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Current Opinion in Biotechnology

Biomass pretreatments capable of enabling lignin valorization in a biorefinery process

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Recent techno-economic studies of proposed lignocellulosic biorefineries have concluded that creating value from lignin will assist realization of biomass utilization into valuable fuels, chemicals, and materials due to co-valorization and the new revenues beyond carbohydrates. The pretreatment step within a biorefinery process is essential for recovering carbohydrates, but different techniques and intensities have a variety of effects on lignin. Acidic and alkaline pretreatments have been shown to produce diverse lignins based on delignification chemistry. The valorization potential of pretreated lignin is affected by its chemical structure, which is known to degrade, including inter-lignin condensation under high-severity pretreatment. Co-valorization of lignin and carbohydrates will require dampening of pretreatment intensities to avoid such effects, in spite of tradeoffs in carbohydrate production.

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Current Opinion in Biotechnology 2016, **38**:39–46

This review comes from a themed issue on **Energy biotechnology**

Edited by **Andrew S Ball** and **Jamie HD Cate**

http://dx.doi.org/10.1016/j.copbio.2015.12.018

Introduction

To cultivate economic value from renewable biomass, pretreatment of incoming biomass is critical to overcome the recalcitrant properties of lignocellulosic biomass for downstream biological conversion. It is well known that lignin can inhibit both enzymatic saccharification and fermentation of carbohydrates, leading to the necessity of biomass pretreatment for lignin removal/disruption [1••]. The diverse array of pretreatments that can be optimized for carbohydrate conversion have been reviewed in recent years [2–12]. In a newly published techno-economic analysis of a hypothetical industrial biorefinery, return on investment was highly susceptible to the incoming carbohydrate fraction in biomass [13••]. In the best case, marginal returns were predicted in addition to addressing the market risks. These findings support the actively occurring paradigm shift in lignocellulosic biorefinery research toward valorization of the lignin fraction from biomass [14–22,23•,24–26].

Despite recently successful investigations into novel methods of valorizing biorefinery lignin by conversion into precursors for different chemical and material applications, the published results remain at the laboratory scale [27–31]. In order to advance lignin-valorizing technologies, a comprehensive understanding of biorefinery lignin streams must be further established. Currently there exists a void of explicit knowledge regarding the modifications to lignin's properties after pretreatment across techniques. This dearth of knowledge leads to techno-economic models of industrial-scale biorefineries treating lignin solely as a power source for the biorefinery itself or as fuel pellets. With a better understanding of how lignin's structure is affected by pretreatment conditions, potential applications beyond combustion would be more readily innovated and developed. Furthermore, if any stream of biorefinery lignin can be valorized, then the profitability of the entire biorefinery would rise.

Two lignin streams: hydrolyzate and residue

The two potential streams from which lignin can be valorized within a biorefinery are pretreatment hydrolyzate (solubilized lignins) and post-saccharification residue (insoluble lignins). It is impossible to correlate the amount of lignin solubilized during pretreatment with valorization potential of soluble and insoluble lignins, due to inadequate data regarding the characteristics of the pretreated lignin. As shown in Table 1, when comparing diverse pretreatment processes and intensities across woody and non-woody biomasses, great variability in lignin solubilization is observed. Aside from percent delignification, there tends to be sparse discussion regarding the chemical properties of the lignin stream. This is mainly because current biorefinery research is focused on carbohydrate utilization with the absence of in-depth knowledge of whole lignin structure. Therefore it can be stated that current knowledge of lignin utilization is only in its fledgling state, marred by selective analysis that yields incomplete understanding of the entire lignin structure after pretreatment.

