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Integrating Separation and Conversion—Conversion of Biorefinery Process Streams to Biobased Chemicals and Fuels

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Abstract The concept of the integrated biorefinery is critical to developing a robust biorefining industry in the USA. Within this model, the biorefinery will produce fuel as a high-volume output addressing domestic energy needs and biobased chemical products (high-value organics) as an output providing necessary economic support for fuel production. This paper will overview recent developments within two aspects of the integrated biorefinery—the fractionation of biomass into individual process streams and the subsequent conversion of lignin into chemical products. Solvent-based separation of switchgrass, poplar, and mixed feedstocks is being developed as a biorefinery "front end" and will be described as a function of fractionation conditions. Control over the properties and structure of the individual biomass components (carbohydrates and lignin) can be observed by adjusting the fractionation process. Subsequent conversion of the lignin isolated from this fractionation leads to low molecular weight aromatics from selective chemical oxidation. Together, processes such as these provide examples of foundational technology that will contribute to a robust domestic biorefining industry.

Keywords Fractionation · Catalysis · Co-Schiff base complex · Lignin · Biorefinery · Organosolv

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Introduction

The last decade has witnessed the advent of biomass (forest resources, agricultural crops such as switchgrass, corn and soybeans, residues, etc.) as a source of renewable carbon, evidenced by a huge upsurge in research and commercial interest. The lignocellulosic *biorefinery* is the construct linking domestic sources of renewable carbon with the technology necessary for their conversion to biofuels and high-value organics (HVOs—i.e., chemicals and materials).

An analogy between the emerging biorefinery and today's petrochemical refinery is appropriate and illustrative. The petrochemical industry, as the nation's primary consumer of nonrenewable carbon, provides the standard for developing and optimizing the biorefining industry. The petrochemical industry is effective because it has achieved a highly integrated value chain based on nonrenewable carbon, from raw material collection and processing to fuel and chemical production. Underpinning this success is the industry's fundamental understanding of broadly applicable conversion technologies capable of transforming hydrocarbons into HVOs and fuels in high yield and efficiency [1]. An integrated, multiproduct approach coupling HVO and fuel manufacture is of particular importance. Even though chemicals account for only 7–8 % of crude oil use in the USA, they provide the key economic driver for overall profitability of the petrochemical industry, which reports US sales of over US$435 billion. Chemicals provide nearly 50 % of the value-added for the industry (US$375 billion) despite their low comparative consumption of crude oil [2, 3].

Integrating multiple HVOs with fuels will also be central to biorefinery development. Although most current biorefinery research is focused on fuel EtOH, analyses reveal that a next-generation biorefinery adopting the petrochemical model of simultaneous fuel and HVO production realizes a much higher return on investment [4–6]. The improved profitability from integrating HVO and fuels will be critical for industrial adoption of carbohydrates and lignin as raw materials. HVOs will provide the financial incentive needed to justify the use of building blocks unfamiliar to industry, development of processes to convert them to final products, and the capital investment necessary to take new technology to commercial scale. Research into the utility of alternative and sustainable sources of carbon is further justified by a 35 % increase in US energy consumption over the last 30 years and more than half of all new energy demand coming from India and China through 2035 [7].

Turning the chemical industry model into a successful and commercially viable biorefining industry requires processes that provide easy access to individual process streams containing the primary components of biomass as well as developing technology tailored for the unique structural features of these materials. This paper reviews our efforts in both of these areas, with a particular focus on solvent fractionation of biomass and processes for the conversion of lignin into HVOs.

Organosolv Fractionation of Lignocellulosic Biomass for Use in the Biorefinery

Biomass, as harvested, is difficult to use directly because it is a complex mixture of several simpler components. Like crude oil, it requires an initial separation and upgrading before it can be converted into HVOs or biobased transportation fuels. Second-generation lignocellulosic biorefineries remain overwhelmingly linked to the production of fuel EtOH to the point that the default operation of these processes has become almost dogmatic: the raw material is first subjected to a *pretreatment* designed to improve access to the polysaccharides present in the biomass. Polysaccharides in the pretreated material are hydrolyzed to monomeric sugars and fermented to EtOH, and the unfermented, lignin-rich residue is typically used as fuel to generate process heat and steam. Pretreatment is arguably the most important step in this process. If the pretreatment is ineffective, hydrolysis and fermentation become much less efficient, driving the overall process costs too high to be industrially viable. Well-known pretreatment methods that are under consideration commercially include dilute acid, steam explosion, hot water, or AFEX (Fig. 1) [8, 9].

