Received: 1 March 2015 ■ *Revised: 26 March 2015* ■ *Accepted: 30 March 2015* ■ *Publication: 19 June 2015*

EJMS EUROPEAN JOURNAL OF MASS SPECTROMETRY

Special Issue Celebrating the 20th Anniversary of *EJMS—European Journal of Mass Spectrometry*

Mass spectrometric studies of fast pyrolysis of cellulose

John C. Degenstein,[a] Matt Hurt,[b] Priya Murria,[b] Mckay Easton,[a] Harshavardhan Choudhari,[a] Linan Yang,[b] James Riedeman,[b] Mark S. Carlsen,[b] John J. Nash,[b] Rakesh Agrawal,[a] W. Nicholas Delgass,[a] Fabio H. Ribeiro[a] and Hilkka I. Kenttämaa[b,*]

[a]School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

[b]Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA. *E-mail: hilkka@purdue.edu

A fast pyrolysis probe/linear quadrupole ion trap mass spectrometer combination was used to study the primary fast pyrolysis products (those that first leave the hot pyrolysis surface) of cellulose, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose, as well as of cellobiosan, cellotriosan, and cellopentosan, at 600°C. Similar products with different branching ratios were found for the oligosaccharides and cellulose, as reported previously. However, identical products (with the exception of two) with similar branching ratios were measured for cellotriosan (and cellopentosan) and cellulose. This result demonstrates that cellotriosan is an excellent small-molecule surrogate for studies of the fast pyrolysis of cellulose and also that most fast pyrolysis products of cellulose do not originate from the reducing end. Based on several observations, the fast pyrolysis of cellulose is suggested to initiate predominantly via two competing processes: the formation of anhydro-oligosaccharides, such as cellobiosan, cellotriosan, and cellopentosan (major route), and the elimination of glycolaldehyde (or isomeric) units from the reducing end of oligosaccharides formed from cellulose during fast pyrolysis.

Keywords: ion trap mass spectrometry, linear quadrupole ion trap, fast pyrolysis, cellulose, cellotriosan

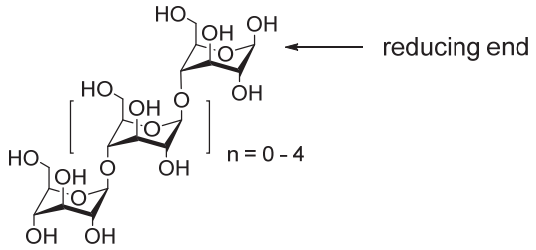
Introduction

Fast pyrolysis (rapid heating in an inert atmosphere) is an attractive alternative for the conversion of biomass into fuels or valuable chemicals because it is a relatively simple and scalable process.[1–4] Most studies thus far have focused on fast pyrolysis of cellulose since it is the simplest polymer in biomass.[1–4] Unfortunately, even for cellulose, the final fast pyrolysis products (often referred to as biooil in the literature) are a complex unstable mixture of molecules having an oxygen content too high to be used (directly) as a fuel.[1–4] Upgrading this mixture is hindered by its extreme complexity, which arises from numerous competing and consecutive reactions both during and after pyrolysis.[1–4] Currently, no agreement exists in the literature on the mechanisms (e.g., radical, ionic, or neither) of the fast pyrolysis reactions of cellulose, the sequence of these reactions, or the identity of the primary products of fast pyrolysis, although anhydro-oligomers, in general, have been proposed as intermediates several times.[1–6]

With the aim of gaining a deeper understanding of the fast pyrolysis of cellulose, which may allow better control over the final products, the primary products of the fast pyrolysis of cellulose, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose (Scheme 1), as well as of cellobiosan, cellotriosan, and cellopentosan, were determined using a previously described mass spectrometry methodology.[7] Primary products, as considered here, are the very first products to evaporate from the hot surface (at 600°C) where pyrolysis occurs.

