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Critical Review

Organosolv Pretreatment of Plant Biomass for Enhanced Enzymatic Saccharification

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The combination of dwindling petroleum reserves and population growth make the development of renewable energy and chemical resources more pressing than ever before. Plant biomass is the most abundant renewable source of energy and chemicals. Enzymes can selectively convert the polysaccharides in plant biomass into simple sugars which can then be upgraded to liquid fuels and platform chemicals using biological and/or chemical processes. Pretreatment is essential for efficient enzymatic saccharification of plant biomass and this article provides an overview of how organic solvent (organosolv) pretreatments affect the structure and chemistry of plant biomass, and how these changes enhance enzymatic saccharification. A comparison between organosolv pretreatments utilizing broadly different classes of solvents (*i.e.*, low boiling point, high boiling point, and biphasic) is presented, with a focus on solvent recovery and formation of by-products. The reaction mechanisms that give rise to these by-products are investigated and strategies to minimize by-product formation are suggested. Finally, process simulations of organosolv pretreatments are compared and contrasted, and discussed in the context of an industrial-scale plant biomass to fermentable sugar process.

1. Introduction

Fossil carbon, while known since ancient times, only overtook terrestrial plants as the principle source of energy and chemicals from the middle of the 19th century. For a century and half, petroleum and its fractionation products have supported phenomenal advancements in all areas of science and technology, and hence human development. However, diminishing global fossil-fuel reserves, economic, social, and political uncertainty, and climate change, are driving the rapid re-evaluation of terrestrial plants as a source of energy and chemicals in the modern context. With an estimated annual production of 80−164 billion tonnes of dry matter, terrestrial plants have the potential to displace a significant proportion of fossil resources as feedstock for the production of fuels and chemicals.[1]

The saccharification of cell wall polysaccharides is essential for the production of biofuels and biochemicals from lignocellulose via microbial fermentation. In plants, enzymes that hydrolyse cellulose and hemicellulose are involved in such diverse processes as the remodelling of the plant cell wall during growth, abscission (*i.e.*, the process by which plants release leaves and fruit), and cellulose synthesis (Fig. 1A).[2, 3] The role of these hydrolytic enzymes in the life cycle of

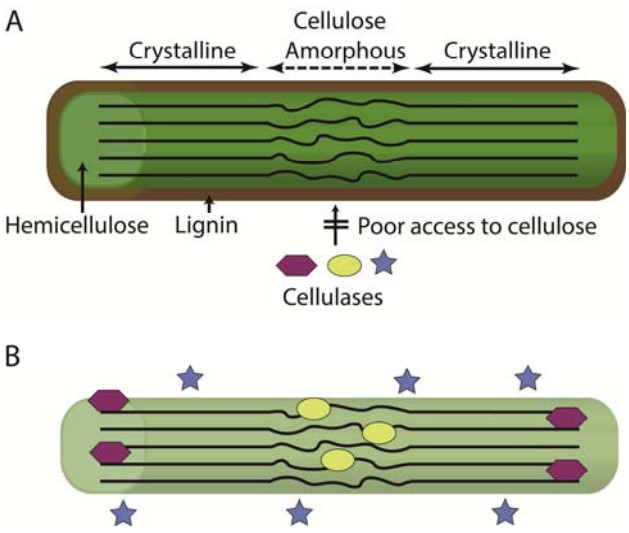


Fig. 1. Enzymatic saccharification of cellulose and hemicellulose. (A) Predominantly crystalline cellulose embedded within an amorphous hemicellulose/lignin matrix and the resultant restriction of cellulase access. (B) Increased cellulase (cellobiohydrolase, purple hexagons; endoglucanase, yellow ovals) access to cellulase after organosolv pretreatment dissolves/modifies lignin and partially dissolves hemicellulose. β-glucosidases (blue stars) hydrolyse cellobiose produced by cellobiohydrolases into glucose.

microbes is equally diverse: many aerobic and anaerobic fungi secrete complex mixtures of proteins that saccharify the plant biomass upon which they reside, while many bacteria deploy cellulases to saccharify plant biomass, participate in cellulose synthesis, and perhaps even evade amoebal encystment.[4, 5] Importantly, the presence of environmental oxygen has played a key role in the evolution of plant cell wall degrading enzymes in microbes; such enzymes from aerobes are either secreted into the extracellular environment or associate with the outer cell membrane, while their counterparts from most anaerobes associate into supramolecular complexes known as "cellulosomes".[6] While complexed cell wall saccharifying enzymes from anaerobes will undoubtedly have a more widespread role in the future, the present review will focus on saccharifying enzymes from aerobic fungi because of their existing use at industrial-scale.

The smallest number of aerobic fungal enzymes required for complete degradation of cellulose to glucose are derived from three functional classes; (i) endoglucanases (endo-1,4-β-D-glucanases, EC 3.2.1.4), (ii) exoglucanases or cellobiohydrolases (exo-1,4-β-D-glucanases), and (iii) β-glucosidases (EC 3.2.1.21).[7] Endoglucanases hydrolyse internal cellulose β1→4 bonds at random, soften and swell the fibres, and expose single cellulose microfibrils.[8, 9] Free chain ends generated by endoglucanases are the sites of action for processive, unidirectional cellobiohydrolases. Cellobiohydrolases act on either the non-reducing (EC 3.2.1.91) or reducing (EC 3.2.1.176) ends of cellulose polysaccharide chains, liberating cellobiose. Endoglucanases further enhance the processivity of cellobiohydrolases by degrading amorphous cellulose, preventing cellobiohydrolase 'stalling' and enhancing cellobiohydrolase recruitment to free chain ends in crystalline cellulose.[8] Cellobiose is hydrolysed by β-glucosidase producing glucose, which prevents feedback inhibition of cellobiohydrolases.[10] Most cellulases have a modular structure consisting of a catalytic domain and a carbohydrate-binding module (CBM), connected by a flexible linker region.[11] CBMs play a key role in cellulase binding to cellulose,[12] and have been utilized more recently as molecular probes of cellulose accessibility[13] and changes in cell wall chemistry after pretreatment.[14] In addition to the enzymes required specifically for the saccharification of cellulose, aerobic fungal enzyme mixtures also contain proteins that act directly on cellulose to enhance saccharification by cellulases including lytic polysaccharide monooxygenases (formerly known as GH61)[15-17] and expansion–like proteins (such as swollenin).[18-20]

Hemicellulose saccharification is intrinsically more complex than that of cellulose because of the heterogeneity of the substrate within a given plant cell, between cells in the same plant, and between cell walls from different plants.[21-23] While hemicellulose removal is rarely complete during biomass pretreatment and commercial fungal cellulase mixtures typically contain numerous hemicellulose-degrading enzymes, the majority of biomass pretreatment processes at least partially solubilize hemicellulose.[24] As a result, we direct the reader to other literature describing the enzymes involved in hemicellulose saccharification.[25-27]

The inherent structural resistance of lignocellulose to enzymatic saccharification makes the cost of fermentable sugars from raw lignocellulose prohibitively expensive. Pretreatment disrupts the structure of lignocellulose and substantially increases enzyme access to hemicellulose and cellulose.[28] As a result, the extent and rate of enzymatic saccharification is enhanced and the economics of enzymatic saccharification of lignocellulose improves dramatically. The choice of pretreatment technology and the pretreatment conditions selected not only impacts upon enzymatic saccharification but also upon the choice of lignocellulose feedstock, handling and processing, pretreatment vessel composition and size, fermentation efficiency, enzyme loading and composition, waste disposal, and opportunities to generate co-products.[29] Therefore, pretreatment is the central technology in a production system based upon the enzymatic saccharification of lignocellulose.

Recent reviews provide a general overview of the different approaches to lignocellulose pretreatment and the reader is directed to them for more detailed information.[29-35] Pretreatment technologies can be categorized as chemical, physical, biological, or combinations thereof. Chemical pretreatments are typically conducted under pressure at temperatures significantly above the boiling point of the solvent (*e.g.*, water or organic liquids), with or without the addition of catalysts. Physical pretreatments include mechanical comminution (*e.g.*, ball-milling and wet disk milling), extrusion, and irradiation (*e.g.*, ultrasound, microwave, γ-rays). Biological pretreatments generally employ white-rot fungi, which act by enzymatic degradation of lignin.[36] Purely physical or biological pretreatments require relatively high energy inputs or long pretreatment times (days or weeks), respectively, in order to improve saccharification yields to a commercially-viable level and are therefore not practical at present for industrial applications. The majority of recent pretreatment studies have focused on physicochemical processes whereby lignocellulosic biomass is chemically deconstructed and then physically processed to reduce particle size. Table 1 presents the attributes, benefits, and drawbacks of leading lignocellulose pretreatments.

Lignocellulose pretreatments that use organic solvents (more commonly known as organosolv pretreatments) have been studied intensively since their development in the pulp and paper industries, and have emerged as one of the most promising pretreatment strategies for the enhancement of enzymatic saccharification of lignocellulose. Organosolv pretreatments utilize solvents such as short chain aliphatic alcohols (*e.g.*, methanol, ethanol), polyols (*e.g.*, glycerol, ethylene glycol (EG), triethylene glycol), organic acids, acetone, dioxane, and phenol. That some of these organic solvents (such as methanol, ethanol, acetone, acetic acid, and glycerol) can be obtained from renewable sources further

Table 1 Impacts of different acid-catalyzed organosolv pretreatments on lignocellulosic biomass

Solvent type	Delignification	Removal of hemicellulose	Decrystallization	Cellulose accessibility
Ethanol	+++	+++	-	+++
Organic acids	+++	+++	-	++
Peroxylic acids	+++	+++	-	++
Glycerol	++	+++	-	+++
EG	+++	+++	-	+++
EC	+++	+++	-	+
EC/EG	+++	+++	-	+++
GC and GC/glycerol	+++	+++	-	+++
MIBK-alcohol	+++	+++	-	+++
2-MTHF	+++	+++	-	+++

+, slightly positive ++, moderately positive, +++, highly positive, - negative

enhances their application to sustainable production of fuels and chemicals. Further, some organosolv pretreatments produce lignin that is relatively pure, low in sulfur, and less condensed than that produced by other lignocellulose pretreatments as a by-product.[37, 38] Such 'high-quality' lignin can potentially be transformed into higher-value products.

More recently, the term "organosolv" has been applied to lignocellulosic biomass pretreatment processes that utilize organic solvents such as alkylene carbonates (ACs), N-methylmorpholine N-oxide (or 4-methylmorpholine 4-oxide, NMMO), methyl isobutyl ketone (MIBK), and 2-methyltetrahydrofurfuran (2-MTHF). Ionic liquids composed of organic cations and anions (*e.g.*, cholinium-amino acid ionic liquids) have also been used to pretreat lignocellulose.[39] However, a number of recent reviews have described ionic liquid lignocellulose pretreatment[40-43] and thus the use of ionic liquids will not be reviewed herein.[44-47] In addition, ionic liquid processes are relatively expensive compared to organosolv processes due to the high costs associated with ionic liquid production and recovery, despite their ability to dissolve and decrystallize the cellulose component of biomass. NMMO has not been included for discussion simply because of its mode of action as a cellulose-dissolving solvent.

