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Minireview

Formation of degradation compounds from lignocellulosic biomass in the biorefinery: sugar reaction mechanisms

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ABSTRACT

The degradation compounds formed during pretreatment when lignocellulosic biomass is processed to ethanol or other biorefinery products include furans, phenolics, organic acids, as well as mono- and oligomeric pentoses and hexoses. Depending on the reaction conditions glucose can be converted to 5-(hydroxymethyl)-2-furaldehyde (HMF) and/or levulinic acid, formic acid and different phenolics at elevated temperatures. Correspondingly, xylose can follow different reaction mechanisms resulting in the formation of furan-2-carbaldehyde (furfural) and/or various C-1 and C-4 compounds. At least four routes for the formation of HMF from glucose and three routes for furfural formation from xylose are possible. In addition, new findings show that biomass monosaccharides themselves can react further to form pseudo-lignin and humins as well as a wide array of other compounds when exposed to high temperatures. Hence, several aldehydes and ketones and many different organic acids and aromatic compounds may be generated during hydrothermal treatment of lignocellulosic biomass. The reaction mechanisms are of interest because the very same compounds that are possible inhibitors for biomass processing enzymes and microorganisms may be valuable biobased chemicals. Hence a new potential for industrial scale synthesis of chemicals has emerged. A better understanding of the reaction mechanisms and the impact of the reaction conditions on the product formation is thus a prerequisite for designing better biomass processing strategies and forms an important basis for the development of new biorefinery products from lignocellulosic biomass as well.

1. Introduction

When lignocellulosic biomass is processed into biofuels—and potentially other biorefinery products—the biomass is usually pretreated in order to make the cellulose and hemicellulose amenable to enzymatic depolymerisation. The pretreatment may be done according to a number of regimes,[1,2] but current large scale pretreatment processes for lignocellulosic biomass generally involve some kind of high temperature treatment. The biomass pretreatment, particularly pretreatment regimes involving acid and/or temperatures above 160–180 °C, induces the formation of degradation products that may inhibit the cellulolytic enzymes (Table 1) and/or the ethanol producing microorganisms (notably yeast, *Saccharomyces cerevisiae*) (Table 2) that are required for the subsequent sugar conversion.

5-(Hydroxymethyl)-2-furaldehyde (HMF) and furan-2-carbaldehyde (furfural) are considered the key primary degradation compounds from the carbohydrate fraction of the lignocellulosic biomass, but several other products, notably other aldehydes, aliphatic and aromatic acids may also form and these compounds have a different inhibitory impact on the enzymes and yeast (Tables 1 and 2).

Knowledge of the degradation routes is therefore obviously an important foundation for controlling the inhibitor reactivity and in turn for improving the current cellulosic ethanol processes.

The advances in the recent two years have also revealed that the chemistry of formation of the putative inhibitors during thermal biomass pretreatment for biofuel production have many features overlapping with the discipline of industrial scale synthesis of biobased platform chemicals from glucose and potentially from other biomass monosaccharides.[3,4] The deliberate production of these type of products from biomass carbohydrates for industrial uses currently only appears feasible via targeted catalytic or biocatalytic technologies.[5] Nevertheless, with regard to the formation of degradation or synthesis compounds two topics are particularly important to understand in detail for making the production of biofuels more cost-effective and for preparing for industrial scale synthesis of chemicals from monosaccharides:

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Table 1
Inhibition of cellulolytic enzyme activity (commercial cellulase preparations) by lignocellulosic biomass degradation products

Inhibitor	Concn (mM)	Commercial cellulases (% activity relative to reference)
Furfural and 5-(hydroxymethyl)-2-furaldehyde (HMF) total	19	~100[a]
Vanillic acid	12	~100[b]
Syringic acid	10	~100[b]
Acetosyringone	5	~100[b]
Syringaldehyde	5/10	~100[b]/~30[c]
Ferulic acid	10	~100[d]
Tannic acid	1	~40[d]
Vanillin	13	~100[d]
Gallic acid	12	~100[d]
Cinnamic acid	14	~100[d]
p-Coumaric acid	12	~100[d]
Sinapic acid	9	~100[d]
4-Hydroxybenzoic acid	14	~100[d]
Lignin derivatives	1	~20-30[c]
Acetic acid	218	95–100[a]
Butyric acid	567	42[e]
Formic acid	326	5–20[b]
Succinic acid	34	~100[b]
Itaconic acid	384	83[e]
Lactic acid	555	87[e]
Propionic acid	675	64[e]

Activity (%) compared to reference hydrolysis with no inhibitor present (data from a,[30] b,[31] c,[32] d,[33] e,[34]).