The reactor configuration utilized in this work was specifically designed[7] to detect the primary products and not to allow them to undergo further reactions. It has been previously reported that the pyrolysis reactor configuration is of critical importance to the product distribution produced from the

ISSN: 1469-0667
doi: 10.1255/ejms1335



Scheme 1. The carbohydrate molecules studied here contain two to six D-glucose units coupled to each other in a linear manner via β(1→4) linkages, just as in cellulose.

fast pyrolysis of cellulose.[1b,4] Hence, the primary products detected here may not be the same as detected in a reactor of a different design. The gaseous molecules were ionized via atmospheric pressure chemical ionization (APCI) using either chloroform in methanol (negative ion mode, Cl^- attachment) or ammonium hydroxide in water (positive ion mode, NH_4^+ or proton attachment) in order to ensure that all the products were ionized and detected.[7] Based on previous model compound studies, both methods have been found[7] to ionize all the major pyrolysis products of cellobiose (some minor products were ionized by only one or the other methods). Hence, only the positive ion mode results are discussed below. The structures of most of the ions formed from cellobiose and cellulose have been examined[7,8] previously by using tandem mass spectrometry (MS^2) experiments [i.e., by isolating them and subjecting them to collision-activated dissociation (CAD)]. When necessary, the structures of the fragment ions were examined by isolating them and subjecting them to CAD (MS^3 experiment).[7] Where possible, structures were confirmed[7] by analyzing authentic compounds. High-resolution mass spectral data needed to determine the elemental compositions of the ions were collected using a Thermo Scientific linear quadrupole ion trap (LQIT)/Fourier-transform ion cyclotron resonance mass spectrometer.[7] Similar studies were carried out in this research for the fast pyrolysis products of cellotriose, cellotetraose, cellopentaose, and cellohexaose, as well as of cellobiosan, cellotriosan, and cellopentosan.

Experimental methods

The pyrolysis method[7] employed here is based on the coupling of a very fast-heating (up to 20,000°C s^{-1}) Pyroprobe 5200 (CDS Analytical, Oxford, PA) to a Thermo Scientific LTQ LQIT mass spectrometer (Waltham, MA) through a custom-built adaptor. The pyrolysis probe uses a resistively heated platinum ribbon (2.1 mm × 35 mm × 0.1 mm). The pyrolysis probe was placed inside the APCI source of the linear quadrupole ion trap and the ribbon was heated up to 600°C at a rate of 1000°C s^{-1}. The primary products of pyrolysis evaporated into a nitrogen atmosphere at 100°C in the ion source and were quenched. The gaseous molecules were ionized via APCI using ammonium hydroxide in water (positive ion mode; NH_4^+ or proton attachment). The structures of the ions were examined by CAD in MS^2 and MS^3 experiments and their elemental compositions were determined by high-resolution measurements using a Thermo Scientific LQIT/Fourier-transform ion cyclotron resonance mass spectrometer. We are currently unable to determine mass balance for this pyrolysis experiment. However, quantitation of the pyrolysis products was performed using a pyrolysis–gas chromatography/mass spectrometry (GC/MS) set-up (see the Supporting Information).

Results and discussion

The primary products of the fast pyrolysis of cellobiose, the simplest compound studied, are shown in Figure 1 (top).[7,8] The relative abundances of the ions reflect the relative abundances of the products that produced them, as verified earlier by using authentic compounds.[7] Only ten major products were observed (with an abundance of at least 10% compared to the most abundant product) and they are consistent with those recently reported in the literature.[7,8] The unambiguously identified[7] products include hydroxymethylfurfural (protonated molecule, *m/z* 127), levoglucosan (NH_4^+ adduct, *m/z* 180), glucose (NH_4^+ adduct, *m/z* 198), β-D-glucopyranosylglycolaldehyde [NH_4^+ adduct, *m/z* 240; note that this product is formed[8] by the loss of two glycolaldehyde units (or isomers) from cellobiose], and cellobiosan (NH_4^+ adduct, *m/z* 342). Based on our preliminary computational studies,[8] the formation of cellobiosan has the lowest energy barrier of these reactions. Two levoglucosan isomers were generated, one that forms an NH_4^+ adduct (*m/z* 180) like the authentic compound and one that does not (protonated molecule, *m/z* 163).[7,8] This finding is in agreement with an earlier report wherein the structure (anhydroglucofuranose) was proposed for the second isomer.[9] It is also noteworthy that levoglucosan is not the major primary product of fast pyrolysis, although it is a major final product.[1,2] In prior reports that utilized on-stream fast pyrolysis-GC/MS, the largest molecules that were observed for cellulose (and oligosaccharide) pyrolysis were levoglucosan and its isomers.[2] This may be explained by the high final temperature of about 300°C typically used in GC analysis, which opens the possibility for secondary reactions of larger primary products. Further, the pyrolysis-MS reactor discussed here achieves both pyrolysis *and downstream analysis* in as little as 125 + 57 ms (see the Supporting Information for details), whereas a pyrolysis-GC/MS reactor requires from two up to 30 minutes, depending on the elution times of the products.