Although research into the application of organic solvents to biomass pretreatment has progressed significantly in recent years, comprehensive reviews describing organosolv pretreatments are limited.[48] In the present review, progress on both well-studied and emerging solvent-based systems for lignocellulose pretreatments are reviewed with a focus on recent developments in our understanding of both how they work and the side reactions arising from the use of a particular solvent. Comparison of organosolv pretreatments with different solvents, process simulation, and future perspectives are also discussed.

2. Plant biomass: a sustainable feedstock for fuels and chemicals

The majority of the dry matter in terrestrial plants is made of plant cell walls which consist of distinct layers; the primary cell wall is laid down first and is therefore farthest from the plasma membrane in the mature cell (Fig. 2). The primary cell walls of dicots, noncommelinoid monocots (*e.g.*, water plantain, onions, and lilies) and gymnosperms (Type I cell walls) consist of cellulose fibres within a xyloglucan, pectin, and structural protein matrix. In contrast, the Type II primary cell walls observed in commelinoid monocots (*e.g.*, palms, grasses, and bananas) consist of cellulose fibres within a glucuronoarabinoxylan matrix with high levels of hydroxycinnamates.[42] Further, the Type II primary cell walls of the grasses (family Poaceae, *e.g.*, wheat, corn, rice, sugarcane) also contain significant amounts of mixed linkage glucans. Once cell growth is complete, additional secondary cell wall layers are deposited between the primary cell wall and plasma membrane. Secondary cell walls consist of cellulose fibres within a matrix of hemicellulose (primarily glucuronoarabinoxylan) and lignin. As with the primary cell wall, plants of different evolutionary origin show significant differences in secondary cell wall composition.[42] Given that secondary cell walls typically constitute the majority of the mass of plant fibre, researchers typically use the term lignocellulosic biomass to describe any plant fibre, regardless of phylogenetic origin or effective absence of lignin in the primarily cell walls contained therein.

Cellulose, a long-chain, unbranched homopolysaccharide composed of glucose monomers linked by β–1,4–glycosidic bonds into cellobiose sub-units (Fig. 2), is the most abundant structural fibre in plants and the most abundant biopolymer on earth.[49, 50] The number of glucose monomers in cellulose polymers (degree of polymerization, DP) varies depending

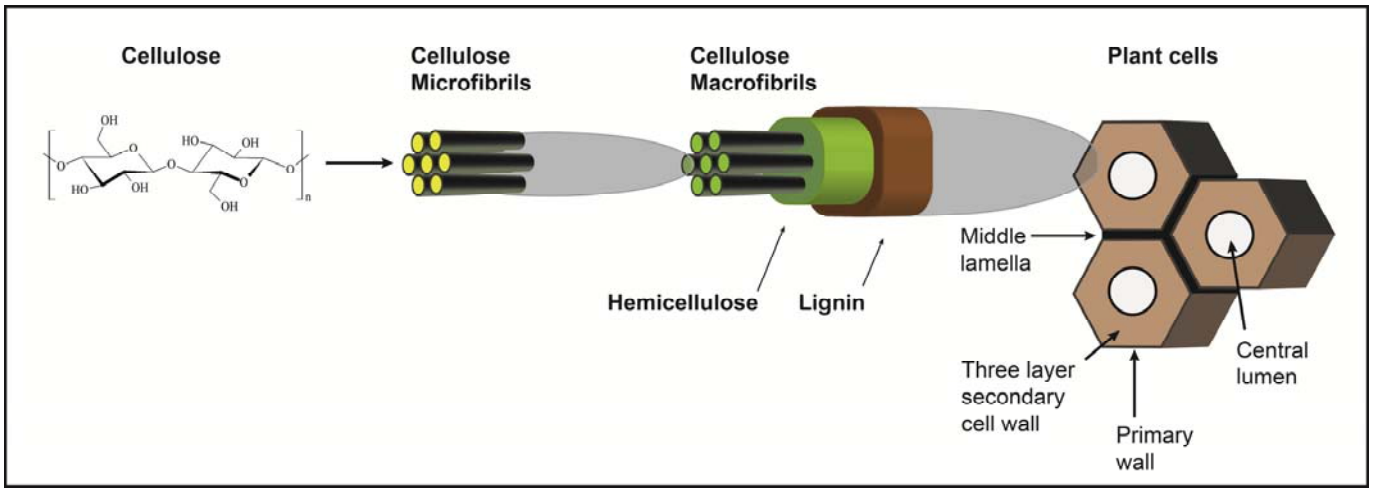


Fig 2. Schematic illustration of plant cell wall architecture.

upon both plant species and the plant cell wall layer in which the cellulose resides.[51, 52] In higher plants, 36 parallel cellulose chains aggregate via hydrogen bonding and van der Waals forces to form microfibrils of 3–5 nm in diameter (Fig. 2).[53, 54] The majority of the cellulose along the length of a microfibril is crystalline in one of two forms (I_α and I_β), with intervening amorphous regions.[49] Cellulose microfibrils are further ordered by hydrogen bonding to hemicellulose into larger aggregates (or macrofibrils) of 50–250 nm diameter and reside within a non-crystalline matrix of both hemicellulose and either lignin or pectin (Fig. 2).[53]

Hemicelluloses are structurally diverse, branched heteropolysaccharides consisting of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids, and include xyloglucans, xylans, mannans, glucomannans, and β–(1→3,1→4)–glucans.[22] The composition of hemicellulose varies dramatically between dicot and monocot (*i.e.*, grass) cell walls.[42] The β–1,4–linkages in the backbone structure of hemicelluloses allow these polysaccharides to form hydrogen bonds both with themselves and with cellulose.[55-57] Unlike cellulose, the structures of hemicelluloses are too variable (both in the nature of backbone linkages and substituents) to form crystalline microfibrils and are best described as amorphous.

Lignin is a complex, cross-linked polymer of phenolic monomers with both aliphatic and aromatic constituents.[58] Lignin is totally amorphous and hydrophobic, and the three major structural units in lignin are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) phenylpropane, which differ in the O-methyl substitution of the aromatic ring.[59] These structural units are connected by a range of ether (*e.g.*, α–*O*–4, β–*O*–4, and 4–*O*–5) and carbon-carbon (β–β, β–5, and 5–5) bonds, the formation of which are catalyzed by laccase and peroxidase enzymes during lignin biosynthesis.[60] Hemicellulose is covalently linked to lignin, thus serving as the connection between lignin and cellulose fibres and giving the cellulose–hemicellulose–lignin network rigidity.[41, 57, 61, 62] As a result of these linkages (either direct or indirect) with other cell wall components, a key challenge in understanding lignin chemistry is the inability to isolate lignin in its native state from plant fibre and what is known about the structure of lignin depends not only on the plant and/or plant tissue from which it originates but also the chemical method used for its extraction.[63, 64]

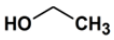
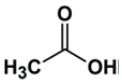
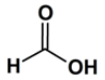
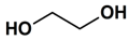
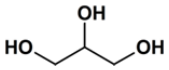
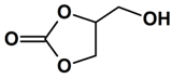
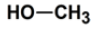
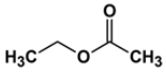
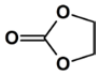
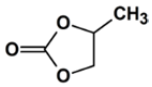
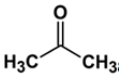
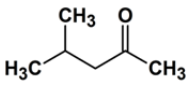
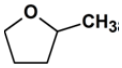
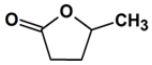
3. Solvent capabilities in biomass pretreatment

Organic solvents have been utilised to improve the conversion of lignocellulosics by increasing solvent penetration and biomass dissolution.[48, 65] Compared to aqueous medium, organic solvents play important roles in hydrogen transport, limiting diffusion effects, and improving reaction performance through increased catalytic activity (by reducing activation energy) and product selectivity.[66] The acid potential in acid-catalyzed reactions in non-aqueous solvents depends on the dielectric constant (relative permittivity, ε_r) of the solvent, and the higher the dielectric constant of the solvent, the higher the acidity.[67]

Cost and ease of recovery (*i.e.,* boiling point, miscibility and partitioning) are important engineering aspects in selecting a suitable solvent. Likewise health (toxicology), safety (*i.e.,* flash point, vapour pressure) and environmental impact are also

important considerations. There is limited understanding of the solvent impacts on biomass pretreatment at the microscopic scale. On a macroscopic scale, solvent properties such as viscosity and molecule size (solvent molar volume) are important to the interactions between solvent and substrate in pretreatment. Solvent penetration into pores resulting in physical changes of the biomass and the substrate architecture are important for lignocellulose deconstruction. Other bonding important solvent properties in pretreatment include hydrogen and polarizability. Solvent performance is classically correlated and described by solubility parameters and solvatochromic parameters. These polarity scales are measured empirically as opposed to the direct measurement of dielectric constant (Table 2). The Hildebrand solubility parameter (δ), perhaps the most widely applied parameter and experimentally determined from viscosity measurements, is a measure used to determine solvent dissolution power.[68] δ is derived from the cohesive energy density of the solvent (equation 1), which in turn is derived from the heat of vaporization and so directly reflects the degree of van der Waals forces holding the molecules of the liquid together.

Table 2 Structure and physical constants for selected organic solvents for pretreatment of biomass

Solvent	Structure	Classification[69]	Boiling point, °C	Relative permittivity, ε_r	Flash point, °C	Vapour pressure, Pa	Green solvent rating[c] Health	Safety	Environment[d]
Ethanol		Amphoprotic	78.3	24.55	13	5,900 (20°C)	4	3	4.0
Butanol		Amphoprotic	117.7	17.5	35	800 (20°C)	3	5	4.3
Acetic acid		Polar structured	117.9	6.17 (20°C)	43.0–44.5	1,530 (20°C)	3	6	5.0
Formic acid		Polar structured[a]	101	58.5 (16°C)	68.9	4,200 (20°C)	2	6	5.3
Ethylene glycol		Polar structured	197	37.7	111.1	8 (20°C)	3	3	4.3
Glycerol		Polar protic	290	47	160	3 (50°C)			
Glycerol carbonate		Polar protic[a]	137–140	109.7	110	not available			
Methanol		Polar protic	64.5	32.66	11–12	12,800 (20°C)	3	5	5.0
Ethyl acetate		Aprotic dipolar	77.1	6.0	-4	7,300 (20°C)	5	4	4.7
THF		Aprotic dipolar	66	7.52	-14	17,600 (20°C)	5	6	4.7
Ethylene carbonate		Aprotic highly dipolar[a]	243	90.0 (40°C)[b]	160	2 (20°C)			
Propylene carbonate		Aprotic highly dipolar	241.7	64.92	132	4 (50°C)			
Acetone		Aprotic highly dipolar	56.1	20.56	-17	24,000 (20°C)	4	4	4.3
MIBK		Aprotic highly dipolar[a]	117.5	13.11 (20°C)	17.8	800 (20°C)	5	6	4.0
2-MTHF		Aprotic highly dipolar[a]	80	6.97	-11.11	not available	5	6	4.0
GVL		Aprotic highly dipolar[a]	207	36.91 (20°C)	81	not available			

Except where noted, physical constants are given for materials at 25 °C and 100 kPa, and boiling point, relative permittivity, vapor pressure, and toxicity were taken from [70].

