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Controlling lignin solubility and hydrogenolysis selectivity by acetal-mediated functionalization†

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Existing lignocellulosic biomass fractionation processes produce lignin with random, interunit C–C bonds that inhibit its depolymerization and constrain its use. Here, we exploit the aldehyde stabilization of lignin to tailor its structure, functionality, and resulting properties, expanding its potential uses. We use bifunctional aldehydes to install specific functionality in lignin and thereby control its physical properties. Rational selection of the aldehyde allows for the formation of acetal-stabilised lignins that are soluble in either polar or non-polar solvents such as water and toluene. Exploiting these novel solubility properties, the effect of solvent on lignin hydrogenolysis is elucidated through the hydrogenolysis of select lignins. Through this study, we notably demonstrate the hydrogenolysis of sodium glyoxylate stabilised lignin in water, opening new avenues for the development of green chemical processes.

Introduction

The increasing political strife and environmental damage associated with the extraction of fossil carbon has prompted a search for renewable reduced carbon sources.[1–3] Lignocellulosic biomass is a potential target as it represents an enormous source of renewable reduced carbon.[4] In this context, new chemical processes and catalysts must be developed to efficiently exploit this material and convert it into the products that we need.[5–9]

Over 80% of the mass of lignocellulosic biomass is composed of three major biopolymers—cellulose, hemicellulose, and lignin. These biopolymers can be separated and depolymerized into their constituent monomers, which include glucose from cellulose, predominantly xylose from hemicellulose, and aromatic molecules from lignin.[10] Of these monomers, both glucose and xylose feed into previously developed biorefinery processes with well-defined products.[11–13] The material properties of lignin and the aromatic molecules that could be produced from it offer several possible avenues for developing low-volume, high-margin products that could make biorefineries economical. However, currently these target products are not well-defined largely due to the lack of diversity of lignin materials available on the market.[14]

This constraint is a consequence of the current industrialized lignin isolation processes, which produce lignin that is highly recalcitrant towards depolymerization. The lignins that are commercially available are also difficult to process due to their limited solubilities, which are constrained by their methods of production. Kraft lignin can be solubilised under alkaline conditions, but not in neutral water. And, it is soluble in polar solvents such as dimethyl sulfoxide, ethylene glycol, and DMF, but has reduced solubility in acetone, ethanol, and THF.[15] In contrast, sodium lignosulfonate can be solubilised in polar protic solvents, but not in aprotic solvents.[16] Due to these limitations, less than 2% of extracted lignin is currently used in commercial products with the remainder being burned to produce heat and power.[17] To generate targetable products, we need highly upgradable and processable lignin, which can only result from the development of novel lignin extraction technologies.

All existing industrial scale biomass valorisation processes have a fractionation or pre-treatment step for the removal of lignin from lignocellulosic biomass.[18] The largest existing industrial scale biomass valorisation processes are the pulp and paper processes, which use the Kraft and sulphite pulping processes.[19] Other large-scale biomass valorisation processes, which typically focus on enzymatically hydrolysing cellulose into glucose, pre-treat the raw biomass with mineral acids at high temperature in water, ionic liquids, or organic solvents.[20–23] Under these conditions, lignin's labile benzylic alcohols eliminate to produce reactive benzylic carbocations or alkenes (Scheme 1).[24] These reactive species rapidly condense under the reaction conditions with adjacent electron-rich guaiacyl or syringyl lignin subunits in electrophilic aromatic substitution reactions.[25,26] The interunit C–C bonds that result from these reactions are highly recalcitrant and prevent the extracted lignin from being efficiently depolymerized by hydro-