All the major products observed upon the fast pyrolysis of cellobiose were also observed for cellotriose, cellotetraose, cellopentaose, cellohexaose, and even cellulose, albeit with different relative abundances. Specifically, the abundances of β-D-glucopyranosylglycolaldehyde [*m/z* 240, dominant product for cellobiose formed via the loss of two glycolaldehyde molecules (or isomers)], glucose (*m/z* 198), cellobiose that has lost a glycolaldehyde molecule (or isomer, *m/z* 300), and cellobiose that has lost both a glycolaldehyde molecule (or isomer) and a

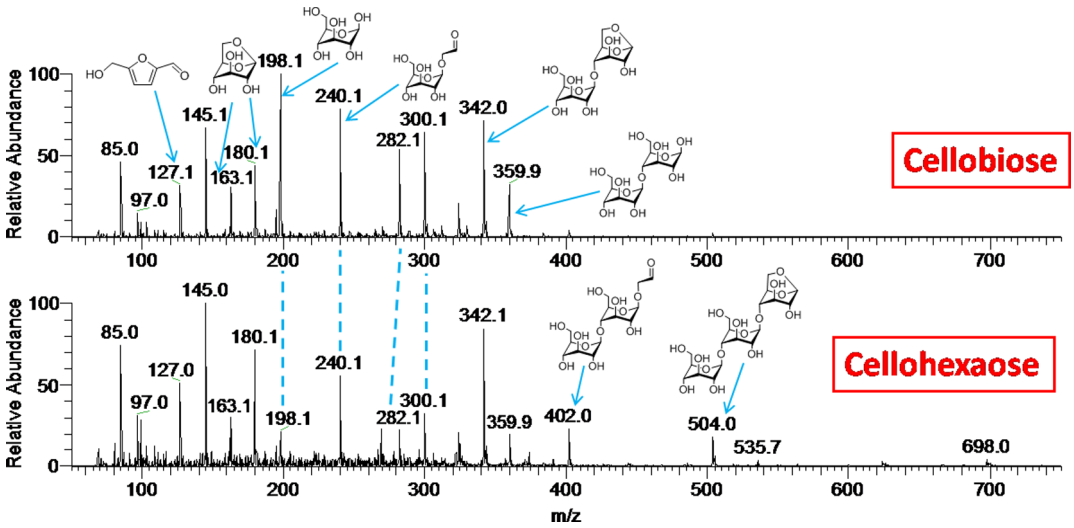


Figure 1. Positive ion mode mass spectra showing the primary products of the fast pyrolysis of cellobiose (top) and cellohexaose (bottom) ionized by APCI with ammonium hydroxide. The ions whose relative abundances differ the most are indicated with dotted lines. Two isomers of levoglucosan were observed, levoglucosan itself (ion of *m/z* 180) and another isomer (ion of *m/z* 163). All the structures shown for cellobiose have been identified[7] by CAD mass spectral comparison using authentic compounds.

water molecule (*m/z* 282) decrease systematically proceeding from the dimer to trimer, tetramer, pentamer, hexamer, and cellulose. For example, Figure 1 shows a comparison of the primary products of the fast pyrolysis of cellobiose (top) and cellohexaose (bottom). It is obvious that the four products listed above (highlighted with dotted lines in Figure 1) have substantially lower abundances for cellohexaose than for cellobiose. For cellulose, their abundances are even lower, as shown in Figure 2 (bottom). These findings suggest that the four products described above are somehow associated with the terminal glucose units because the ratio of the terminal units to the total number of glucose units decreases as the size of the oligomer increases. Indeed, the ratio of the end group to the monomer has been reported[3] to be a vital descriptor of cellulose pyrolysis chemistry.