Lignin properties for high-value applications

Some of the potential applications for biorefinery lignin including Kraft lignin utilization [32–35] are under

Table 1

Summary of pretreatments, severities, delignification, and impacts on lignin structure

Pretreatment	Conditions	pH	Biomass	Wt% delignification	Impact on lignin structure	Ref.
Dilute acid (sulfuric acid)	130°C, 60 min	Acidic	Rape straw	42%	–	[59]
	30°C, 7 h	Acidic	Banana peel	38%	–	[60]
	190°C, 1 min	Acidic	Switchgrass	0%	Cβ in β-O-4, Cα in β-5 and β-β 0.74 (untreated); 0.54 (pretreated) Cγ in β-5 and β-O-4 with Cα=O in G and S units 0.35 (untreated); 0.20 (pretreated) Cγ in β-O-4 without Cα=O 0.39 (untreated); 0.25 (pretreated)	[61]
	100–190°C, 2 h	Acidic	Poplar	–	Nitrobenzene oxidation products Vanillin 53.3%, syringaldehyde 22.0% (100°C) Vanillin 41.9%, syringaldehyde 16.8% (170°C) Vanillin 17.8%, syringaldehyde 12.6% (190°C)	[62]
Steam explosion	170°C, 3 min	Acidic	Wheat straw	64%	–	[63]
	185°C, 5 min	Acidic	Aspen	10%	Total β-O-4 54/100 Ar (untreated) 42/100 Ar (pretreated)	[64]
	200°C, 15 min	Acidic	Aspen	20%	18/100 Ar (pretreated)	
	180°C, 10 min	Acidic	Sugarcane bagasse	9%	Total β-O-4 25.3–31.7/100 Ar (untreated) 16.7–20.7/100 Ar (pretreated)	[65]
Autohydrolysis	177°C, 3.5 h	Acidic	Aspen	62%	Total β-O-4 54/100 Ar (untreated) 34/100 Ar (pretreated)	[57]
	195°C, 6 min	Acidic	Wheat straw	42%	–	[63]
	180°C, 15 min	Acidic	Eucalyptus alkali lignin	26%	Total β-O-4 61.2/100 Ar (untreated) 30.8/100 Ar (pretreated)	[66]
Organosolv (methyl isobutyl ketone, ethanol, water, sulfuric acid)	140°C, 56 min	Acidic	Mixed hardwoods	97%	–	[67]
	160°C, 56 min	Acidic	Mixed hardwoods	98%	–	[67]
	140°C, 56 min	Acidic	Switchgrass	64%	Total β-O-4 37/100 Ar (untreated) 17/100 Ar (organosolv lignin)	[68]
	160°C, 56 min	Acidic	Switchgrass	73%	4/100 Ar (organosolv lignin)	[68]
	190°C, 1 h	Acidic	Switchgrass	61%	Total phenolic OH 0.86 mmol/g of lignin (untreated) 1.90 mmol/g of lignin (organosolv treated) 1.65 mmol/g of lignin (organosolv lignin)	[69]
Alkaline green liquor (sodium sulfide and sodium carbonate)	160°C, 60 min	Alkaline	Poplar	18%	–	[70]
	140°C, 60 min	Alkaline	Miscanthus	54%	–	[70]
	170°C, 3 h	Alkaline	Oil palm frond	–	Nitrobenzene oxidation products Vanillin 0.5%, syringaldehyde 0.7% (Kraft) Vanillin 0.7%, syringaldehyde 1.5% (Soda)	[71]
	190°C, 1 h	Alkaline		–	Vanillin 1.6%, syringaldehyde 4.6% (Organosolv)	
Mild alkaline (sodium hydroxide; 15% soda charge)	175°C, 15 min	Alkaline	Eucalyptus	36%	–	[72]
	175°C, 15 min	Alkaline	Sugarcane bagasse	80%	–	[72]
Ionic liquid and alkaline	110°C, 12 h 75°C, 3 h		Poplar	–	Relative abundance of β-O-4 79.0% (untreated); 80.2% (pretreated)	[73]
Ionic liquid	110°C, 12 h		Birch	26%	Total β-O-4 65/100 Ar (cellulolytic lignin) 56/100 Ar (ionic liquid lignin) 59/100 Ar (residual lignin)	[74]