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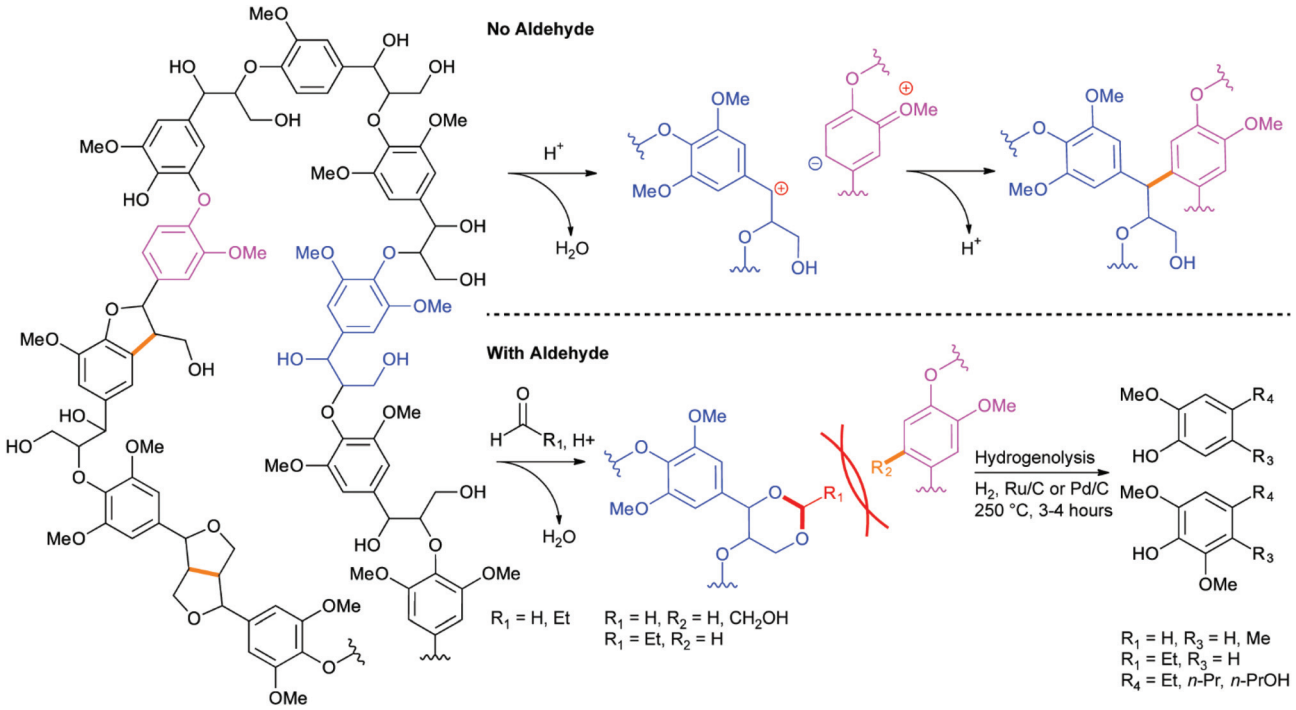


Scheme 1 Valorisation and extraction of lignin with or without stabilising aldehydes. (Left) A model structure of native lignin illustrating the free diol (blue) and electron rich guaiacyl subunit (pink). Without the stabilising aldehyde, the benzylic alcohol of the free diol is eliminated producing a benzylic carbocation that can undergo electrophilic aromatic substitution with a nearby guaiacyl or syringyl subunit, forming an irreversible C–C bond that prevents the depolymerization of the lignin post extraction. In the presence of an aldehyde a 1,3-dioxane is formed, preventing the elimination of the benzylic alcohol and any subsequent C–C bond forming reactions. The resulting aldehyde-stabilised lignin yields a variety of monomers after hydrogenolysis. If formaldehyde is used, the aromatic subunits can be hydroxymethylated, doubling the number of possible monomers. 4-(3-Hydroxypropyl)-2-methoxyphenol was not observed as a product of the biomass used in this manuscript.

genolysis (see Fig. 3 for yields of monomers from Kraft lignin and sodium lignosulfonate). They can be broken by catalytic hydrotreatment, but this typically requires supercritical conditions (≥300 °C, ≥20 bar H_2) and produces a complex mixture of products.[27–30]

As an alternative to these lignin separation processes, we previously introduced a lignin-first strategy that uses aldehydes to stabilise the benzylic alcohol of lignin during extraction, allowing for the full fractionation of lignocellulosic biomass into cellulose-rich solids, aldehyde-stabilised xylose, and aldehyde-stabilised lignin.[31] In this protocol, which we have dubbed Aldehyde Assisted Fractionation (AAF), the aldehyde prevents the elimination of the benzylic alcohol of lignin through the formation of an acetal (1,3-dioxane in red, Scheme 1) with the free diol on the lignin side chain (highlighted in blue, Scheme 1).[32] The viability of this strategy was demonstrated using formaldehyde and propionaldehyde, achieving monomer yields of 94% and ≥95 mol% respectively using birch as measured against the achievable monomer yield of that feedstock as determined by hydrogenolysis of the raw biomass.[26,33–35]

Both the formaldehyde and propionaldehyde stabilised lignins can be isolated as high-quality, uncondensed, bench-stable solids. Using the propionaldehyde stabilization protocol, one can affect the efficient fractionation of the biomass, recovering 103 wt/wt% of the Klason lignin as the propionaldehyde stabilised lignin, 94 wt/wt% of the glucan (cellulose) as glucose, and 82 wt/wt% of the xylan (hemicellulose) as either xylose or dipropylxylose as performed on a sample of birch wood. This procedure is routinely used to isolate gram-scale quantities of propionaldehyde protected lignin and has been scaled to 1 kg of biomass.[36] It has also been independently reproduced by other laboratories.[37]

Given the scalability and efficiency of the aldehyde-facilitated lignin extraction process, we decided to probe the steric and electronic effects of the aldehyde backbone on the properties of the resulting lignin. Simultaneously, we explored the use of bifunctional aldehydes to access unique lignin properties that allow for control of both its solubility and the products of its hydrogenolysis.