In addition to the products observed for cellobiose, the oligomers studied generated two larger products: a molecule likely to be β-D-cellobiopyranosylglycolaldehyde (NH_4^+ adduct, *m/z* 402) and cellotriosan (NH_4^+ adduct, *m/z* 504, verified by comparison of its CAD mass spectrum to that of an authentic sample). Cellulose also produced a very small amount of cellotetrosan [NH_4^+ adduct, *m/z* 666, verified by comparison of its CAD mass spectrum to an authentic sample (Figure 2, bottom)]. Hence, cellotriosan appears to be the largest product with a significant abundance that is efficiently able to escape the hot pyrolysis surface for cellotriose and the larger oligosaccharides as well as cellulose during the fast pyrolysis at 600°C.

Inspired by the above observations, the fast pyrolysis of cellotriosan was also performed. Cellobiosan dominates this

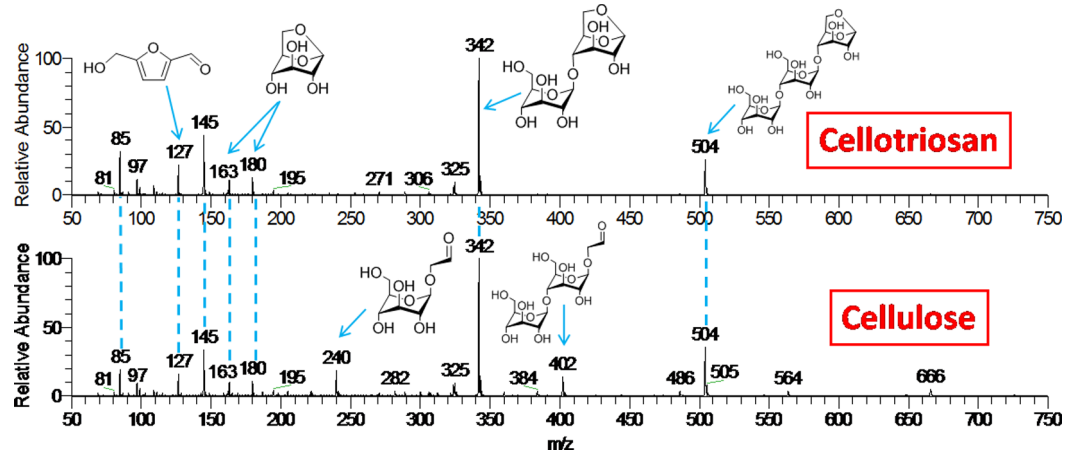


Figure 2. Positive ion mode mass spectra showing the primary products of the fast pyrolysis of cellotriosan (top) and cellulose (bottom) ionized by APCI with ammonium hydroxide. Some of the ions having the same *m/z* ratio are indicated with a dotted line.