[a] Predictions by the authors; [b] Ethylene carbonate is a solid at room temperature; [c] values obtained from American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable; [d] Average of air, water, and waste impact scores.

Table 3 Solubility and polarity parameters for selected organic solvents for pretreatment of biomass[71, 72]

Solvent	Hildebrand solubility parameter ($MPa^{½}$)	Hansen solubility parameters ($MPa^{½}$)			Kamlet-Taft empirical polarity			Molar volume (cm^3/mol)	Empirical polarity E_T^N (kcal/mol)
		Dispersion component	Polar component	Hydrogen bonding component	π* (dipolarity/ polarizability)	α acidity (HBD)	β basicity (HBA)		
Ethanol	26.5	15.8	8.8	19.4	0.54	0.86	0.75	58.4	0.654
Butanol	23.1	16.0	5.7	15.8	0.47	0.84	0.84	91.5	0.586
Acetic acid	21.4	14.5	8.0	13.5	0.64	1.12	0.45	57.2	0.648
Formic acid	24.9	14.3	11.9	16.6	0.65	1.23	0.38	37.7	0.833
Ethylene glycol	32.9	17.0	11.0	26.0	0.92	0.9	0.52	55.9	0.79
Glycerol	36.1	17.4	12.1	29.3	0.96	1.06	0.66	73.1	0.817
Glycerol carbonate								84.3	
Methanol	29.6	15.1	12.3	22.3	0.6	0.98	0.66	40.5	0.762
Ethyl acetate	18.1	15.8	5.3	7.2	0.55	0	0.45	98.2	0.228
THF	19.4	16.8	5.7	8.0	0.58	0	0.55	88.1	0.207
Ethylene carbonate	29.6	19.4	21.7	5.1			0.41	66.7	0.552
Propylene carbonate	27.2				0.83	0	0.4	84.4	0.472
Acetone	20.0	15.5	10.4	7.0	0.67	0.08	0.48	73.4	0.355
MIBK	17.0	15.3	6.1	4.1				124.9	0.269
2-MTHF	17.4				0.53	0	0.58	112.5	0.179
GVL					0.83	-	0.6	95.7	-

$$\delta = \sqrt{c} = \left[\frac{\Delta H - Rt}{V_m}\right]^{1/2} \quad (1)$$

where c is the cohesive energy density ($MPa^{1/2}$), ΔH is the heat of vaporization (J/mol), R is the gas constant (8.314 J/K.mol), t is the temperature (°C), and V_M is the molar volume (cm^3/mol).

If δ is similar to the substrate then good dissolution is expected. While δ values are not available for cellulose and lignocellulose, lignin has an estimated value of 22.5 which is close to that of many organosolv solvents (Table 3) and explains their behaviour in regards to lignin.

For polar and more complicated molecules Hansen solubility parameters are commonly used. Hansen parameters divide the total Hildebrand value into three parts: a dispersion force component, a hydrogen bonding component, and a polar component as follows[73]:

$$\delta^2 = {\delta_D}^2 + {\delta_P}^2 + {\delta_H}^2 \quad (2)$$

where δ_D is the dispersion component calculated using a homomorph method, δ_P is the polar component, and δ_H is the hydrogen bonding component with the latter parameters determined from best reflecting empirical evidence.

While solubility parameters are particularly useful in predicting substrate solubility, other solvent reactivity phenomena such as cellulose swelling are less well correlated. In this situation, more comprehensive solvatochromic measurements are generally used. Linear solvation energy relationship (LSER) methods, such as those developed by Kamlet and Taft, have shown successful quantitative treatment of solvation effects. These methods involve multiple linear regression analysis to calculate properties from wavelength shifts of different solvatochromic dyes in the solvent. The Kamlet-Taft empirical polarity parameter (γ) has the following form[74]:

$$\gamma = \gamma_0 + s\pi^* + A\alpha + B\beta \quad (3)$$

where γ_0 is the regression value based on a reference solvent, π^* is an index of the solvent dipolarity/polarizability, α is a measure of the solvent hydrogen-bonding donor (HBD) acidity, β is a measure of the solvent hydrogen-bonding acceptor (HBA) basicity, and s, A and B are regression coefficients.

Table 4 Ethanol lignocellulosic biomass pretreatments for saccharification

Biomass	Ethanol, %	Catalyst	T, °C	t, min	Cellulose yield, %	Hemicellulose removal, %	Delignification, %	Cellulose digestibility,%	Ref.
Barley straw	50[a]	1.6% $FeCl_3$	170	60	83	0	76	89	75
		0.98% H_2SO_4			-	-	-	55	
Lodgepole pine	65[b]	1.1% H_2SO_4	170	60	71.5	89.0 (93.3)	73.8	~100	76
		1.1% SO_2			71.2	87.5 (92.9)	72.3	~71	
		20% NaOH			63.7	48.2 (73.9)	83.3	~35	
	78[b]	0.24% $MgCl_2$	205	30	72.7	89.1 (88.4)	67.4	~65	
Buddleja davidii	50[b]	1.75% H_2SO_4[d]	180[g]	40	85	78	36	98	77
	65[b]	1.50% H_2SO_4[d]	195	60	86	84	69	98	
Eucalyptus	25[a]	1% CH_3COOH	200	60	-	-	-	~100	78
Japanese cypress	50[c]	0.4% HCl	170	45	~65	100 (100)	~67	~70	79
Liriodendron tulipifera	50[a]	1% H_2SO_4	140	50	~91	66.5	43.4	~67	80
	50[a]	1% NaOH	140-160	50				66-68	81
Loblolly pine	65[c]	1.1% H_2SO_4[d]	170	60	79.3	96.1 (97.9)	61.2	67.9	82
Miscanthus	80[b]	1% H_2SO_4[d]	170	60	-	-	~93	~45 (~75[e])	83
	80[c]	0.5% H_2SO_4	170	60	95.0	88.8	70.3	80 (98[f])	84
Pitch pine	50[b]	1% H_2SO_4	180	0	~82	100	~9	56.7	85
		1% $MgCl_2$	210	10	~97	100	~1	61.1	
		2% NaOH	190	20	~93	100	~55	~57	
Sugarcane bagasse	50[b]	1.25% H_2SO_4[d]	175	60	-	-	-	46 .0	86
	50[b]	1.25% H_2SO_4[d]	175	60	110.5	51.4	9.3	26.5	87
		1.25% NaOH[d]			102.6	20.2	9.4	38.4	
Wheat straw	50[a]	-	210	90	94.9	95.3	75.8	85.9	88
	60[a]	0.29% H_2SO_4	190	60	91.1	81.4	59.1	89.4	

[a] Weight ratio; [b] Volume ratio; [c] Concentration (ratio) unit not specified; [d] On dry biomass; [e] With enzymatic prehydrolysis; [f] With presoaking; [g] Heating was stopped when reaction temperature reached 180°C.

Here, the empirical polarity is a linear combination of three common solvent properties but additional descriptors including the Hildebrand solubility parameter[89] can also be added as terms to the equation.[90] In addition to the Kamlet-Taft parameters, $E_T(30)$ data, a measure of both polarity and acidity together is often used.[72] It is calculated from the wavelength of maximum absorbance of Reichardt's dye (RD) and generally normalized (E_T^N) where tetramethyl silane and water are arbitrarily chosen as 0.0 and 1.0 values for the scale as follows[71]:

$$E_T^N = (E_T(30) - 30.7)/32.4 \quad (4)$$

and

$$E_T(30) = 28591/\lambda_{max,Z} \quad (5)$$

Cellulose swelling has been correlated using LSER methods to multiple solvatochromic parameters with the best correlations based on dipolarity/polarizability, $E_T(30)$, solvent acidity, solvent basicity and molar volume.[91, 92] Solubility and solvatochromic parameters for selected organosolv solvents are presented in Table 3.

4. Organosolv pretreatments: new interest in an old technology

The majority of organic solvents used for lignocellulose pretreatments are either polar protic or polar aprotic solvents (Table 2). This results in a cellulose-rich fraction, an organosolv lignin fraction, and a water soluble fraction containing sugars (mainly hemicellulose-based sugars), acid soluble lignin, carbohydrate degradation products, organic acids, and other components. Most of the organic solvents used are bulk commodity chemicals, and so their cost is low relative to cellulose dissolving solvents such as ionic liquids. Despite this, the cost of organosolv pretreatments and corrosion issues continue to be factors affecting their large-scale adoption and effective recovery and recycling strategies are required.

4.1. Alcohols

4.1.1 Ethanol

Ethanol is a low cost, renewable solvent and is the most commonly used low boiling point solvent for pretreating/pulping lignocellulosic biomass. The application of ethanol to pulping began in the 1940s[93] and the resulting

ethanol-based organosolv process was further developed by the Canadian pulp and paper industry (*i.e.*, the Alcell pulping process).[94] Research into ethanol-based organosolv pretreatment of lignocellulosic biomass for enhanced enzymatic hydrolysis began in the 1980s.[93] Some twenty-five years later, an ethanol-based biorefinery process to produce lignin and fermentable sugars was developed and is known as the Lignol process.[95]

Acid catalysts are preferred for ethanol pretreatment of lignocellulose (Table 4). As with other organosolv pretreatment systems, the addition of acid catalyst delivers comparable glucan digestibility in the residue to that of either ethanol alone or base-catalyzed ethanol but at reduced temperature and reaction times (Table 4). The results of these studies reveals that the improvement in glucan digestibility with the addition of acid catalyst is not dependent upon increases in delignification efficiency; rather the improvement arises from a reduction in degree of cellulose polymerization (with a concomitant increase in cellulose chain 'ends' that are accessible to cellobiohydrolases), reduced average fibre length, and increased substrate porosity of pretreated biomass obtained under acidic conditions. All of these effects can lead to increased cellulose accessibility to hydrolytic enzymes.

The use of organic acid or inorganic salts as catalysts during ethanol pretreatment of biomass rather than mineral acid catalysts offers the opportunity to significantly reduce corrosion, a key parameter for the scale up of pretreatment technology from the laboratory to commercial-scale.[75, 76, 85] An assessment of six inorganic salts ($FeCl_3$, $Fe_2(SO_4)_3$, $FeSO_4$, $AlCl_3$, $Al_2(SO_4)_3$, $MgSO_4$) as catalysts for the ethanol pretreatment of barley straw revealed that $FeCl_3$ is the most effective and improves glucan digestibility in the residual fibre by ~30% when compared to 1% H_2SO_4 (Table 4).[75] $FeCl_3$ improves pretreatment effectiveness as it catalyzes carbohydrate dehydration.[75] Replacing H_2SO_4 catalyst with $FeCl_3$ also reduces the formation of carbohydrate degradation products, hydroxymethylfurfural (HMF) and furfural,[75] because of reduced acidity. Organic acid catalysts also have significant value in organosolv pretreatment systems; the presence of acetic acid catalyst during pretreatment of bagasse and eucalyptus reduces the ethanol content required by more than 80% without increasing initial reaction pressure or negatively effecting glucan digestibility.[78, 96] The combination of this process with ball milling[97, 98] or twin-screw extrusion[99] further improves glucan digestibility, although the high energy demand during physical pretreatment precludes practical industrial application.