Results and discussion

Acetaldehyde was previously used in the extraction of lignin from lignocellulosic biomass and provides a monomer yield of ≥95 mol% when compared with the Reductive Catalytic Fractionation (RCF) monomer yield of the same birch wood feedstock. Using it as a template, a series of aldehydes substituted at the alpha position was selected to probe the steric and

electronic effects of the aldehyde-backbone on the lignin extraction using the same lignocellulosic biomass source (Fig. 1). To determine the efficacy of the extraction and stabilisation, the resulting lignins were hydrogenolysed and their monomer yields as percentage of the whole dry biomass were compared. This yield provides an indirect measure of the degree of stabilisation because condensation, which increases the fraction of interunit linkages that are connected by C–C bonds (*i.e.* C–C content), rapidly reduces the maximum attainable monomer yield that is thought to be proportional to (1 − [C–C content]^2).[38–40] Based on this series of aldehydes, the determining factor in the degree of condensation in the extraction of aldehyde-stabilised lignin was found to be the electrophilicity of the aldehyde, and not the steric bulk of its backbone. Acetaldehyde, propionaldehyde, isobutyraldehyde, and pivaldehyde all produced lignins that yielded approximately the same quantity of lignin monomers upon hydrogenolysis while chloroacetaldehyde, dichloroacetaldehyde, and chloral produced lignins that yielded fewer lignin monomers with increasing chlorine content suggesting that electron withdrawing groups on the aldehyde-backbone produce a more condensed lignin.

Exploring this further, a series of aldehydes was selected to probe the effect of chain length and aromaticity of the aldehyde on the extraction of the lignin. Extraction of the biomass with octanaldehyde yielded an uncondensed lignin with a monomer yield approaching that of acetaldehyde, but systematic increases in the chain length beyond that resulted in an increasingly condensed lignin. As steric effects were previously ruled out, this likely resulted from solubility issues of the aldehyde at the biomass interface. Benzaldehyde stabilization did produce a slightly more condensed lignin as would be predicted by the electron-withdrawing effect of the benzene ring and the previous observation of the impact of chlorine substituents alpha to the carbonyl. However, in contrast to this observation, electron withdrawing groups on the benzene ring slightly improved the yield of monomers as compared to electron donating substituents.

The presence of a reactive functional group such as a phenol or carboxylic acid on the aldehyde backbone led to a decrease in yield of monomers produced from the isolated lignin. We hypothesize that the reduction in yield of monomers that can be produced from these lignins likely stems from competing substitution reactions by the functional groups with the reactive benzylic alcohols of the lignin. The resulting ethers or esters would inhibit the formation of an acetal but could still be readily eliminated under the acidic conditions of the biomass fractionation, forming reactive benzylic carbocations. The subsequent reaction of these benzylic carbocations can be prevented if the aldehyde portion of the bifunctional molecule forms an acetal with the lignin. Such interceptions are likely proximity dependent. This proximity effect can be best observed in the hydrogenolysis yields of the *ortho*, *meta*, and *para*-hydroxybenzaldehyde stabilised lignins (Fig. 1C). As the phenol approaches the aldehyde, the hydrogenolysis yield of the isolated lignin increases. This is likely due to the increased ability of the aldehyde to intercept the reactive carbocations, which result from the ether elimination, by immediately creating an acetal (Scheme S1†). The substitution of the *p*-hydroxybenzaldehyde with a methoxy group (vanillin and syringaldehyde) also reduces the impact of the free phenol on the yield of lignin monomers by sterically hindering the ether formation, which competes with the acetal formation.

Carboxylic acids do not impact the yield of the lignin monomers to the same extent that phenols do, presumably due to their reduced nucleophilicity. The modest yields of the glycolaldehyde (2-hydroxyacetaldehyde) stabilised lignin, which has a free alcohol, can be attributed to the fact that the aldehyde is added as a cyclic dimer (1,4-dioxane-2,5-diol), which hydrolyses under the reaction conditions to produce the free aldehyde.

Many aldehydes undergo homoaldol reactions under acidic conditions. Consequently, to achieve good stabilisation of the β-O-4 subunit of lignin we used a substantial excess of the aldehyde. However, if the aldehyde doesn't have hydrogens alpha to the carbonyl, it cannot enolize and therefore it cannot undergo a homoaldol reaction. When using these aldehydes, their loading can be substantially reduced (≥75% reduction).

Having created this library of acetal-stabilised lignins, we explored the effects of using bifunctional aldehydes on the final properties of the resulting aldehyde-stabilised lignins, with a specific focus on solubility. In addition to being generally recalcitrant to depolymerization, commercially available lignins also have generally poor solubilities in most solvents outside of polar organic solvents. These limitations have limited research on the development of lignin biocatalysis as most enzymes are insoluble in organic solvents, and they have limited the use of lignin as a drug delivery substrate or UV absorber.[41,42] Lignosulfonates are water soluble, but as our results show (Fig. 3), they are highly recalcitrant to depolymerization. Aldehydes can alter the structure of the lignin allowing for various targeted properties, notably solubility, to be imparted to the material as it is extracted from the biomass by simply choosing the structure of the aldehyde.