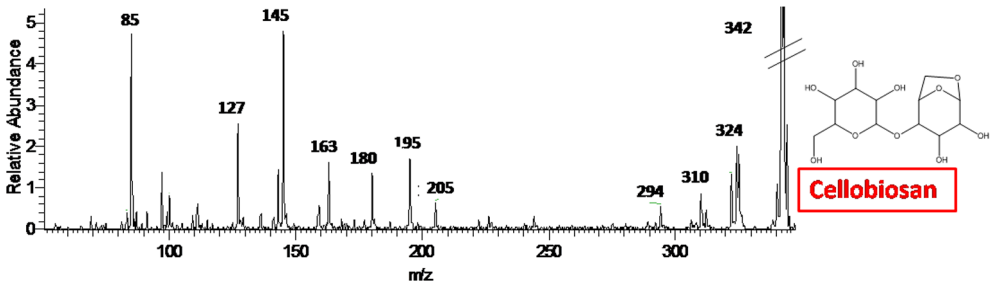
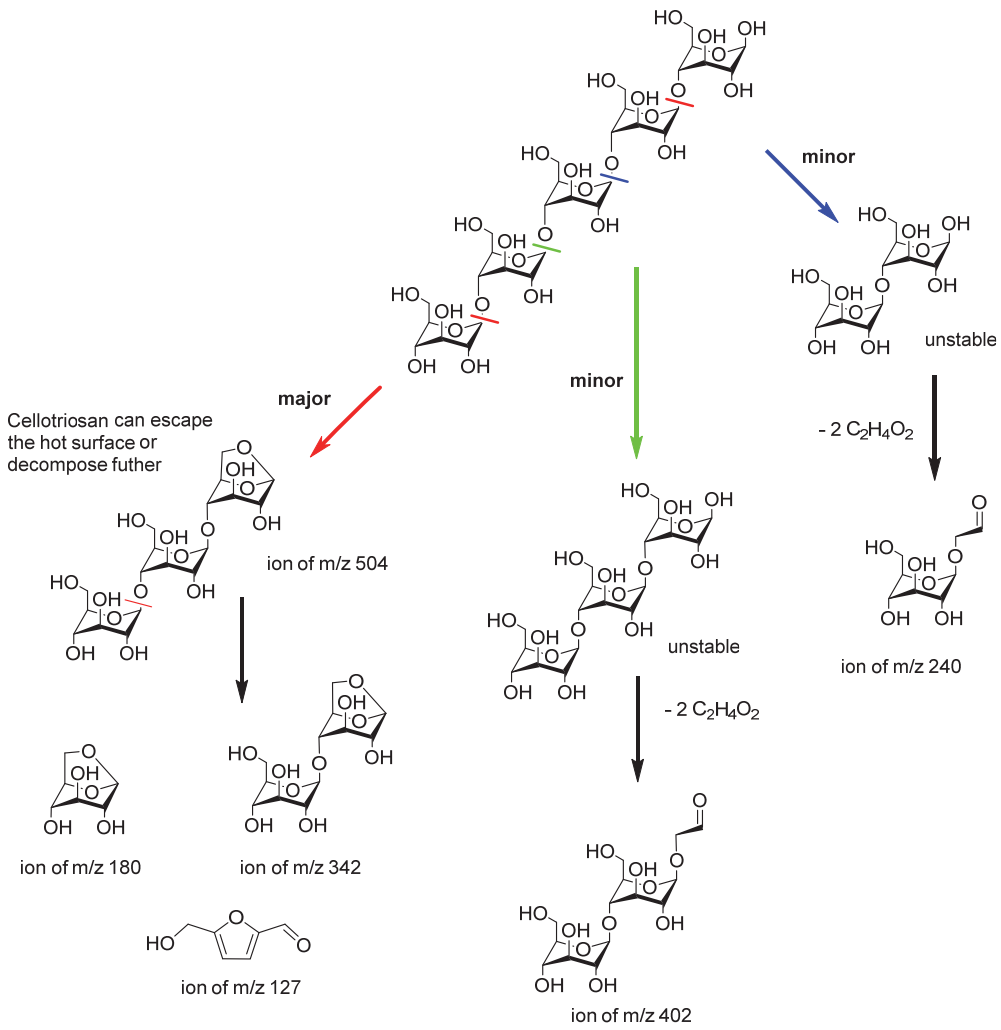


Figure 3. A positive ion mode mass spectrum showing the primary products of the fast pyrolysis of cellobiosan (*m/z* 342) ionized by APCI with ammonium hydroxide. The ions of *m/z* 85, 127, 145, 163, 180, and 195 are also formed for cellotriosan, cellopentosan and cellulose. The ion of *m/z* 324 results from the loss of H_2O from the ion of *m/z* 342.

product distribution. However, all the major products observed for cellobiose and the oligomers were also observed, with the following exceptions: glucose (*m/z* 198), β-D-glucopyranosylglycolaldehyde (*m/z* 240), the product corresponding to cellobiose that has lost a glycolaldehyde molecule (or isomer, *m/z* 300), and the product corresponding to cellobiose that has lost both a glycolaldehyde (or isomer) and a water molecule (*m/z* 282). These are the four products mentioned above as



