. Na^+ ion has the appropriate ionic electronegativity for the preferred binding at ring oxygen site, such that it helps hinder protonation at the ring oxygen (and thereby inhibiting ring-opening and consequent reactions). Solution-phase optical rotation data indicated that excess amount of Na^+ reduced the reaction rate of acid-catalyzed glucose mutarotation (as a proxy of ring opening), through the competition with H^+ for the ring oxygen. The Na_2SO_4-H_2SO_4 system can also be applied to more complex substrates such as cyclodextrin and cellulose to greatly improve the yield of levoglucosan during pyrolysis. The addition of an acid and a salt enables the high-yield synthesis of LGA and other anhydrosugars from carbohydrate pyrolysis.

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