Using the library of aldehyde-stabilised lignins, we performed an assay to determine the relationship between the structure of the aldehyde and the solubility of the isolated lignin (Fig. 2, select lignins; see Fig. S1 and S2† for the full solubility table). In general, aldehydes with non-polar tails (*e.g.*, octanaldehyde, decanaldehyde, and dodecanaldehyde) led to lignins with increased solubility in non-polar solvents such as toluene. In contrast, aldehydes with ionic functionality (*e.g.*, sodium glyoxylate and sodium formylbenzoate) led to lignins with significant solubility in water. These two different solubilities are unprecedented both for lignins that represent most of the plant's native lignin and for lignins that remain upgradeable at high yields. Presumably, this reflects the difficulty of solubilizing the native lignin structure and the importance of functionalisation to assist in this regard.

The solubilities of the intermediately functionalised lignins were less intuitive, but in general they were soluble in tetra-

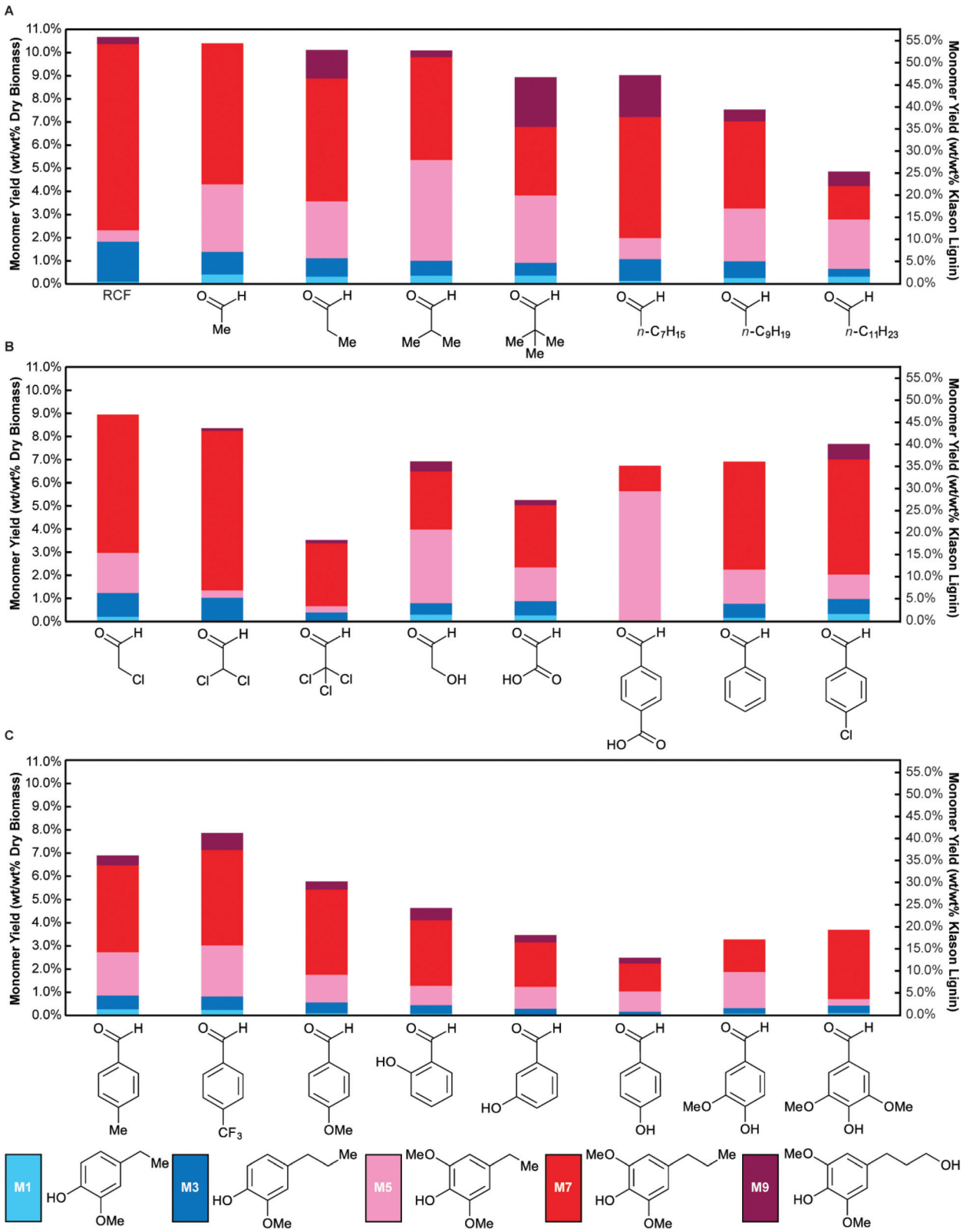


Fig. 1 Hydrogenolysis data for various aldehyde stabilised lignins. These plots summarize the yields of lignin monomers produced from the hydrogenolysis of lignin extracted from birch wood using the aldehyde fractionation protocol. Biomass was extracted using aldehydes that varied in (A) steric and (B and C) electronic parameters to elucidate the relationship between the stabilization efficacy and aldehyde structure. The hydrogenolyses were performed after isolating the lignin from the reaction liquor by precipitation. In the top left-hand corner (Panel A), the reductive catalytic fractionation (RCF) of the birch wood in methanol is provided, which is a good estimate of the highest achievable monomer yield from this biomass source. The yields are reported on a whole dry biomass basis (left) and based on the Klason lignin content of the original biomass (right).

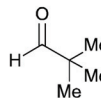
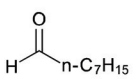
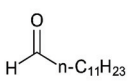
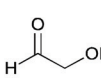
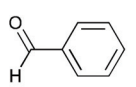
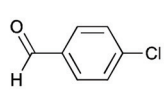