Scheme 2. A simple schematic of the major fast pyrolysis pathways proposed for oligosaccharides formed from cellulose during fast pyrolysis upon addition of water. The cleavages indicated in red are thought to occur in the middle of a cellulose chain. The cleavages indicated in blue and green likely occur only at the reducing terminals, which for long chains of cellulose represent a small overall fraction of the total units. Hence, they are minor pathways.

being somehow associated with the terminal glucose units. As the reducing end in cellotriosan has been modified compared to that in cellotriose, and cellotriose yields these four products but cellotriosan does not, the formation of these four products is likely to depend on the presence of the reducing end in cellotriose. The same is true for cellobiosan (Figure 3) except that no ions larger than *m/z* 342 (ionized cellobiosan) were observed. The mechanisms of these fragmentations are currently being investigated using quantum chemical calculations. The most surprising finding made in this study is that the fast pyrolysis product distribution of cellotriosan (and cellopentosan) is nearly identical to that of cellulose (Figure 2). The most significant differences are the formation of β-D-glucopyranosylglycolaldehyde (*m/z* 240) and β-D-cellobiopyranosylglycolaldehyde (*m/z* 402) for cellulose but not for cellotriosan (or cellopentosan).These two products correspond to cellotriose that has lost two glycolaldehyde molecules (or isomers) (*m/z* 402) and cellobiose that has undergone the same losses (*m/z* 240). These findings suggest that the fast pyrolysis of cellulose may be initiated predominantly via two competing processes—the formation of anhydro-oligosaccharides, such as cellobiosan, cellotriosan, and cellopentosan (major route), and the elimination of glycolaldehyde (or isomeric) units from the reducing end of oligosaccharides formed from cellulose during fast pyrolysis [minor route leading to products of *m/z* 240 and *m/z* 402 (Scheme 2)].

Conclusions

The results suggest that molecules larger than cellotriosan are not able to leave the heated surface efficiently during fast pyrolysis of oligosaccharides at 600°C. Instead, they undergo further degradation on the hot surface. The observation of very similar primary product distributions for the fast pyrolysis of cellotriosan and cellulose suggests that cellotriosan presents an excellent small-molecule surrogate for cellulose, and it should be a much better choice than glucose, which has been considered previously.[3]

Based on the primary products observed for cellotriosan and cellulose, the fast pyrolysis of cellulose under the conditions used here may be initiated predominantly via two competing pathways. One involves the formation of small anhydro-oligosaccharides (but not predominantly levoglucosan, as suggested in the literature[1–3]) that either evaporate from the hot pyroprobe surface or degrade to yield most of the other primary products (major pathway). The other involves the elimination of glycolaldehyde (or isomeric) molecules from the reducing end of small oligosaccharides formed from cellulose during the pyrolysis to yield volatile β-D-cellobiopyranosyl-glycolaldehyde and β-D-glucopyranosylglycolaldehyde molecules (ions of *m/z* 240 and *m/z* 402 (Scheme 1)). Reactions of the primary products of fast pyrolysis are currently under investigation in order to understand better how the final fast pyrolysis products are formed. These reactions may explain why levoglucosan is a major final fast pyrolysis product but not a major primary product.

Supporting information

Detailed descriptions of the pyrolysis probe/tandem mass spectrometry and gas chromatography/mass spectrometry (GC/MS) experiments and quantitative product distribution determined using GC/MS experiments can be found in the online version at http://dx.doi.org/10.1255/ejms.1335.

Notes

The authors declare no competing financial interest.

Acknowledgments

The authors gratefully acknowledge partial financial support by the Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0000997. The work by John C. Degenstein was supported by the National Science Foundation EFRI (0938033-DGE).