Additional processes prior to ethanol pretreatment offer opportunities to improve glucan digestibility relative to single-stage, ethanol pretreatments. Such processes include refluxing in aqueous acid and enzymatic hydrolysis.[83, 84] Not surprisingly, refluxing in dilute acid solubilizes ~56% of the arabinoxylan in milled *Miscanthus*, resulting in significantly increased lignin solubilization during subsequent ethanol pretreatment.[84] The addition of a commercial lignocellulose hydrolysis enzyme mixture appears to disrupt the lignocellulose matrix and enhances subsequent ethanol pretreatment despite having only minimal impact on fibre structure and composition.[83]

Ethanol concentration has a significant effect upon delignification in the presence of an acid catalyst; at lower ethanol concentrations acid-catalyzed cleavage of α- and β-ether linkages in the lignin[100] produces lignin fragments with smaller molecular weights that become soluble whereas higher ethanol concentrations increase solubilization of the lignin without the need for fragmentation.[101, 102] Cleavage of β-O-4 ether linkages is the major step for lignin depolymerization in various biomasses including *Miscanthus*, Loblolly pine, *Kanlow switchgrass* and *Buddleja davidii* with acidified ethanol solutions.[103-106] However, El Hage *et al.*[107] reported cleavage of α–ether linkages as the primary cause of lignin depolymerization during acid-catalyzed ethanol pretreatment of *Miscanthus*, which is inconsistent with their early conclusion[103] despite the similar reaction conditions. This may be because the α–ether linkages are weaker than the β-linkages, and so are easier to breakdown, but does not necessarily lead to depolymerization.

Lignin condensation is observed in acid-catalyzed ethanol pretreatment of biomass.[104, 107] Under such conditions, increasing pretreatment severity increased dehydration of the side chains and condensation of *Miscanthus* lignin, increased the concentration of phenol groups, and decreased the molecular mass of lignin fragments, but core lignin structure was not altered.[103, 107] Although highly-condensed lignin is formed during ethanol pretreatment of *Buddleja davidii* biomass, delignification efficiency is not impaired.[106] Intriguingly, it has been suggested that condensed lignins with an abundance of phenols and carboxylic acids, and low aliphatic carbon content produced during ethanol pretreatment of Loblolly pine may have utility as antioxidants or other value-added products.[104]

While delignification is the major feature of ethanol pretreatment, the process also has impacts on cellulose and hemicellulose, although the effects are not uniform. For example, increased cellulose crystallinity is observed after acid-ethanol pretreatment of Lodgepole pine as a result of hydrolysis of amorphous hemicellulose and cellulose, and removal of lignin.[108] In contrast, cellulose crystallinity remains effectively unchanged after acid-ethanol pretreatment of Kanlow switchgrass under similar pretreatment conditions.[109] Further, removal of hemicellulose and alterations to the structure of cellulose are perhaps as equally important as delignification when considering efficiency of enzymatic saccharification of cellulose in ethanol-pretreated lignocellulosic biomass.[77] For example, conversion of crystalline cellulose dimorphs (I_α and I_β) to more easily degradable para-crystalline and amorphous forms with a decrease in the degree of polymerization has been observed during ethanol pretreatment of biomass.[77] Interestingly, there is no correlation between glucan digestibility and either delignification of empty palm fruit bunch or hemicellulose solubilization in *Eucalyptus* wood during ethanol pretreatment.[96, 110] Collectively, these studies confirm that the accessibility of cellulose saccharifying

enzymes to their substrate, which is affected by delignification, particle size, hemicellulose removal, and/or biomass porosity, is the key factor that determines glucan digestibility in ethanol pretreated fibre.[111]

The mass balances of carbohydrates, and in particular xylan, in acid-catalyzed ethanol pretreatments are typically poor, an observation attributed to formation of the pentose/xylan degradation product furfural and/or xylan oligomers.[76, 77, 110, 112, 113] However, it is more likely that poor xylan mass balance arises because of the formation of ethyl xyloside during pretreatment (Fig. 3). Ethyl glycosides can also be generated via a similar mechanism and such compounds have been observed at yields comparable to free monosaccharides during acid-catalyzed ethanol pretreatment of spruce wood.[114] While vexatious for mass balance, the formation of xylosides and glycosides protects xylose and glucose from degradation into furfural and 5-hydromethyl furfural, respectively, and opens the possibility of exploiting such compounds for the synthesis of sustainable, relatively high-value chemicals.[114, 115]

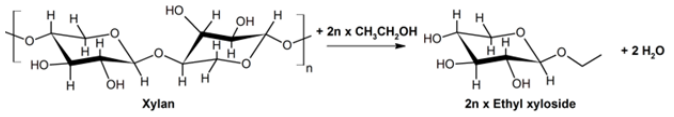


Fig. 3 Formation of ethyl xyloside during ethanol pretreatment

4.1.2 Methanol

The mechanism of methanol biomass pretreatment is very similar to that of ethanol.[93] Under acidic conditions, methyl glycosides can be produced, presumably via a similar reaction to that which gives rise to ethyl glycosides during ethanol pretreatment (Section 3.1.3).[116] Due to its inherent toxicity and flammability, research into methanol pretreatment for biomass saccharification has been minimal in recent years.[117]

4.2 Polyhydric alcohols

4.2.1 Glycerol

Glycerol is a non-toxic, viscous, organic solvent and can be produced by saponification of triglycerides in fats and oils, or from propylene via synthetic chemistry. As a result, crude glycerol is produced as a by-product of biodiesel production and increased biodiesel production has significantly reduced the price of industrial-grade glycerol. Glycerol has a long history as a solvent for the isolation of lignin from wood and as a pulping agent, but has only relatively recently been used in organosolv pretreatment of lignocellulosic biomass to enhance enzymatic saccharification. Glycerol can be used as a standalone solvent[118,119] or combined with alkali catalysts[120-122] for pretreatment of lignocellulosic biomass to produce readily digestible solids. However, glycerol pretreatment of lignocellulosic biomass is more frequently undertaken in the presence of an acid catalyst (Table 5).

Table 5 summarizes the results of glycerol-based pretreatments to improving cellulose digestibility. In the absence of catalyst, Sun and Chen[118] observe that a reaction temperature of 220 °C and reaction time of 3 h under atmospheric pressure are required to achieve 70% hemicellulose removal, 65% delignification, and 90% glucan digestibility after pretreatment of wheat straw with glycerol. With crude glycerol containing impurities such as water, salts and others, atmospheric pretreatment of wheat straw with 220 °C for 3h leads to cellulose digestibility of 72-75%.[123] Likewise, glucan digestibility of 98% and 64.3% delignification of *Eucalyptus* wood is only achieved after ~70 min of pretreatment at 200 °C in glycerol in the absence of catalyst.[119] In the presence of 10% KOH, pretreatment of softwood (Norway spruce) at 210 °C for 15 min leads to a cellulose digestibility of 97%[120] while pretreatment of hardwood (beech) at 190 °C for 15 min results in cellulose digestibility of 95%.[121]

Compared to alkaline-catalyzed glycerol pretreatment of lignocellulosic biomass, the acid-catalyzed process requires relatively low pretreatment temperatures and/or relatively short pretreatment times and/or relatively low concentrations of catalyst in order to achieve higher glucan digestibility (Table 5). Efficient pretreatment of lignocellulosic biomass with acidified glycerol generally requires reaction temperatures of < 200 °C (Table 5).[124-127] For example, 90% glucan digestibility in sugarcane bagasse after pretreatment in glycerol at 190 °C for 60 min with 0.94% H_2SO_4 catalyst has been achieved (Table 5).[125] The combination of acidified glycerol and microwave irradiation further reduces reaction times; total reducing sugar yields of 79% can be achieved after only 6 min pretreatment of Japanese cedar at 180 °C in the presence of acidified (0.1% HCl) glycerol.[124] HCl is a more effective as a catalyst for glycerol pretreatment processes than other acids, including H_2SO_4 (Table 5) because of its low pKa (~–6) and thus high acidity.

Our research team has evaluated pretreatment of sugarcane bagasse at relatively low temperatures (≤130 °C) using acidified glycerol at the laboratory-scale (*i.e.*, 4 g dry mass in 40 g liquid).[127] Pretreatment of sugarcane bagasse with glycerol containing ≤20% water and 1.2% HCl at 130 °C for 60 min results in fibre with glucan digestibility of ≥88%, despite relatively low (<40%) delignification (Table 5).[127] Furthermore, we have demonstrated acidified glycerol pretreatment at the pilot-scale in a horizontal, stirred reactor[127] and, despite a significant reduction in reaction time (from 60 min to 15 min), acid catalyst concentration (from 1.2% to 0.4% HCl), and liquid/solid ratio (from 10:1 to 6:1), are able to obtain comparable glucan digestibility (90%) to that obtained at the laboratory-scale (Table 5). We attribute the increased efficiency of pretreatment at the pilot-scale to improved mixing and heat transfer in the horizontal reactor.

Complex, commercial enzyme mixtures for saccharification of biomass contain enzymes that hydrolyze cellulose and hemicellulose, as well as enzymes that modify lignin. The ability of such enzyme mixtures to saccharify biomass is an important measure of pretreatment efficiency but the use of such mixtures precludes assessment of the effect of pretreatment on individual classes of enzymes (*e.g.*, cellulases)

Table 5 Glycerol lignocellulosic biomass pretreatments for saccharification

Biomass	Glycerol/water, w/w	Catalyst	T, °C	t, min	Cellulose yield, %	Hemicellulose removal, %	Delignification, %	Cellulose digestibility, %	Ref.
Eucalyptus globulus	56:44	-	200	69	92	82	64.3	98	119
Japanese cedar	91:9	0.1% HCl	180[a]	6	-	-	50.2	79.0[b]	124
		0.1% H_2SO_4			-	-	45.3	49.9[b]	
Sugarcane bagasse	80:20[c]	-	190	240	92	-	79.9	-	128
	80/20	1.1% H_2SO_4	194	100	-	-	66.7	97.6	126
	80:20	0.94% H_2SO_4	190	60	87	96	54	91	125
		3% NaOH	190	60	100	8	48	66	
	88.8:10	1.2% HCl	130	60	92.1	92.4	37.9	97.1	127
	78.8:20	1.2% HCl	130	60	94.0	79.2	33.5	87.9	
	89.6:10	0.4% HCl	130	60	94.2	75.3	35.2	80.1	
	~83:17	0.4% HCl	130	15	-	-	-	90.4[d]	
Wheat straw	70:30	-	220	180	~98	~70	~65	~90	118
	Crude glycerol (40-50% and impurities)	-	220	180				~75	
Softwood (Norway spruce)	100:0	-	210	15	-	-	-	97	120
Hardwood (beech)	100:0	-	190	15	-	-	-	95	121

[a] Microwave heating; [b] Yield of reducing sugars (compared to total reducing sugars in pretreated biomass); [c] Volume ratio; [d] Pilot-scale pretreatment in a horizontal reactor.

or individual enzymes. Therefore, we investigated the effect of pretreatment on saccharification of sugarcane bagasse by both complex and simple enzyme mixtures.[129] Sugarcane bagasse pretreated with acidified glycerol (0.4 wt% HCl) and subsequent steam explosion is saccharified more readily with a binary cellulase mixture (CBH I and βG) than that pretreated with either dilute acid or NaOH combined with steam explosion.[129] These results indicate that acidified glycerol pretreatment offers the opportunity to simplify the complexity of enzyme mixtures required for saccharification of lignocellulosic biomass, which may lead to a significant reduction in process cost. In addition, acidified glycerol pretreatment of biomass generates lower levels of sugar degradation products (*i.e.*, furfural and HMF) than dilute acid pretreatment at a similar level of glucan digestibility.[127] The low levels of sugar degradation products is possibly due to the production of glycerol glycosides (glucosides and xylosides), which protect the degradation of sugars.