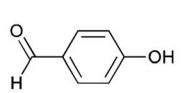
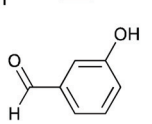
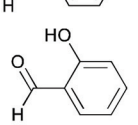
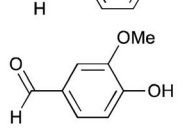
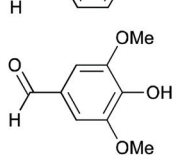
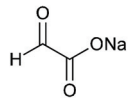
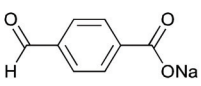
Stabilising Group	Toluene	Et_2O	Me-THF	THF	EtOAc	1,4-Dioxane	EtOAc: MeOH (50:50)	*i*PrOH	EtOH	MeOH	Water	HSP[a]
	Insoluble	Insoluble	≥10.0%	≥10.0%	5.1%	≥10.0%	8.1%	0.2%	1.5%	1.7%	Insoluble	δ_d = 17.99 δ_p = 9.10 δ_h = 9.60 R = 7.4
	3.5%	2.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	≥10.0%	2.2%	2.2%	2.1%	Insoluble	δ_d = 18.18 δ_p = 8.84 δ_h = 6.27 R = 8.6
	9.9%	1.9%	≥10.0%	≥10.0%	9.9%	≥10.0%	9.0%	1.0%	1.5%	1.9%	Insoluble	δ_d = 18.18 δ_p = 8.84 δ_h = 6.27 R = 8.6
	≥10.0%	≥10.0%	≥10.0%	≥10.0%	9.4%	≥10.0%	≥10.0%	2.2%	4.0%	2.0%	Insoluble	δ_d = 17.52 δ_p = 8.91 δ_h = 6.23 R = 8.7
	Insoluble	Insoluble	≥10.0%	≥10.0%	8.3%	≥10.0%	≥10.0%	0.4%	2.3%	3.9%	Insoluble	δ_d = 17.99 δ_p = 9.10 δ_h = 9.60 R = 7.4
	Insoluble	Insoluble	Insoluble	6.3%	Insoluble	≥10.0%	5.4%	Insoluble	0.7%	3.0%	1.6%	δ_d = 19.02 δ_p = 8.80 δ_h = 9.99 R = 7.7
	Insoluble	Insoluble	≥10.0%	≥10.0%	4.6%	≥10.0%	≥10.0%	1.0%	Insoluble	1.9%	Insoluble	δ_d = 17.99 δ_p = 9.10 δ_h = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0 %	3.7%	≥10.0%	8.1%	0.8%	Insoluble	0.8%	Insoluble	δ_d = 17.99 δ_p = 9.10 δ_h = 9.60 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	6.9 %	≥10.0%	≥10.0%	3.0%	7.0%	9.3%	Insoluble	δ_d = 15.79 δ_p = 8.70 δ_h = 13.24 R = 10.0
	Insoluble	Insoluble	≥10.0%	≥10.0%	7.0%	≥10.0%	≥10.0%	0.6%	3.0 %	6.2%	Insoluble	δ_d = 17.94 δ_p = 9.09 δ_h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	4.4%	≥10.0%	≥10.0%	1.0%	1.0%	3.9%	Insoluble	δ_d = 17.94 δ_p = 9.09 δ_h = 9.81 R = 7.4
	Insoluble	Insoluble	≥10.0%	≥10.0%	6.6%	≥10.0%	≥10.0%	1.5%	4.7%	8.3%	Insoluble	δ_d = 15.79 δ_p = 8.70 δ_h = 13.24 R = 10.0
	Insoluble	Insoluble	≥10.0%	≥10.0%	3.5%	≥10.0%	7.7%	1.5%	0.4%	4.3%	Insoluble	δ_d = 17.94 δ_p = 9.09 δ_h = 9.81 R = 7.4
	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	1.2%	≥10.0%	δ_d = 15.14 δ_p = 13.85 δ_h = 32.32 R = 10.3
	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	5.3%	≥10.0%	δ_d = 15.14 δ_p = 13.85 δ_h = 32.32 R = 10.3

