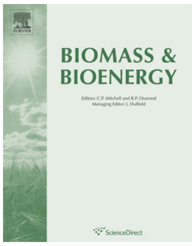
BIOMASS AND BIOENERGY 74 (2015) 1–5

Available online at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe



Tandem mass spectrometric characterization of the conversion of xylose to furfural

Nelson R. Vinueza [a,1], Eurick S. Kim [a], Vanessa A. Gallardo [a],
Nathan S. Mosier [b], Mahdi M. Abu-Omar [a,c], Nicholas C. Carpita [d],
Hilkka I. Kenttämaa [a,*]

[a] *Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA*
[b] *Department of Agricultural and Biological Engineering, Laboratory of Renewable Resources Engineering, Purdue University, West Lafayette, IN 47907, USA*
[c] *School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA*
[d] *Department of Botany and Plant Pathology and Bindley Biosciences Center, Purdue University, West Lafayette, IN 47907, USA*

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form
14 October 2014
Accepted 16 October 2014
Available online

Keywords:
Xylose
Furfural
Tandem mass spectrometry
Catalytic conversion
Maleic acid
^{13}C labeling

ABSTRACT

Thermal decomposition of xylose into furfural under acidic conditions has been studied using tandem mass spectrometry. Two different Brønsted acids, maleic and sulfuric acids, were used to demonstrate that varying the Brønsted acid does not affect the mechanism of the reaction. Two selectively labeled xylose molecules, 1-^{13}C and 5-^{13}C-xyloses, were examined to determine which carbon atom is converted to the aldehyde carbon in furfural. This can be done by using tandem mass spectrometry since collision-activated dissociation (CAD) of protonated unlabeled furfural results in the loss of CO from the aldehyde moiety. The loss of a neutral molecule with MW of 29 Da (^{13}CO) was observed for protonated furfural derived from 1-^{13}C-labeled xylose while the loss of a neutral molecule with MW of 28 Da (CO) was observed for protonated furfural derived from 5-^{13}C labeled xylose. These results support the hypothesis that the mechanism of formation of furfural under mildly hot acidic conditions involves an intramolecular rearrangement of protonated xylose into the pyranose form rather than into an open-chain form.

1. Introduction

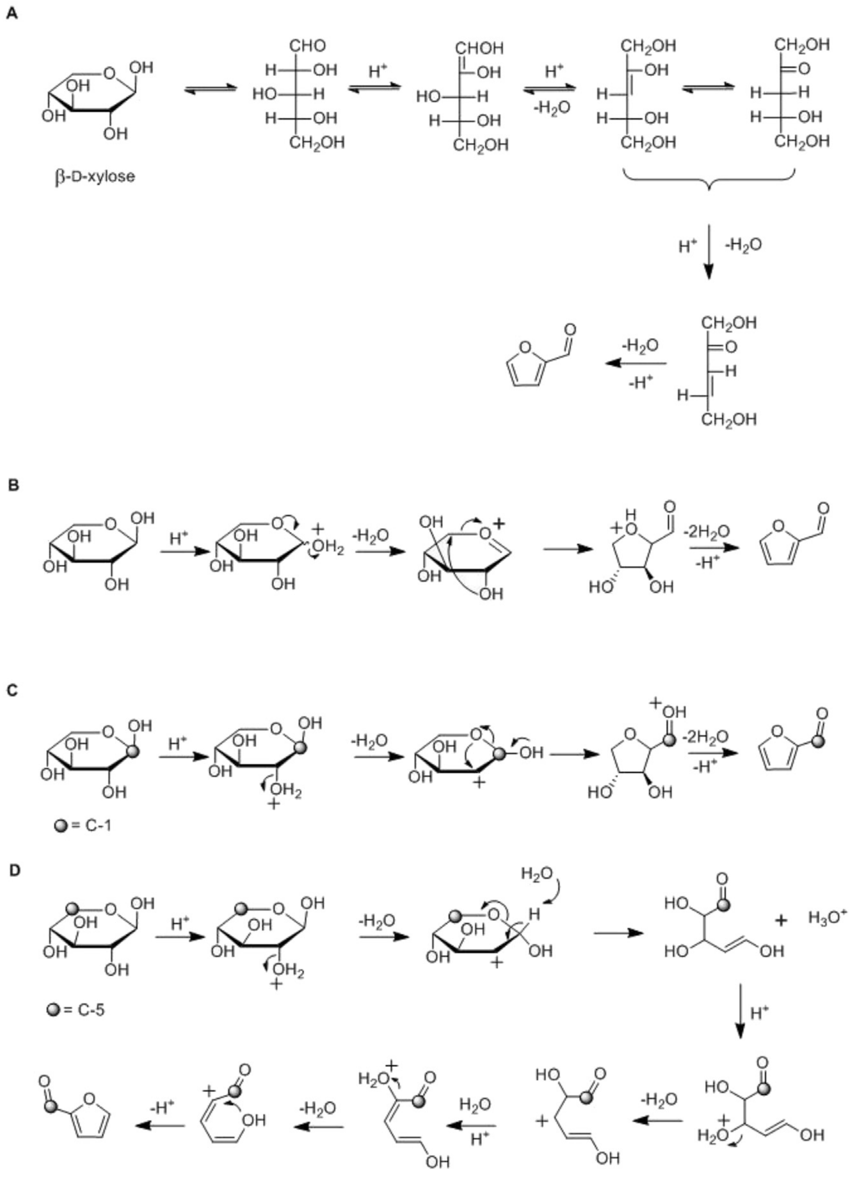
Plant biomass, mostly plant secondary cell walls, represents an important renewable source of energy as well as valuable organic chemicals [1–3]. For most plants, lignocellulosic biomass consists of cellulose (35–50%), non-cellulosic glycans (25–37%), as well as lignin and other phenolic substances (15–30%) [3]. Cellulose microfibrils give plant cell walls their foundational structure. Glucose derived from cellulose is the major substrate for fermentation of biomass to bioethanol [3]. However, for grasses and certain hardwoods, glucuronoxylan is the principal glycan that coats cellulose microfibrils and interacts with lignin and other phenolic substances to