Glycerol organosolv pretreatment functions through a combination of delignification, particle size reduction, and improvement of cellulase access to cellulose. It is expected that the mechanisms of delignification in glycerol pretreatment are similar to other organosolv processes; that is, cleavage of aryl-ether linkages in lignin and cleavage of ether bonds between carbohydrate and lignin. However, detailed information on the extent of cleavage of these linkages and lignin condensation is unavailable. Delignification with acid-catalyzed glycerol pretreatment (Table 5) is generally lower than that obtained with acid-catalyzed ethanol pretreatment (Table 4) or EG[130] for reaching the similar level of cellulose digestibility. The relatively low solubility of lignin in glycerol is the most likely cause for this observation.[131] The average biomass particle length of acidified glycerol pretreated bagasse is much shorter than that of acidified EG pretreated bagasse. Carbohydrate-binding modules (CBMs) are protein domains that play a key role in mediating cellulase binding to cellulose.[132] Recombinant CBMs have been used to probe enzyme accessibility in softwood pretreated with acidified glycerol and the results indicate that cellulase accessibility (and hence glucan digestibility) in the resulting residue is greater than that obtained from other polyol pretreatments, including EG.[124]

Although glycerol-based and other organosolv pretreatments have been extensively reported, few studies have reported the effects of residual glycerol (and other solvents) on enzymatic hydrolysis and microbial fermentation. In our recent study (Zhang et al., 2015),[133] we found that the presence of 2% glycerol inhibited enzymatic hydrolysis, resulting in a reduction in glucan digestibility of ~2%. However, the inhibitory effect of glycerol on cellulose enzymes was reversible and dilution of glycerol resulted in increased glucan digestibility. Furthermore,

ethanol fermentation of glycerol-pretreated sugarcane bagasse by yeast was sensitive to glycerol and up to 5% glycerol had no significant effect on ethanol production and final ethanol yield.

There is a paucity of information about the chemical composition of the hydrolysate produced during glycerol pretreatment.[127] We have characterized hydrolysates produced during acidified glycerol pretreatment of sugarcane bagasse and found that, although the majority of the hemicellulose (>90%) is removed from sugarcane bagasse, the yields of monomeric sugars are <50%.[127] Subsequent analysis revealed the presence of glycerol glycosides that likely formed via a reaction mechanism similar to that which gives rise to EG-glycosides and ethyl glycosides during cellulose liquefaction and biomass pretreatment in acidified EG and ethanol.[114, 127, 134] As is the case with ethyl glycosides,[115] glycerol glycosides can potentially be recovered as intermediate for the production of high value chemicals and their formation may explain the low levels of sugar degradation observed during acidified glycerol pretreatment.[127]

Catalytic efficiency is not the only factor effecting choice of acid catalyst in the glycerol pretreatment system; while HCl gives a higher sugar yield than sulfuric, phosphoric, malonic, maleic, lactic, citric, and acetic acids during glycerol pretreatment of softwood,[124] we observe the formation of glycerol chlorination products, such as 3-monochloropropane-1,2-diol (3-MCPD), during HCl-catalyzed glycerol pretreatment of sugarcane bagasse under similar conditions.[127] Despite the fact that increasing water content and reducing HCl concentration reduces the extent of glycerol chlorination, we recommend the use of acid catalysts other than HCl for glycerol pretreatment of biomass because chlorinated glycerol compounds are carcinogenic.[127]

4.2.2 Ethylene glycol

EG is also a well-known biomass pulping solvent and is a more effective delignification agent than glycerol during pretreatment under the same conditions.[130] For example, pretreatment of waste newspaper with non-aqueous EG solution in the presence of 2% H_2SO_4 at 150 °C for 15 min results in 94% glucan digestibility in the resulting fibre.[135] We have demonstrated that glucan digestibility of sugarcane bagasse after acid-catalyzed EG pretreatment is highly dependent upon the extent of delignification.[130] We have also observed strong linear correlation ($R^2 = 0.984$) between glucan digestibility and delignification.[130] As is the case with other alcohol pretreatments, EG glycosides are likely to be produced in significant amounts during pretreatment under acidic condition.[130]

4.3 Alkylene carbonates

Alkylene carbonates (ACs), such as glycerol carbonate (GC), ethylene carbonate (EC), and propylene carbonate (PC), are commercially-available solvents used in a wide range of industrial applications.[136] These ACs have high dielectric constants (ε) and can be synthesized from their corresponding polyols (Table 2).[137, 138]

EC has been used previously for liquefaction of woody biomass to produce hydroxyl rich compounds for the synthesis of polymers.[67, 139] Complete biomass liquefaction in acidic EC occurs at relatively low (≤ 150 °C) temperature and ~8 fold faster than is observed for EG.[67] Further, mixtures of EC and EG improve the extent of biomass liquefaction under acidic conditions compared to either EC or EG alone.[67] Given that the goal of biomass pretreatment for improved cellulose saccharification is the removal and/or modification of lignin and removal of hemicellulose, biomass pretreatment using ACs is conducted at lower temperatures than are used for biomass liquefaction.

Our research team has demonstrated that biomass pretreatment with mixtures of EC and EG is more effective than either of the individual components alone.[140] Pretreatment of sugarcane biomass with acidified EG at 90 °C for 30 min in the presence of 1.2% H_2SO_4 resulted in 65% delignification but only 13% glucan digestibility.[140] The addition of EG significantly improved both delignification and glucan digestibility, and maximal delignification (93%) and glucan digestibility (93%) were observed at an EC:EG weight ratio of 4:1 after pretreatment at 90 °C in the presence of 1.2% H_2SO_4. Further, we demonstrated that EC/EG pretreatments were more effective than those using PC/propylene glycol (PG) for sugarcane bagasse.[140] However, while EC is considered to have low toxicity, we would urge caution in the industrial use of EC/EG pretreatment systems; EG is toxic to humans and can be generated during EC decomposition,[67] and long-term exposure to EG is associated with metabolic acidosis, cardiopulmonary failure and acute renal failure.[141]

GC is a cyclic alkylene carbonate that can be produced sustainably from CO_2 and glycerol[142, 143] and is considered to have low toxicity.[137] Unlike EC, the decomposition product of GC (*i.e.*, glycerol) is also considered to have low toxicity. Pretreatment of sugarcane bagasse using acidified GC at 90 °C results in 90% glucan digestibility in the resulting residue,[144] which is ~6 fold higher than the glucan digestibility of fibre pretreated under similar conditions using EC (16%). Similarly to the EC/EG pretreatment system, GC can be partly replaced by glycerol without negative impact on biomass pretreatment effectiveness; however, the GC/glycerol pretreatment system is generally less effective than EC/EG.[144] Pretreatment of a model substrate (*i.e.*, microcrystalline cellulose) with EC does not improve glucan digestibility but glucan digestibility is improved by pretreatment with GC or a mixture of EC/EG, which likely relates to increased cellulose surface area. Under optimal conditions,[144] pretreatment of biomass with mixtures of ACs and alkylene glycols does not produce 5-hydroxymethyl furfural (a glucose degradation product) at levels that are detectable in the hydrolysate and only produces furfural (a xylose degradation product) at very low levels (≤0.3% of initial mole xylose).[140, 144]

The effectiveness of pretreatment using alkylene carbonates arises from their relatively high relative permittivity, ε_r (also well known as dielectric constant); EC, PC and GC have dielectric constants of 90.0 (at 40 °C), 65.5 (at 25 °C) and 109.7

Table 6 Organic acid/peroxylic acid biomass pretreatments at atmospheric pressure for saccharification

Biomass	Solvent	T, °C	time, h	Cellulose yield, %	Hemicellulose removal, %	Delignification, %	Cellulose digestibility, %	Ref.
Corn cob	88%[a] FA[b] + 0.2% HCl	60	6	-	85	70	-	145
Corn stover	88% FA[c]	80[d]	3	89.5	79.8	65.6	62.8	146
Palm fruit bunch	86.25% AA[ce] + 0.25% HCl	BP	2	-	-	80	-	147
Miscanthus	40% FA + 40% AA + 20% water[f]	107	3	85.1	78.8	79.6	75.3	148
	90 % FA[a] + 0.4% H_2O_2	80[d]	2	74.8[g]	-	84.3	-	149
Sugarcane bagasse	78% FA[c]	107	1	88.0	89.2	80.7	88.0	150
				88.3	89.0	81.5	89.8[h]	
				90.0	88.1	82.5	91.3[i]	
	88% FA[c]			87.5	88.6	86.4	53.2	
				85.0	90.3	87.6	90.1[h]	
				86.5	91.6	87.8	97.7[i]	
	50% PAA[a] (on biomass)	80	2	-	-	82.0	82	151
	15% PAA[c] (on biomass)	75	2.5	104.7	-	96.9	90.0[j]	152
Wheat straw	30% FA + 55% AA + 15% water[c]	105[d]	3	88.6	69.6	95.5	-[k]	153

[a] Concentration (ratio) unit not specified; [b] Formic acid; [c] Weight ratio; [d] Pretreatment pressure not specified; [e] Acetic acid; [f] Volume ratio; [g] Polysaccharide yield; [h] Deformylation with $Ca(OH)_2$ incubation at 120 °C for 1 h; [i] Deformylation with NaOH incubation at 120 °C for 1 h; [j] Alkaline-peracetic acid process; [k] Pulping was followed by H_2O_2 delignification.