Fig. 2 Tabulated solubility data for select aldehyde stabilised lignins. Birch wood was fractionated using the aldehydes identified on the left-hand-side of the table and the aldehyde-stabilised lignins were isolated as bench-stable solids. These aldehyde-stabilised lignins were dissolved in various solvents or solvent-mixtures at room temperature (~23–30 °C) and passed through syringe filters into tared vials. The vials were dried overnight in a vacuum oven at 45 °C and 20 mbar and re-tared to determine the quantity of lignin in the solvent. Concentrations exceeding 10.0 wt/wt% were often observed, but highly concentrated solutions became viscous, almost gel-like. Consequently, the maximum concentration targeted was 10 wt/wt%. Each reported number represents the average of three measurements and is reported as a wt/wt%. None of the lignins were soluble in hexanes. [a] Hansen Solubility Parameters (HSP). See Fig. S1 and S2† for the full solubility table.

hydrofuran, methyl tetrahydrofuran, and 1,4-dioxane and insoluble in hexanes, toluene, diethyl ether, and water, which is typical of extracted lignins. Ethyl acetate was able to solubilise almost all the acetal-stabilised lignins, but alcohols were mostly poor solubilisers. Mixtures such as 50 : 50 ethyl acetate and methanol were broadly able to solubilise all the lignins. Unfortunately, due to esterification reactions with the free carboxylic acids, it was not possible to determine the solubilization of the glyoxylic acid or 4-carboxybenzaldehyde stabilised lignins by some of the alcohols (Fig. S1†). From this data, we have determined the Hansen Solubility Parameters for the lignins (Fig. 2).

With these novel acetal-stabilised lignins, we can also explore the effect of solvent and aldehyde structure on lignin hydrogenolysis by observing the lignin monomer yields and distributions in various solvents. In previous work we explored the hydrogenolysis of propionaldehyde stabilised lignin in isooctane, in which the lignin is insoluble.[43] This insolubility led to reduced monomer yields (~70%) and shifted the monomer distribution such that predominantly hydrodeoxygenation (HDO) products were observed. Here, using our expanded lignin library, which includes highly water-soluble sodium glyoxylate stabilised lignin (≥10 wt/wt%), we can observe the true effect of converting a (solubilised) lignin in a non-polar solvent.

From these lignins, we selected two aldehyde-stabilised lignins with opposing affinity for solvents in terms of polarity —octanaldehyde and sodium glyoxylate—as well as a functionalised lignin with intermediate properties: acetaldehyde-stabilised lignin. We also selected two technical lignins—Kraft lignin and sodium lignosulfonate—as representative samples of current industrial feedstocks. The acetal stabilised lignins were carefully triturated to ensure that they did not contain any residual sugars, ethers, or alcohols that could perturb the results. This purification removed lower-molecular weight lignin fragments that were partially soluble in the trituration solvent, which in turn reduced the observed yield of monomers. The technical lignins were used without any further purification. All the lignins were then hydrogenolysed in isooctane, toluene, tetrahydrofuran (THF), and water using ruthenium on carbon (5 wt/wt%) as the catalyst (Fig. 3).

In all solvents, the technical lignins produced consistently poor yields of lignin monomers, confirming the formation of highly recalcitrant C–C bonds during their formation. As for the acetal stabilised lignins, in THF, the monomer distributions for the octanaldehyde and acetaldehyde stabilised lignins were similar to those of the unpurified, isolated lignins (Fig. 1A), but their yields were reduced due to losses during purification (13% and 22% lower respectively, Fig. 3). In contrast, the sodium glyoxylate stabilised lignin saw a 48% reduced yield of lignin monomers *versus* that observed in water, consistent with its insolubility. Given that we do see monomer production despite its insolubility, we hypothesise that the lignin may either form a melt or pyrolyzes to produce soluble lignin fragments that can react in the pores of the catalyst. Surprisingly, the monomers that were produced were exclusively alcohols suggesting that the structure of the lignin, beyond determining its solubility, also influences the product distribution.