Table 2
Ethanol yields (g ethanol/g consumed glucose) relative to reference fermentation

Inhibitor compound	Concn (mM)	*S. cerevisiae* (Baker's yeast)
Furfural	21–65	82–50
5-(hydroxymethyl)-2-furaldehyde (HMF)	8–57	50
4-Hydroxybenzaldehyde	4–17	50
Vanillin	1–18	~50–100
Syringaldehyde	1–25	50
Levulinic, acetic and formic acids	Total <100	Increase in yield
	Total >100	Decrease in yield

Data adapted from Refs. 35,36.

1. The degradation products and their routes of formation.
2. The influence of process parameters and pretreatment on the degradation product profile.

In the literature, different authors promote different degradation routes for biomass monosaccharides, with the degradation routes for xylose to furfural and for glucose to HMF appearing to be particularly disputed.[6–10] In the present treatise we will critically discuss the recently proposed degradation mechanisms and routes and show that several degradation routes for glucose and xylose are in fact possible. We will also highlight how a combination of advanced modelling and systematic analytical approaches has recently cast new light on the details of the molecular reactions, and underline how this understanding can pave the way for the industrial production of new chemicals in the biobased economy.

2. Biomass degradation during hydrothermal treatment

2.1. Cellulose and hemicellulose

The D-glucose originating from cellulose can be thermally degraded directly during the biomass pretreatment. In this type of degradation, D-glucose is firstly dehydrated to HMF, which can then further degrade to formic acid and levulinic acid[8] (Fig. 1). As the monomeric substituents in hemicellulose include both hexoses and pentoses, hemicellulose may also give rise to HMF, formic acid and levulinic acid (Fig. 1). In contrast, furfural is formed exclusively from pentoses, that is, mainly from D-xylose and L-arabinose released from the hemicellulose (Fig. 1).

Hydrothermal biomass pretreatment can also lead to cleavage of the acetyl linkages in xylan and presumably also induce hydrolytic cleavage of the acetyl substitutions in, for example, acetylated galacto-glucomannans, leading to the formation of free acetic acid[11] (Fig. 1).

Although it is generally acknowledged that phenolics found in biomass liquors stem from lignin, early reports show that various phenolic compounds may also form as degradation products from D-glucose, D-xylose and L-arabinose[12,13] (Fig. 1). Recently this formation of phenolics has been confirmed by demonstration of pseudo-lignin generation from model substrates of cellulose (i.e., Avicel), xylan and D-xylose.[14] These findings mark a significant 'game-changer' in the field, since they show that phenolics can originate from carbohydrates.

2.2. Lignin

The aromatic residues in lignin can be degraded to different types of phenolic structures depending on the type of structural monomeric unit in the lignin.[15] Furthermore it cannot be excluded that acetylated lignin[16] liberates acetic acid when thermally treated (Fig. 1).

2.3. Degradation product inter-reactions

The degradation compounds shown in Figure 1 are moreover able to undergo various reactions with each other. Such intermolecular reactions can lead to several new products and polymerisation reactions.

2.3.1. Pseudo lignin

Pseudo lignin is an aromatic material containing hydroxyl and carbonyl functional groups. In this way pseudo lignin resembles native lignin but is not derived thereof. Sannigrahi et al.[17] proposes the broad definition of pseudo-lignin to be an aromatic material that yields a positive Klason lignin value and is not derived from native lignin. The existence of pseudo lignin has been recognised because the amount of Klason lignin in pretreated