References

1. (a) D. Shen, R. Xiao, S. Gu and K. Luo, "The pyrolytic behavior of cellulose in lignocellulosic biomass: a review", *RSC Adv.* **1,** 1641 (2011). doi: http://dx.doi.org/10.1039/c1ra00534k (b) G. Huber, S. Iborra and A. Corma, "Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering", *Chem. Rev.* **106,** 4044 (2006). doi: http://dx.doi.org/10.1021/cr068360d

2. (a) R. Vinu and L.J. Broadbelt, L. "A mechanistic model of fast pyrolysis of glucose-based carbohydrates to predict bio-oil composition", *J. Energy Environ. Sci.* **5,** 9808 (2012). doi: http://dx.doi.org/10.1039/c2ee22784c (b) H.B. Mayes and L.J. Broadbelt, "Unraveling the reactions that unravel cellulose", *J. Phys. Chem. A* **116,** 7098 (2012). doi: http://dx.doi.org/10.1021/jp300405x

3. (a) M.S. Mettler, S.H. Mushrif, A.D. Paulsen, A.D. Javadekar, D.G. Vlachos and P.J. Dauenhauer, "Revealing pyrolysis chemistry for biofuels production: conversion of cellulose to furans and small oxygenates", *Energy Environ. Sci.* **5,** 5414 (2012). doi: http://dx.doi.org/10.1039/C1EE02743C (b) M.S. Mettler, A.D. Paulsen, D.G. Vlachos and P.J. Dauenhauer, "The chain length effect in pyrolysis: bridging the gap between glucose and cellulose", *Green Chem.* **14,** 1284 (2012). doi: http://dx.doi.org/10.1039/c2gc35184f

4. (a) P.R. Patwardhan, D.L. Dalluge, B.H. Shanks and R.C. Brown, "Distinguishing primary and secondary reactions of cellulose pyrolysis", *Biores. Tech.* **102,** 5265 (2011) doi: http://dx.doi.org/10.1016/j.biortech.2011.02.018. (b) P.R. Patwardhan, J.A. Satrio, R.C. Brown and B.H. Shanks, "Product distribution from fast pyrolysis of glucose-based carbohydrates", *J. Anal. Appl. Pyrolysis* **86,** 323 (2009). doi: http://dx.doi.org/10.1016/j.jaap.2009.08.007

5. V. Agarwal, P.J. Dauenhauer, G.W. Huber and S.M. Auerbach, "*Ab initio* dynamics of cellulose pyrolysis: nascent decomposition pathways at 327 and 600°C", *J. Am. Chem. Soc.* **134,** 14958 (2012). doi: http://dx.doi.org/10.1021/ja305135u

6. J. Piskorz, P. Majerski, D. Radlein, A. Vladars-Usas and D.J. Scott, "Flash pyrolysis of cellulose for production of anhydro-oligomers", *J. Anal. App. Pyr.* **56,** 145 (2000). doi: http://dx.doi.org/10.1016/S0165-2370(00)00089-9

7. M.R. Hurt, J.C. Degenstein, P. Gawecki, D.J. Borton II, N.R. Vinueza, L. Yang, R. Agrawal, W.N. Delgass, F.H. Ribeiro and H.I. Kenttämaa, H. I. "On-line mass spectrometric methods for the determination of the primary products of fast pyrolysis of carbohydrates and for their gas-phase manipulation", *Anal. Chem.* **22,** 10927 (2013). doi: http://dx.doi.org/10.1021/ac402380h

8. J.C. Degenstein, P. Murria, M. Easton, H. Sheng, M. Hurt, A.R. Dow, J. Gao, J. Nash, R. Agrawal, W.N. Delgass, F. Ribeiro and H.I. Kenttämaa, "Fast pyrolysis of ^{13}C-labeled cellobioses: gaining insights into the mechanisms of fast pyrolysis of carbohydrates", *J. Org. Chem.* **80,** 1909 (2015). doi: http://dx.doi.org/10.1021/jo5025255

9. Q. Lu, X. Yang, C. Dong, Z. Zhang, X. Zhang and X. Zhu, "Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: analytical Py-GC/MS study", *J. Anal. Appl. Pyr.* **92,** 430 (2011). doi: http://dx.doi.org/10.1016/j.jaap.2011.08.006