In toluene, the monomer yields of the octanaldehyde-stabilised lignin were identical to those in THF, but the acetaldehyde and sodium glyoxylate-stabilised lignins were reduced by 9%, and 60% respectively *versus* their maximum yields. While the yield of the octanaldehyde-stabilised lignin and the substantially reduced yield of the sodium glyoxylate stabilised lignin can be rationalised from their respective solubilities in toluene, the only minor reduction in yield for the acetaldehyde-stabilised lignin stands as an outlier for it is insoluble in toluene at room temperature. This could suggest that at the elevated temperature and pressure of the hydrogenolysis the properties of toluene and lignin change sufficiently that dissolution of the acetaldehyde-stabilised lignin occurs. In all cases, HDO products were not observed presumably due to preferential reduction of the toluene.

None of the lignins were soluble in isooctane and correspondingly, the hydrogenolyses of the lignins in these solvents saw the greatest reductions in yield. The octanaldehyde, acetaldehyde, and sodium glyoxylate stabilised lignins yielded 59%, 76%, and 99% fewer monomers respectively, corresponding to their relative lipophilicities.

As for the reactions in water, the monomer yields of the octanaldehyde and acetaldehyde stabilised lignins were reduced by 60% and 56% respectively, which again was consistent with their insolubilities. However, instead of predominantly aromatic lignin monomers produced in toluene and THF, the products were largely cyclohexanes, which results from HDO – a process that does not appear to be suppressed by water. Some aromatic lignin monomers were observed in the case of octanaldehyde stabilisation, which could have resulted from the solubilization of a portion of the lignin in the lignin oil that was being produced over the course of the reaction. In that medium, we would expect the solubilised lignin to react largely as it would in THF, suppressing the formation of HDO products.

Due to its solubility in water, the sodium glyoxylate stabilised lignin produced its highest yield of lignin monomers. However, in contrast to the octanaldehyde and acetaldehyde stabilised lignins, cyclohexanols were produced almost exclusively (91% selectivity). It is possible that the pH of the solution (9 in the case of the sodium glyoxylate stabilised lignin) could be influencing the selectivity. However, the effect of water as suppressant for the final dehydration of lignin monomers has previously been observed in the hydrogenolysis of lignin pyrolysis oils and on model compounds.[44–46]

This represents the first demonstration of the direct production of cyclohexanols from lignin as the only commercially available water–soluble lignin, sodium lignosulfonate, does not yield them (Fig. 3). Furthermore, while the yield of lignin monomers was low (39% of the RCF yield), it was still 6.3-fold greater than that observed with sodium lignosulfonate. The hydrogenolysis of a lignin solubilised in water with these