(at 25 °C), respectively.[136] In contrast, the dielectric constants of EG, PG and glycerol are respectively 37.0 (at 25 °C), 32 (at 20 °C) 42.5 (at 25 °C). The high dielectric constant increases the acid potential of the solvent. Stronger acidity promotes the cleavage of ether linkages of lignin and the hydrolysis of hemicellulose, thus improving delignification and hemicellulose removal.100 This also explains why delignification and hemicellulose removal after pretreatment of sugarcane bagasse with a mixture of EC/EG is more significant than that obtained from pretreatment with a mixture of PC/PG at the same acid concentration and temperature.[140]

Pretreatment by acidified EC alone does not lead to high glucan digestibility despite the high level of delignification.[140] EG acts by delignification and by swelling fibres during biomass pretreatment,[130, 154] and the addition of EG to EC during biomass pretreatment results in biomass swelling and further enhances delignification and hence improves glucan digestibility in the resulting fibre.[140] In contrast, GC has a similar structure to PC (Table 1), with one hydrogen from the methyl group in PC replaced by a hydroxyl group. The presence of a hydroxyl group in GC possibly provides the ability to dissolve the lignin components and to swell the cellulose fibre, and thus improves the glucan digestibility.[144]

In summary, the studies on pretreatment by EC/EG, PC/PG, and GC/glycerol demonstrate (i) the high ε value of the solvents provide the ability to significantly cleave the lignin ether bonds and glycosidic bonds, which results in improved delignification and biomass particle size reduction in acidic conditions, (ii) the ability of the solvent to swell biomass, and (iii) the synergetic effects of the above during pretreatment.

Although AC/AG biomass pretreatment systems are effective, AC decomposes under acidic conditions, resulting in the production of the corresponding AG and CO_2.[140, 144] For example, 2–6% of ACs decomposes to polyol and CO_2 during pretreatment of sugarcane bagasse in the presence of 1.2% H_2SO_4 at 90 °C for 30 min.[140, 144] The gradual decomposition of AC to AG may favor the biomass pretreatment as shown in previous study where adding AG in AC improves the pretreatment with ACs such as EC and PC.[140] Although AC can be regenerated by reacting AG with CO_2,[142] the reformation of AC after acidic AC/AG biomass pretreatment adds an extra step, and therefore expense, to the process. Further, as is the case in other biomass pretreatments using alcohols as solvents,[114] polyols added to biomass pretreatments as part of an AC/AG mixture or generated from AC during pretreatment can react with sugars to produce of glycol glycosides.[140] The low yields of sugar degradation products such as furfural and 5-hydromethyl furfural are possibly attributed to the production of glycosides, which protect the sugar degradation.

4.4. Organic acid and peroxylic acid

Acetic acid and formic acid are the best studied organic acid co-solvents for organosolv pretreatment of biomass. Acetic acid and formic acid have boiling points of 118 °C and 100.8 °C, respectively. As a result, biomass pretreatments utilizing these co-solvents can be conducted at relatively low temperatures (*i.e.*, close to their boiling points) under atmospheric

pressure.[145-147, 150, 155, 156] Formic acid and acetic acid react with hydrogen peroxide to form peroxyformic acid and peroxyacetic acid (peracetic acid). These peroxylic acids are strong oxidants and very effective delignification agents; as a result, formic acid and acetic acid in combination with hydrogen peroxide have been used for biomass pretreatment/pulping.[149, 152, 157-161]

Organic acid organosolv pretreatment can be undertaken with or without mineral acid catalyst or in the presence of hydrogen peroxide (Table 6). However, it should be noted that esterification (*i.e.*, formylation) of cellulose during formic acid pretreatment can limit cellulose digestibility despite the removal of lignin and hemicellulose.[93, 162] While cellulose digestibility after formic acid pretreatment can be improved by alkaline deformylation (Table 6), the improvement in glucan digestibility arising from post-pretreatment deformylation depends upon the extent of formylation which, in turn, depends on the concentration of formic acid used during pretreatment (Table 6).[150] Combinations of organic acids have also been used for organosolv pretreatment of lignocellulosic biomass.[148, 153] For example, Vanderghem *et al.*[148] predict maximal cellulose digestibility of 75.3% in *Miscanthus* × *giganteus* biomass after pretreatment with a mixture of formic and acetic acid using response surface analysis (Table 6). By combining mixtures of organic acids for pretreatment and post-pretreatment delignification with H_2O_2, Snelders *et al.*[153] demonstrated 95.5% delignification of wheat straw (Table 6). Optimized, single stage peracetic acid pretreatment of sugarcane bagasse is able to deliver 82% glucan digestibility (Table 6).[151] Furthermore, Zhao and Liu[152] combined peroxylic acid pretreatment with alkaline pretreatment in a two-stage process, which reduces the amount of peroxylic acid required from 50 wt% to 15 wt% but improved glucan digestibility to 90% (Table 6).

Organic acids and lignin have similar Hildebrand's solubility parameters ($(cal/cm^3)^{1/2}$); 12.1 (24.9 $MPa^{1/2}$) for formic acid, 10.1 (21.4 $MPa^{1/2}$) for acetic acid, and ~11 (~23.0 $MPa^{1/2}$) for lignin.[93] As a result, lignin is readily soluble in these organic acids and this is a contributing factor to the efficiency of organic acid lignocellulosic biomass pretreatment. Cleavage of α–aryl ether bonds is primarily responsible lignin fragmentation during H_2SO_4-catalysed acetic acid delignification pretreatment of sugarcane bagasse, although cleavage of β–aryl ether linkages also plays an important role.[100, 163] In addition, condensation and precipitation of residual lignin may also have an impact on glucan digestibility and contribute to the observation that highest glucan digestibility is not observed when lignin and xylose contents are at their lowest.[164]

High molecular mass lignin is removed during peroxyformic acid and peracetic acid lignocellulosic biomass pretreatment by ^{+}OH ions, which form *in situ* from the reaction between carboxylic acid and hydrogen peroxide.[157] Enhanced glucan digestibility in the residue produced by peracetic acid pretreatment arises from delignification, as well as increased surface area and exposure of the cellulose fibres.[93] The incorporation of an alkaline pretreatment step prior to peracetic acid pretreatment also serves to remove lignin and swell the biomass fibres.[159]

Acetic acid pretreatment of Douglas fir wood results in cellulose acetylation; this modification to the surface of cellulose reduces the effectiveness of acetic acid pretreatment relative to ethanol pretreatment by either reducing the ability of cellulases to bind to cellulose or preventing cellulose chains from forming a productive complex with enzymes.[165] Acetylation of cellulose and its negative impact on enzymatic saccharification is reversible; alkaline deacetylation under mild conditions (1 wt% NaOH, 50 °C, 2 h) increases glucan digestibility after 72 h from ~10% to ~60%.[165] Similarly, formylation of cellulose during formic acid pretreatment decreases the surface area of the biomass and thus inhibits enzymatic saccharification.[162] Although alkaline deformylation of formic acid pretreated biomass is able to restore enzymatic saccharification, pretreatment of biomass with high concentrations of formic acid is not recommended because formic acid can be liberated during enzymatic saccharification and inhibit the growth of microorganisms in subsequent fermentation.[150] Recently, Zhao *et al.* developed a kinetic model for polysaccharide dissolution from lignocellulosic biomass during acetic acid pretreatment and proposed reaction mechanisms for the acetylation of cellulose and xylose in the presence of H_2SO_4 catalyst.[161] Formylation of cellulose during formic acid pretreatment is expected to proceed via a similar mechanism.

Decomposition of peroxylic acid to its corresponding organic acid during peroxylic acid biomass pretreatment is accompanied by the production of water and oxygen.[151] The esterification of cellulose during peroxylic acid pretreatment arises from the presence of these organic acids at relatively high concentration and can have a profound effect on enzymatic saccharification above a critical threshold.[151]

4.5 Solvents used for biphasic fractionation systems

4.5.1 Methyl isobutyl ketone

Methyl isobutyl ketone (MIBK) is synthesised from acetone and has been used in combination with water and alcohol for biomass fractionation into pulp and lignin.[65, 166] In recent years, the MIBK-based process has been adapted to pretreat lignocellulosic biomass for the production of fermentable sugars and "clean" lignin.[167-170] Such a process begins with the adjustment of the ratio of MIBK, water, and alcohol (usually ethanol) such that a single phase is formed for biomass digestion at elevated temperature.[65, 166] Replacing alcohol (*i.e.*, ethanol) with acetone in an MIBK-based process increases the efficiency of fractionation.[171] After pretreatment, the solid and liquid are separated by filtration and the cellulose-rich solid residue is converted to glucose by enzymatic saccharification. The pretreatment liquid is mixed with water, resulting in phase separation and resolution of lignin-rich MIBK from aqueous alcohol containing hemicellulose/soluble sugars. The addition of mineral salt (*e.g.*, NaCl) improves phase separation.[171] MIBK is then recovered by distillation, which allows for MIBK

re-use and recovery of lignin. Such a system was used by Brudecki *et al.*[167] for the pretreatment of prairie cordgrass and results in a glucose yield of 84% and an acid insoluble lignin yield of 87%.

4.5.2 Ethyl acetate

Ethyl acetate can replace MIBK for biomass fractionation in order to lower toxicity and solvent cost.[172] Fractionation process conducted at optimised conditions (140 °C for 20 min; 0.46% H_2SO_4 in ethyl acetate/ethanol/water (36.7/25.0/38.3 mass ratio)) leads to lignin recovery of 59%, xylose yield of 44% and glucose enzymatic yield of 84.8%.[172] Ethyl acetate is expected to have higher affinity for lignin based upon its Hildebrand's constant.[172] However, it is well known that esters such as ethyl acetate can be hydrolysed under acidic conditions, which may result in poor solvent recovery and recycling.

4.5.3 2-Methyltetrahydrofuran

2-Methyltetrahydrofuran (2-MTHF) is a bio-based solvent and can be synthesized by catalytic hydrogenation of furfural (a xylose degradation product) or levulinic acid (an organic acid derived from glucose).[173] In a process similar to that deployed for MIBK biomass pretreatment,[167] vom Stein *et al.*[174] reported a one-step process for fractionation of beech wood using a mixture of oxalic acid, water, and 2-MTHF. At mild temperatures (80–140 °C), oxalic acid selectively hydrolyses hemicellulose to soluble sugars in aqueous solution while the cellulose-pulp remains solid and is inaccessible to the acid catalyst. Lignin partitions into the 2-MTHF phase and is directly separated from the pulp and the soluble carbohydrate. The cellulose pulp is subjected to enzymatic saccharification while hemicellulose sugars are recovered from the aqueous fraction. Oxalic acid catalyst is recovered from the aqueous phase by crystallization and 2-MTHF is recovered by distillation, which also recovered lignin. The amount of lignin recovered directly after evaporation of 2-MTHF reaches up to ~60–70% of the theoretical maximum.

4.6 Other solvents

4.6.1 Acetone

The use of acetone for pretreatment of biomass was assessed in the 1980s[93], and has been re-evaluated recently.[175, 176] As with ethanol pretreatment, mineral acids are typically added to acetone pretreatments to promote delignification. For example, Araque *et al.*[175] pretreated wood chips (*Pinus radiata* D. Don) using acetone:water (1:1, v/v) containing 0.9 wt% H_2SO_4 at 185–195 °C and achieved 90–99% ethanol yields after simultaneous saccharification and fermentation of the pretreated biomass. However, as with methanol, there are challenges associated with the use of the solvent for biomass pretreatment (*i.e.*, high flammability and high vapor pressure at elevated temperature).