But widely recognized pretreatments must be differentiated from fractionation processes necessary for integrated fuel and chemical operations. In EtOH-centric processes, *access* to sugars is paramount—separation is not a goal as it can add costs that cannot be accommodated within the severe economic restrictions of a fuel-only operation. Indeed, pretreated material sent to hydrolysis and fermentation operations frequently contains significant levels of lignin and hemicellulose [10–12]. For optimal use of domestic renewable carbon, a transition from simple pretreatment processes to fractionation processes within a multiproduct context is needed. Fractionation processes that provide selective access to individual process streams of cellulose, hemicellulose, and lignin (or other components present in biomass) will not only enable and improve the ability to manufacture fuels, but will lead to a profitable portfolio of chemical products able to provide financial incentive for an entire biorefining industry by producing the high purity process streams demanded by the chemical industry. Adoption of multiproduct fractionations as part of biorefinery development may increase the complexity and cost of operation. Nonetheless, a positive tradeoff results from the inclusion of high-value products because the biorefinery can use their higher profitability to offset more costly, but also more selective and flexible fractionation technologies. Key characteristics of fractionation technology designed for multiproduct operation include selective separation of each component of a biomass feedstock, easy access to and isolation of the components after separation, and recovery of each component in high yield.

Organosolv processes have been identified as able to meet many of these requirements [13–18]. Since 1993, we have been developing a separation process for biomass using organic solvents that can convert this complex starting material into three individual process streams—cellulose, hemicellulose, and lignin—each of which can serve as a starting material for the production of biobased chemicals and fuels [19]. Our process normally heats biomass with a 16/34/50 (by weight) mixture of methyl isobutyl ketone, ethanol, water in the presence of an acid catalyst. This solvent mixture selectively dissolves lignin and hemicellulose, leaving the cellulose as an undissolved material that can be washed, fiberized, and further purified. The soluble component is separated into individual lignin and hemicellulose fractions simply by adding NaCl and removing excess solvent (Fig. 2).

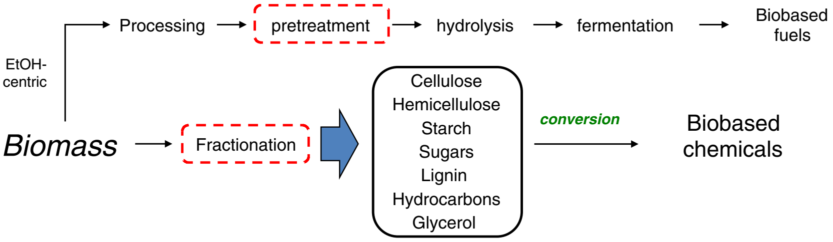


Fig. 1 The integrated biorefinery will evolve from pretreatment to fractionation

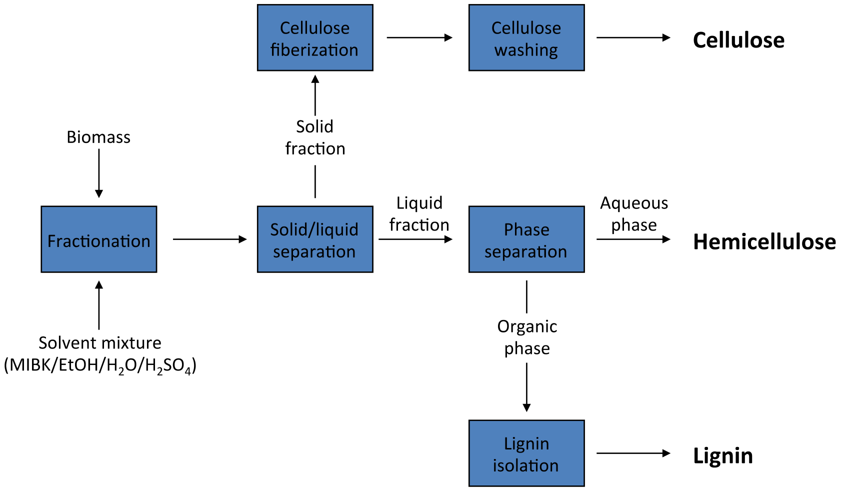


Fig. 2 Schematic of the solvent fractionation process

The process is efficient. Greater than 95 % of the components present in the starting feedstock is isolated after fractionation, which is important for their eventual use as chemical building blocks. Importantly, the process works well on switchgrass and poplar, two renewable feedstocks important to the southeast USA as candidates for large-scale bioenergy crop production.