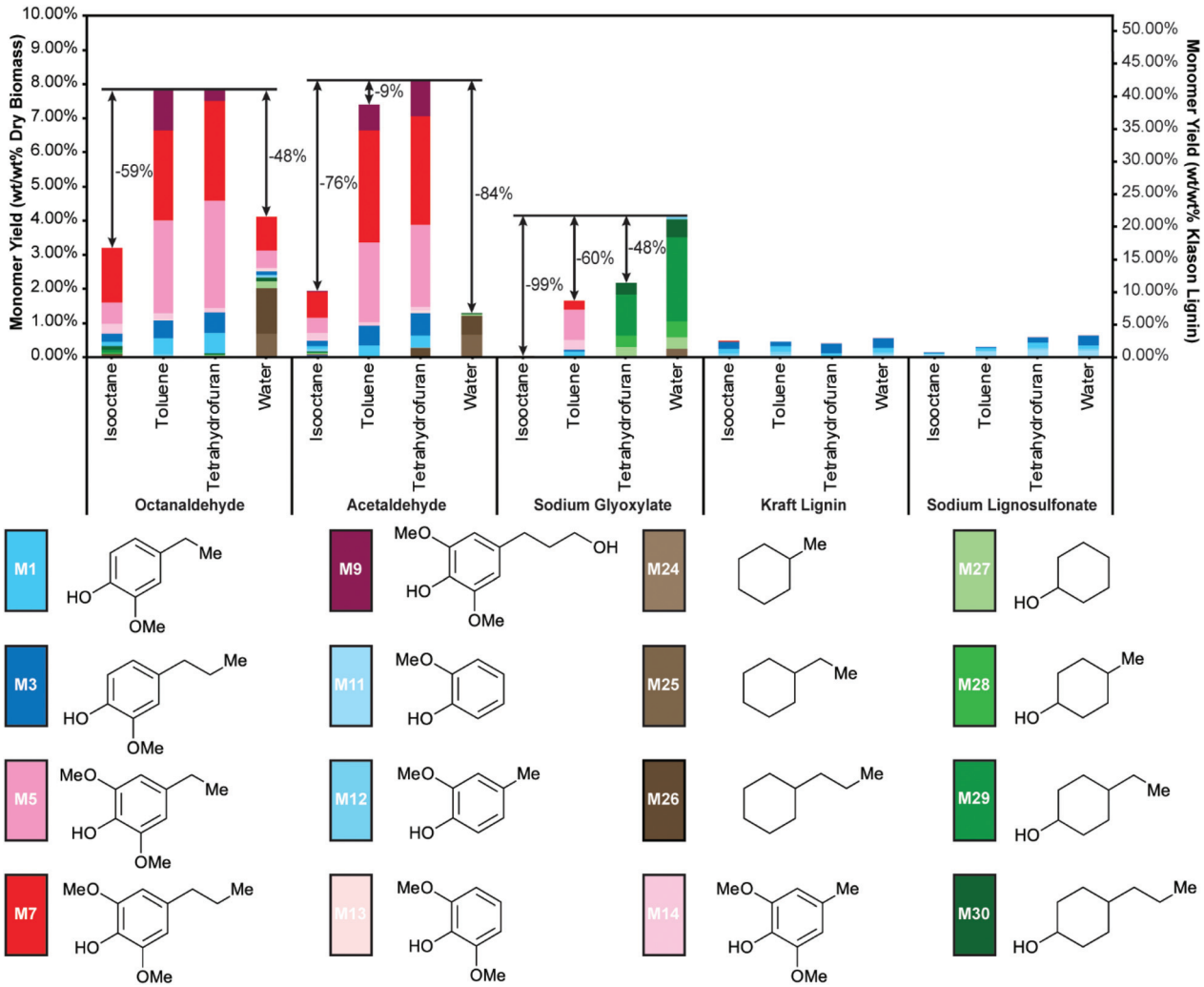


Fig. 3 Yield of lignin monomers from the hydrogenolysis of different lignins in isooctane, toluene, tetrahydrofuran, and water. Select purified aldehyde-stabilised lignins derived from birch wood and technical lignins (Kraft lignin and sodium lignosulfonate) were hydrogenolysed using ruthenium on carbon (5 wt/wt%) in isooctane, tetrahydrofuran, and water at 250 °C under 40 bar of H_2 for three hours. The sodium glyoxylate stabilised lignin was produced from the glyoxylic acid-stabilised lignin and the yields were corrected for the difference in mass between the sodium cation and proton. The yields are the sum of the monomers' reconstituted molecular masses weighted against the whole dry biomass (left) the Klason lignin of the original biomass (right). For more details on these calculations, please see the ESI.† The yields of the acetaldehyde and octanaldehyde-stabilised lignins were reduced *versus* those shown in Fig. 1 due to the washing steps that were performed to remove residual sugars and aldehydes that may have co-precipitated with the lignin during the initial precipitation. These washing steps also removed low-molecular weight lignin fragments that were partially soluble in the trituration solvent (diethyl ether for acetaldehyde, dibutyl ether for octanaldehyde).

yields is unprecedented and could have significant implications for green chemistry.

Conclusions

The stabilisation of lignin with aldehydes during the fractionation of biomass affords a unique opportunity to rationally control the properties and upgradability of the extracted lignin. Lignin monomer production can be optimised by selecting a stabilising aldehyde without electron-withdrawing groups, long alkyl chains, or additional nucleophilic functionality as they produce an acetal-stabilised lignin that is more condensed, yielding fewer lignin monomers upon hydrogenolysis. Aldehydes also dictate the solubility of the lignin. Stabilising lignin with an aldehyde that has a long alkyl chain produces a material that can be solubilised in non-polar solvents such as toluene. Water solubility can also be achieved by stabilising lignin with an aldehyde that has additional ionic functionality. Both the solubility of the lignin and its degree of condensation become relevant during in its hydrogenolysis. Acetaldehyde stabilised lignin gives excellent yields of lignin monomers when hydrogenolysed in tetrahydrofuran, but poor yields in water (84% lower) due to its insolubility. Sodium lignosulfonate is highly soluble in water but produces few monomers upon hydrogenolysis due to its substantial condensation.

These limitations can be overcome by using sodium glyoxylate stabilised lignin, which is soluble in water and produces a substantially higher yield of lignin monomers upon hydrogenolysis (6.3-fold greater than sodium lignosulfonate), while selectively forming cyclohexanols. The relatively high monomer yield produced from the hydrogenolysis of this lignin demonstrates that a uniquely upgradeable water-soluble lignin can be produced during biomass fractionation, which presents opportunities for both green processing and potentially, biocatalysis.

Author contributions

GRD and JSL conceived of the project and designed the research. GRD and AOK performed the experiments and analyses and curated the data. Both GRD and JSL drafted, reviewed, and edited the publication.

Conflicts of interest

GRD and JSL are inventors on a European patent application (EP19202957) on the acetal-stabilisation of lignin using aldehydes with functional groups. J. S. L. is an inventor on a European patent application (EP16165180.7) that covers methods for producing lignin monomers from biomass during biomass depolymerization JSL is co-founder and part owner of Bloom Biorenewables Ltd. that aims to commercialize the aldehyde assisted fractionation process.

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