---

* *Corresponding author*. Fax: +1 765 494 0239.
E-mail address: hilkka@purdue.edu (H.I. Kenttämaa).

[1] Present address: Department of Textile Engineering, Chemistry and Science, North Carolina State University, Raleigh, NC 27695, USA.

http://dx.doi.org/10.1016/j.biombioe.2014.10.012



Scheme 1 – Proposed mechanisms for the formation of furfural from xylose. Mechanism A,[11–14] B,[15] C,[15] and D.[17].

establish the fundamental architecture of the secondary wall [4]. Hence, the conversion of xylan to more useful molecules is critically important if biomass feedstocks, such as corn and sorghum stover, switchgrass, sugarcane bagasse and poplar, are to be used as a source of energy or as starting materials for valuable organic compounds [6–9].

Furan derivatives, such as furfural and 5-(hydroxymethyl) furfural, have great potential as precursors for different chemicals, including pharmaceuticals, plastics and polymers [6–9]. Furfural, obtained by dehydration of xylose and xylan, is perhaps the most common industrial chemical derived from lignocellulosic biomass [10]. Conversion of xylose under acidic catalyst conditions is the most common method used to generate furfural [11–14]. However, the mechanism of formation of furfural under these conditions is still a subject of debate. Different mechanisms proposed for this reaction [11–13,15,17] are shown in Scheme 1. A quantum mechanical study ruled out mechanisms A and B shown in Scheme 1 and suggested that protonation of C2-OH followed by ring-contraction (mechanism C) is the most likely pathway [17].

Hence, the mechanism for formation of furfural most likely begins with a cyclic form of xylose (cyclic form of xylose, pyranose, is presented based on the mechanism studies by Antal et al. [15] and NMR studies by Drew et al. [16]), which is in agreement with kinetic studies of the conversion of xylose into furfural [15]. According to mechanism C, C-1 of xylose becomes the carbon at the aldehyde moiety in furfural (Scheme 1). However, another mechanism of conversion of xylose to furfural has been proposed [17] (mechanism D, Scheme 1), which was not discussed in the quantum mechanical study mentioned above [18]. Based on this fourth mechanism, C-5 of xylose becomes the carbon at the aldehyde group in furfural.

Further, maleic acid catalyzed dehydration of xylose has been shown to result in a higher selectivity toward furfural production than sulfuric acid catalyzed dehydration [19].