The purity of the fractions is also quite high (Table 1). Analysis of the cellulose fractions from typical separation of poplar or mixed hardwoods using a variety of conditions showed high proportions of glucan (frequently >98 %). The level of hemicellulose sugars was normally no greater than a few percent and often less than 0.1 %. The amount of residual lignin (measured as total Klason lignin) was also low, between 2 and 5 %. The lignin displays high purity, with the amount of residual sugar present in the lignin at a level of 0.5 % or less.

Coupling this separation to eventual downstream HVO manufacture requires knowledge about the discrete molecular level structure of the process streams so that appropriate conversion technology can be tailored. For the lignin fraction, nuclear magnetic resonance (NMR) analysis has been proven useful for the evaluation of the structural impact resulting from organosolv separation and for understanding the mechanism of organosolv fractionation processes. Two-dimensional heteronuclear multiple-quantum correlation (HMQC) has demonstrated that key functional groups within lignin undergo reaction, cleavage, or consumption as a function of the fractionation severity. This analysis also supports

Table 1 Analysis of typical cellulose and lignin from solvent fractionation

Cellulose analysis	Saccharides (%)					Klason lignin (%)		
Separation conditions [acid (M)/time (min)/temp (°C)]	Glu	Xyl	Gal	Ara + Man	Total saccharides	Acid insoluble	Acid soluble	Total
0.1/56/160	103.8	0.0	0.00	0.00	103.8	1.4	0.5	1.9
0.1/56/140	97.0	1.5	0.00	0.00	98.5	2.0	0.8	2.8
0.15/56/130	93.1	2.6	0.00	0.00	95.7	4.4	0.9	5.3
0.2/56/140	99.4	0.19	0.00	0.00	99.6	1.1	0.6	1.7
0.2/76/140	102.1	0.12	0.00	0.00	102.2	1.2	0.6	1.8
0.2/76/140	103.5	0.36	0.00	0.00	103.9	2.0	0.6	2.6
Lignin analysis	Tulip poplar sample 1	Tulip poplar sample 2	Tulip poplar sample 3	Mixed oak sample 1	Mixed oak sample 2	Alcell	Kraft	
Wood sugars	0.57	0.46	0	0.2	0.48	<0.5	Low	
Glucose	<0.1	<0.1	nd	<0.1	<0.1			
Mannose	nd	<0.1	nd	nd	nd			
Xylose	0.47	0.26	nd	<0.1	0.38			

nd not detected

acid-catalyzed solvolysis as the primary mechanism for inter-unit cleavage reactions. Figure 3 shows the approximate point of appearance and disappearance of various functional groups in a series of switchgrass lignins [20].

At low severities, crosslinking ferulates and extractives are observed, and their removal is maintained across a wide range of fractionation conditions. In contrast, we observe the disappearance of β-O-4 linkages and the appearance of alkoxy substitution at the α-position of the lignin C_9 side chain only at increasing fractionation severity. At highest severity, the disappearance of typical aromatic ring signals suggests the possible alkylation of lignin's aromatic units via electrophilic aromatic substitution processes. These observations are important for the development of subsequent lignin conversion processes, as knowledge regarding the presence or absence of various functional groups helps to determine the design of optimal processes for the transformation of lignin to HVOs.

Our current effort in biomass fractionation incorporates experimental design for optimization of the process using mixtures of switchgrass and poplar as the raw material supply [21]. Feedstock mixtures are of importance because a wide variety of bioenergy crops within an economically feasible transportation distance may be considered as part of the biorefinery's raw material supply. The use of herbaceous and woody mixtures tolerates variations in weather conditions that other annual agricultural crops such as corn cannot and offers mixed feedstock solutions that are beneficial to the sustainable supply required by a viable biorefinery. For example, a recent study found that the delivered cost of raw material was lower when wood and herbaceous biomass were combined rather than delivered as single feedstocks [22]. Thus, knowledge regarding the performance of mixed feedstock supplies in typical biorefinery operations would provide useful information regarding their viability as a raw material source.