4.6.2 Tetrahydrofuran

Tetrahydrofuran (THF) is low viscosity solvent that can be derived sustainably from biomass via catalytic decarbonylation and hydrogenation of furfural.[177] Unlike MTHF, THF is water miscible and its low boiling point (66 °C) allows for facile recovery, albeit with similar process safety challenges as acetone. When coupled with dilute acid, very high lignin removal and high solubilisation of hemicellulose is achieved using THF as a co-solvent. For example, Nguyen *et al.*[177] pretreated corn stover using THF:water (1:1, v/v) containing 0.5 wt% H_2SO_4 at 150 °C and achieved ~95% yield of combined sugars (glucan, xylan, and arabinan). The high lignin removal with THF resulted in higher accessibility and less inhibition towards enzymes compared to dilute acid treatment alone. When translated to simultaneous saccharification and fermentation, ethanol yields of over 90% were achieved at an enzyme loading of 5 mg protein g^{-1} glucan.

4.6.3 γ-valerolactone

Recently, the bio-derived solvent γ-valerolactone (GVL) has received significant attention as a co-solvent because it can achieve complete saccharification of biomass at low acid concentrations (<0.1 wt% H_2SO_4).[178] This approach differs from the traditional organosolv process as it produces soluble sugars rather than a cellulose-rich substrate for subsequent saccharification. Luterbacher *et al.*[179] reacted various biomass sources (corn stover, maple wood and loblolly pine) with GVL:water (80:20, w/w) and 0.5 wt% H_2SO_4 at 160-200 °C to recover 89% pentoses and 80% hexoses. Yields increased to 90-95% of the carbohydrate content when dehydration products such as furfural, HMF, and levulinic acid were included. The dehydration products, as well as GVL solvent, can inhibit microbial activity and hence require separation prior to subsequent saccharification and fermentation.

A number of solvent recovery methods have been demonstrated from GVL-water hydrolysate mixtures including biphasic separation with addition of NaCl, or liquid CO_2, but multiple extraction stages are required to reduce the GVL concentration in the aqueous phase.[179] Alternatively solvent extraction methods have been effective in recovering both the solvent and furanic inhibitors.[180] The high boiling point of GVL also provides thermal stability, a key parameter in solvent recycling. Another advantage of GVL as solvent is that lignin can be precipitated (~95% recovery) from GVL-water mixtures through addition of water and this simple separation may be attractive for transformation of lignin into higher-value products.

4.6.4 Others

Although other organic solvents such as 1-propanol, isopropanol, 1-butanol, 1,4-dioxane, phenol, and diethylene glycol have been used for biomass pulping, studies describing their application to biomass pretreatment for enzymatic saccharification are very limited,[76, 181] possibly due to the high process cost (*e.g.*, the cost of solvent and its recovery) and/or solvent toxicity (*e.g.*, phenol).

4.7 The application of severity factors to organosolv pretreatment

Severity factor (originally described as reaction ordinate, R_0) is the combination of lignocellulose pretreatment reaction time and temperature relative to the boiling point of pure water into a single parameter, and is calculated using the following equation:[182]

$$R_0 = t \cdot \exp\left(\frac{T(t)-100}{14.75}\right) \quad (6)$$

where t is the residence time (min) and T is the pretreatment temperature (°C). Initially, severity factor was developed to enable both process control and the prediction of cellulose, hemicellulose, and lignin yield and/or purity after pretreatment, and assumes that pretreatment effects follow first-order kinetics and obey the Arrhenius equation.[182]

Equation (6) was to modified to equation (7) to account for the addition of acid or base catalysts.[183, 184] This modified severity factor (M_0) is calculated using the following equation:[183, 184]

$$M_0 = R_0 \cdot C^n \quad (7)$$

where C is the catalyst concentration (wt%), and n is an arbitrary constant. The n-values for sulfuric acid and sodium hydroxide derived from linear models of modified severity factor and experimentally-observed xylan solubilization and reduction in lignin content in cotton stalk are 0.849 and 3.90, respectively.[185] It is not clear if variations in biomass composition substantially impact upon the n-values for these catalysts.

Combined severity factor (CSF) is an alternative, and more commonly employed approach, to combine lignocellulose pretreatment reaction time, temperature, and the addition of acid or base catalysts into a single factor.[117, 184, 186]. In the presence of acid catalyst, CSF is calculated as:[187]

$$\mathrm{CSF} = \log(R_0) - \mathrm{pH} \quad (8)$$

The modification of equation (8) to equation (9) allows CSF to be derived regardless of the nature of the catalyst:[186]

$$\mathrm{CSF} = \log(R_0) + |\mathrm{pH} - 7| \quad (9)$$

In terms ethanol-based pretreatment, it was found that generally cellulose digestibility increased with increasing CSF (< 2.0).[78, 96] However, the cellulose digestibility could reduce if the CSF was too high (*e.g.*, CSF > 2.04 for the pretreatment of empty fruit bunches).[70] Increase in CSF usually resulted in increased delignification for acid-catalyzed ethanol pretreatment.[96, 110] Goh *et al.* observed a good linear correlation between CSF and delignification at a sulfuric acid concentration of >1.0%.[70] However, delignification was not always correlated with CSF.[110, 112] With a sulfuric acid concentration of <1.0%, Goh *et al.* found that there was no obvious trend between CSF and delignification.[70] CSF could not be correlated with delignification in the studies where different concentrations of ethanol were used.[112] The reason is possibly due to the ignorance of the effect of various organic solvent concentrations on lignin dissolution. Hemicellulose removal can not to be correlated with CSF in pretreatment of Eucalyptus wood[96] although Goh *et al.* showed a good linear correlation with pretreatment of empty palm fruit bunch.[70]

In a recent study with methanol-based pretreatment of hemp hurds increase in CSF led to decrease in both lignin and hemicellulose content.[117] CSF has also been used as an integrated indicator in "Clean Fractionation" pretreatment with MIBK/acetone (ethanol)/H_2O solutions though the correlations between CSF and pretreatment effectiveness have not reported.[171]

The use of severity factor R_0 and modified severity factor M_0 are also occasionally used in recent organosolv pretreatments.[97, 120, 121] The studies on alkaline glycerol pretreatments of softwood and hardwood show a significant dependency of delignification on the severity factor with pretreatments by a glycerol/KOH (10:1 mass ratio) mixture.[120, 121] However, the study with acidified ethanol solutions containing different ethanol concentrations does not show correlations of M_0 and the contents of lignin and hemicellulose[97]. Nevertheless, all these studies show that cellulose digestibility/glucose yield increases with increasing severity factor.[97, 120, 121]

In summary, severity factor and its derivation forms are useful parameters for assessing pretreatment severity and effectiveness. Different observations on correlations of severity factors and pretreatment effectiveness (cellulose digestibility, delignification, hemicellulose removal, lignin content and hemicellulose content) are possibly related to the examined operational condition ranges (*e.g.*, pH, temperature), solvent concentrations (whether the same organic solvent concentration is used) and other unknown factors which has not been able to be included in the CSF.

5. General reaction mechanisms during organosolv pretreatment

The majority of organosolv pretreatments are primarily delignification processes that proceed via cleavage of ether linkages in lignin, production of low molecular weight lignin fragments and phenolics, and lignin dissolution. Lignin functions as a barrier that prevents enzymes from accessing polysaccharides in untreated biomass and delignification can have a profound, positive impact on enzyme access to cell wall polysaccharides and hence saccharification.[188] Cellulases can bind non-productively to both native lignin and residual lignin post-pretreatment,[189, 190] and the addition of non-saccharifying proteins has been shown to enhance the enzymatic hydrolysis of pretreated plant biomass by commercial enzyme mixtures by binding to lignin in place of cellulases.[191-193] Lignin removal does not always correlate with increases in rate and/or extent of enzymatic saccharification, however, and chemical

modification of exposed lignin surfaces to reduce non-specific protein binding may prove as important in enhancing enzymatic saccharification as delignification.[194-196] A summary of the impacts of major organosolv pretreatments on lignocellulose is shown in Table 1. In contrast, a conventional ionic liquid-based process dissolves lignocellulosic biomass; ionic liquid cations form strong hydrogen bonds with hydroxyl groups, thereby deconstructing the hydrogen bond network, especially in cellulose.[44]

The properties and proportion of organic solvent in an organosolv pretreatment and reaction pH combine to (ultimately) determine the extent and rate of lignin dissolution, lignin fragmentation, and lignin condensation.[100] Without the addition of catalyst, organosolv pretreatment begins with the autoionization of water. The resulting hydronium ions and acetic acid released from hemicellulose serve as catalysts that promote the hydrolytic cleavage of both α– and β–aryl ether linkages in lignin (Fig. 4), although α–aryl ether linkage cleavage dominates. It is the cleavage of these ether linkages that is primarily responsible for lignin breakdown prior to dissolution of the fragments. The cleavage of γ–ether linkages (Fig. 4) plays a minor role in lignin fragmentation during organosolv pretreatment of biomass.[107]

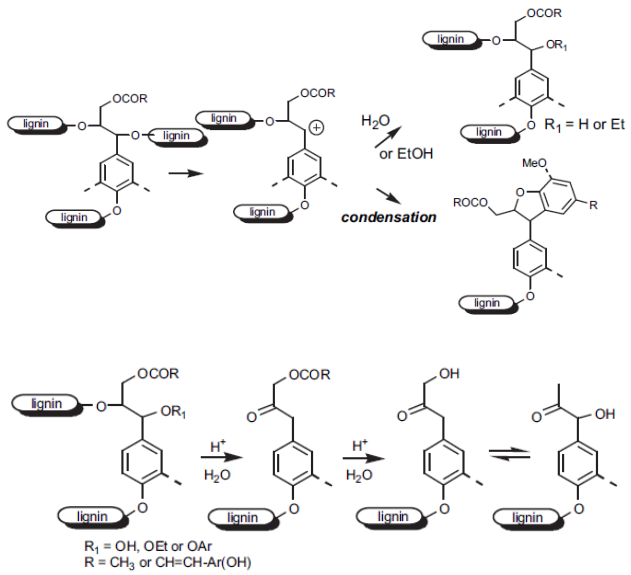


Fig. 4 Mechanisms of cleavage of (top) α, (bottom) β and γ ether linkages in acid-catalyzed ethanol pretreatment of biomass.[107]

Delignification during organosolv pretreatment in the presence of an acid catalyst occurs via a mechanism similar to that observed in the absence of catalyst, albeit at a greatly enhanced rate and extent.[100] However, higher initial acid concentrations increase the likelihood of β-aryl ether bond cleavage.[100, 197] In addition to delignification, amorphous hemicellulose and a small portion of cellulose (usually amorphous) are hydrolyzed and the degree of cellulose polymerization is reduced. Removal of amorphous components in biomass generally leads to an increase in cellulose accessibility. Solvent properties such as the ability to (i) dissolve and prevent lignin condensation, (ii) swell cellulose, and (iii) react with cellulose can therefore also be important factors affecting cellulose accessibility, and hence cellulose digestibility, after acid-catalyzed organosolv pretreatment. Acid-catalyzed processes are the most attractive and well-studied organosolv pretreatments because they allow reduced pretreatment temperatures and reaction times without sacrificing glucose yield.