We have employed Taguchi Robust Product Design [23] to define conditions optimal for separation of mixed switchgrass/poplar feedstocks and to obtain the highest yield of lignin from our solvent fractionation process. The Taguchi experimental design identifies a maximum signal to noise within a matrix of dependent and independent variables. Identification

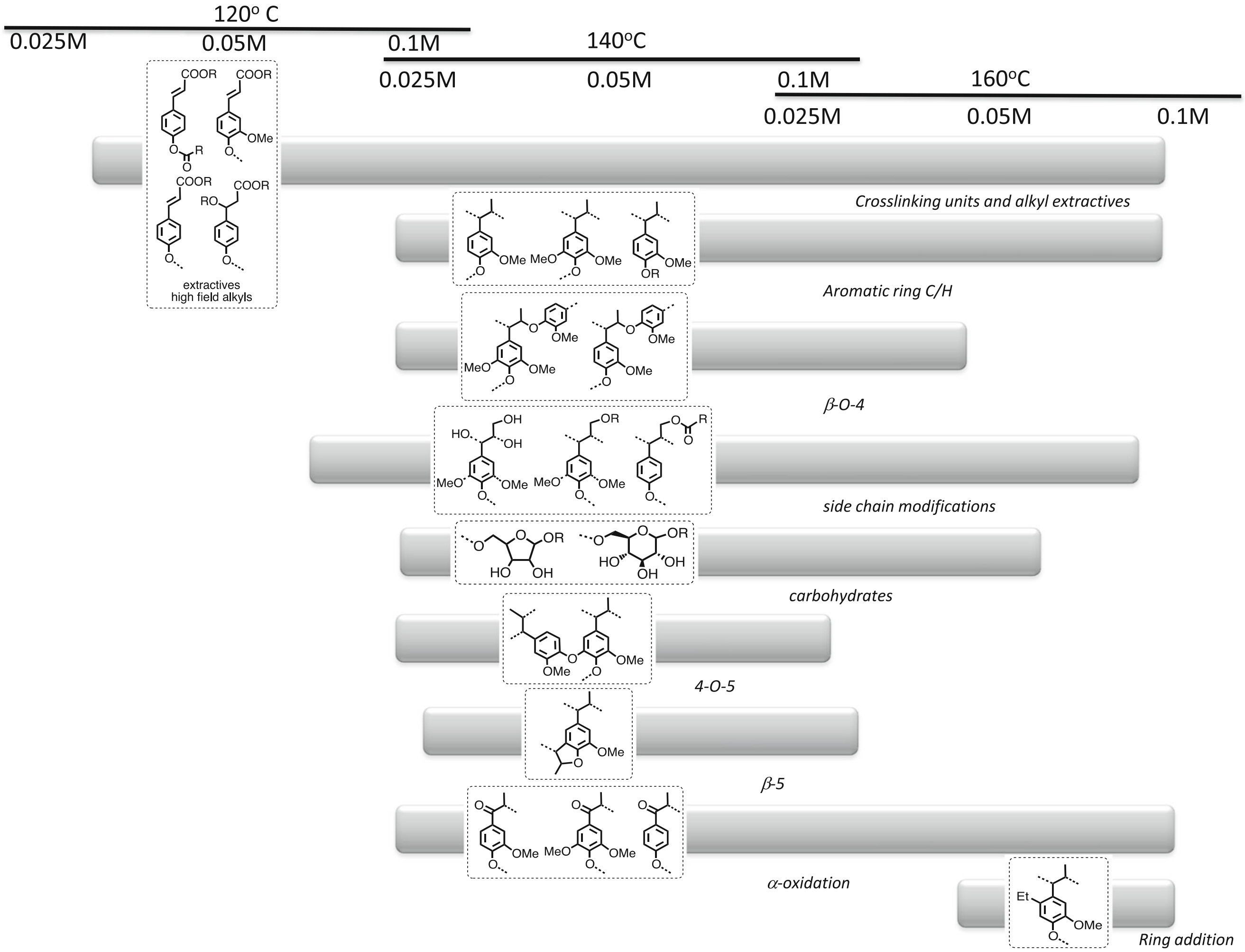


Fig. 3 Summary of structures observed in HMQC evaluation of lignin samples from switchgrass as a function of fractionation conditions

Table 2 Integration of ^{13}C peak clusters in several lignin samples

	NMR region (ppm)				
Run conditions[a]	162–140	123–102.5	88–77	77–65	65–58
120 °C/0.1 M (organic fraction)	100.00	89.80	30.61	1.02	53.06
140 °C/0.1 M (organic fraction)	100.00	93.94	17.17	1.01	31.31
160 °C/0.1 M (organic fraction)	100.00	87.63	4.12	3.09	49.48
Ball-milled switchgrass lignin	100.00	110.53	36.84	50.72	43.54