6. Industrial implementation of organosolv pretreatment processes

6.1 Pretreatment process principles

Organic solvent recovery and re-use is essential in an economic organosolv process and Fig. 5 presents a schematic for general organosolv processes. The efficiency with which an organic solvent can be recovered depends upon its physical properties and its interaction with other components in the pretreatment solution. In order to enhance revenue, solvent recovery should be combined with recovery of hemicellulose sugars and lignin for the production value-added products. Ultimately, process configuration, energy requirements for solvent recovery, and potential hazards associated with organosolv pretreatment depend upon the choice of organic solvent.

Biomass pretreatments using either low boiling point organic solvents (such as ethanol or acetone) or high boiling point organic solvents (such as glycerol or ethylene glycol) share a common set of process steps (Fig. 5a, solid lines). Pretreatment using either solvent type is followed by solid/liquid separation; the solid is washed and subjected to enzymatic saccharification, while the liquid stream is diluted and the lignin is recovered. Two distillation steps are then used to recover water and solvent in separate recycle streams, and a mixture of products (*i.e.*, soluble sugars, phenolics, organic acids *etc.*) are recovered. During biomass pretreatment with low boiling point solvents, the solvent is recovered in the first distillation and water is recovered in the second (Fig. 5a, dotted line). During biomass pretreatment with high boiling point solvents, the converse applies (Fig. 5b, dashed line). The main advantage of using low boiling point solvents is their simple recovery following pretreatment whereas the major drawbacks are the risks associated with volatility and flammability of the solvents and high pressure operation.[198] For organosolv processes using high boiling point solvents, solvent recovery requires more energy than is required for low boiling point solvents.[199]

6.2 Biphasic pretreatment/separation system

Biphasic pretreatment systems (such as those utilizing MIBK or 2-MTHF) offer finer control over biomass fractionation into lignin, cellulose pulp, and hemicellulose-

Critical Review

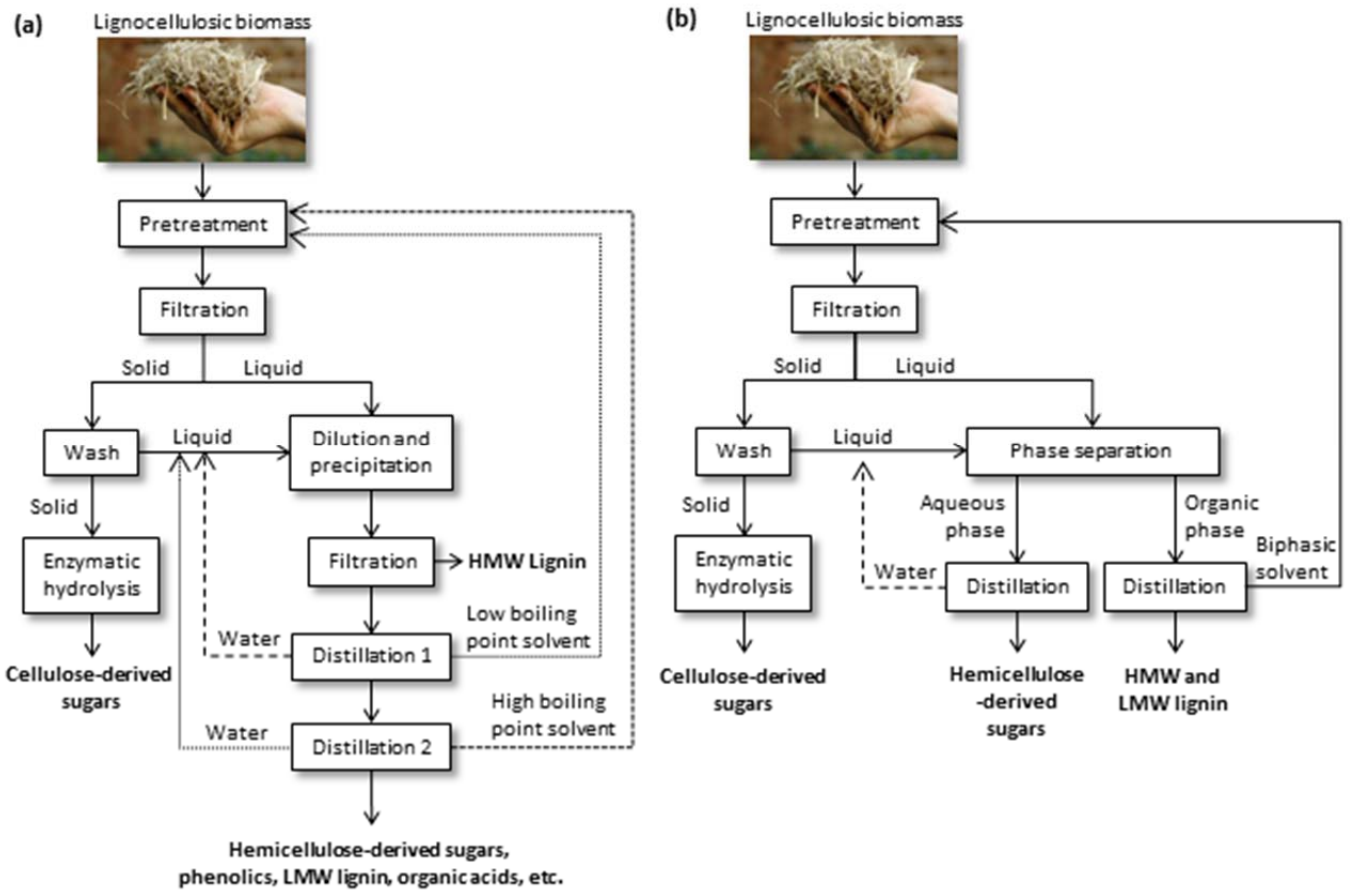


Fig 5. Schematic illustration of pretreatment processes using (a) low (dotted line) or high (dashed line) boiling point solvents or (b) biphasic systems. High molecular weight (HMW) and low molecular weight (LMW) lignins are recovered separately using non-biphasic solvent.

derived sugars than conventional organosolv pretreatments (Fig. 5b).[65] As with pretreatment processes utilizing low and high boiling point solvents (Fig. 5a), post-pretreatment solid/liquid separation and enzymatic saccharification of the solid residues occur during biphasic pretreatment systems. However, the fate of the liquid phase is significantly different; phase separation generates an aqueous phase containing hemicellulose-derived sugars and an organic phase containing lignin. Distillation of the organic phase to recover is simpler because there is little or no water present and both low- and high-molecular weight lignin are recovered together, resulting in higher total lignin recovery.

6.3 Process simulation and economic viability analysis

No single organosolv pretreatment technology (or pretreatment technology of any kind, for that matter) will deliver maximum economic returns in all locations. Regional variations in feedstock availability (both in nature and quantity), chemical and equipment costs, and opportunities for inter-industry interaction render the search for such a technology (ultimately) unproductive. As a result, it is critical to simulate organosolv pretreatment processes in the regional context in which they are being considered. Process simulation identifies the key parameters of a given biomass pretreatment that have an impact (positive or negative) on the economic feasibility of the process. Such parameters include mass flow balances, composition of each process stream, energy analysis, solvent recovery, byproduct isolation and yield, and operation conditions, and these parameters cannot be accurately assessed using laboratory-scale pretreatment experiments.[199] As a result, despite numerous studies on organosolv pretreatment of biomass in recent years, there are only limited number of studies describing process simulation and technoeconomic analysis.

Process simulation for acid-catalyzed ethanol pretreatment of hardwood predicts that bioethanol production from the resulting residue is not energy self-sufficient and that external fuel is required to cover steam demand during (primarily) solvent recovery.[200] Further, the authors determined that such an ethanol organosolv process will consume 34% more energy than an equivalent process based on the use of dilute acid. Process simulation also predicts higher overall energy consumption during bioethanol production using ethanol pretreatment, compared to a soda process, despite optimization of the heat exchanger network using Aspen HX-Net software.[201] Importantly, such analyses highlight the need to balance the production of pure lignin and other co-products against decreased ethanol yield, increased energy consumption, and increased capital expenditure.[200]

Ultimately, process simulations of different processes that convert biomass to renewable fuels, chemicals, and materials allow key technology gaps to be clearly identified. For example, conceptual design of integrated biorefineries built around either ethanol-water or biphasic 2-MTHF pretreatment processes using wood as the feedstock identifies by-product formation, product isolation from complex mixtures, and solvent recovery as the key challenges to profitability, irrespective of scale.[202] As a result, it is clear that significant improvements in process chemistry, equipment design, energy efficiency, and process design are necessary to establish economically-attractive organosolv processes.

6.4 Commercialization

Although continuous efforts have been made on organosolv processes for the production of pulp, fermentable sugars and lignin from lignocellulosic biomass, commercialization of these processes are currently limited. Some organosolv processes studied or being developed towards commercialization include the alcohol-based Alcell™ (Lignol Innovations, Canada) and ECN (Netherlands), Organocell (Germany), American Science and Technology (AST)'s (USA), organic acid-based CIMV (France) and Chempolis (Finland), and glycerol-based Glycell™ (Leaf Resources, Australia) processes. Commercialization of organosolv processes is still facing the challenges including high process cost (e.g. solvent and solvent recovery) and subject to the fluctuation of fossil oil price.

7. Future research and conclusion

The cost of pretreatment (including organosolv) is a major hurdle to commercial production of energy and chemicals from lignocellulosic biomass. Research in the following areas will further the development of biomass pretreatment processes and associate technologies to progress towards commercial outcomes:

(1) Understand the effect of organosolv pretreatment (using a system that is representative of lignocellulose chemical pretreatment that has attributes of acid, base and organic-solvent processes) on the nanoscale architecture of lignocellulose. The study should include structure-property evaluations and an understanding of the mechanisms of the pretreatment process. This could lead to the identification of low cost and more effective solvent systems.

(2) Understand the molecular interactions of enzymes with lignocellulose before and after organosolv pretreatment. Techniques such as atomic force microscopy should be used to determine (i) the adhesion forces between cellulases and either isolated cellulose or lignin, before and after organosolv pretreatment, and (ii) to study the chemical moieties involved in binding of cellulase to lignin.

(3) On the basis of (1) and (2) develop low temperature and/or atmospheric pretreatment processes with low energy consumption and low equipment cost.

(4) Develop tunable solvents that would reduce the amount of solvent required and allow ease of separation.

(5) Investigate and understand the effects of residual solvents on enzymatic hydrolysis and fermentation.

(6) Develop effective, low cost solvent recovery technologies.

(7) Develop substrate-specific low cost enzyme cocktails for efficient saccharification of biomass pretreated by organic solvent.

(8) Develop integrated processes for the production of fermentable sugars and other value-added products from lignin and hemicellulose.

Notes and references

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