[a] Temperature/acid concentration

of these high *S*/*N* realms defines operating parameters that afford significantly lower variability in the process response, i.e., greater assurance that a given set of conditions will lead to reproducible results. A critical advantage of the Taguchi methodology is that it can be successful with a dramatically lower number of experimental runs when compared to a complete factorial design. The full results of these studies will be reported in due course, but we observe that a maximum isolated lignin yield (defined as the percent of total lignin in the starting feedstock) was found upon treatment of the mixed feedstock with the solvent mixture for 90 min at 160 °C, using 0.1 M H_2SO_4 and a feedstock composition of 90% switchgrass/10 % tulip poplar. Preliminary statistical simulation of 5,000 additional runs predicted a mean lignin yield of 74.4 wt%, comparable to the mean lignin yield of 78.6 wt% at the maximum found in our investigation.

Selective Cobalt-Catalyzed Oxidation of Lignin and Lignin Models

Development of successful integrated biorefinery operations will result in the inevitable availability of an enormous amount of lignin both as fractionation processes are more widely employed and as an outcome of federal legislation. The US Renewable Fuels Standard mandates the production of 16 billion gallons of lignocellulosic biofuels by 2022. Using that standard as a basis for production, and with the assumption that a commercial biorefinery produces 80 gallons biofuel/t from biomass that averages 20 wt% lignin, operation of integrated fuel/chemical biorefineries at these levels will afford 40 million tons of lignin on an annual basis. Moreover, this lignin will be inexpensive. Multiple evaluations project an internal transfer cost for lignin of \$0.03–0.06/lb [24–26]. From the viewpoint of renewable carbon availability, these remarkable features offer an attractive raw material source for downstream chemical processing and conversion to HVOs. In addition, development of solvent fractionation processes leads to lignin supplies of high purity. A specific focus of our research effort is the production of HVOs by developing new catalytic processes able to transform structural units common to all isolated lignins. In particular, we are examining selective catalytic oxidations, as the electron-rich arenes of lignin should be excellent substrates for such conversions.

The heterogeneous structure of lignin has long frustrated efforts to selectively convert this abundant biopolymer into low molecular weight aromatics [27]. One source of heterogeneity is the biosynthetic path to lignin, which occurs via the random polymerization of aromatic monolignols [28]. But in the context of chemical production, a second source of heterogeneity is equally important. Both pretreatment and fractionation processes as shown in Fig. 1 lead to different distributions of substructural units within isolated lignin as a function of both the lignin source and the methodology employed in its isolation [20, 29]. The recognition that biomass can serve as a viable source of chemicals and fuels has brought significantly increased interest in lignin, but surprisingly, the dramatic change that can occur in lignin's structure during its isolation is frequently overlooked. For example, recent reports describe systems that deconstruct lignin models, using a variety of metal-catalyzed processes with the goal of producing new, lignin-derived HVOs [30–33]. These studies focus on the cleavage of β-aryl ethers, representative of lignin's β-O-4 linkage, which can account for 50–65 % of the interunit bonding present in native lignin [34].

Native lignin, however, does not retain its original substructural profile when it is isolated from a lignocellulosic matrix. For example, quantitative ^{13}C NMR was used to track the amount of β-O-4 linkages in switchgrass samples during solvent fractionation at a variety of severities (Table 2) [20].

The integrations were normalized to the oxygenated aromatic signals between 162 and 140 ppm, and the β-O-4 signals between 88 and 77 ppm were then compared. Depending on the severity of the fractionation, the isolated lignin might retain little or none of the β-O-4 units present in the native material. Similar observations are made when acid hydrolysis or steam explosion is used as a biomass pretreatment [35, 36]. Moreover, as these units are cleaved, the number of free phenolic –OH groups present the lignin increases dramatically. Aromatic units in native lignin contain 7–13 % phenolic –OH depending on the source [37], but as lignin transitions from the growing plant to a biorefinery

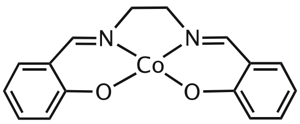


Fig. 4 Co(salen) as a typical example of a Co-Schiff base complex

feedstock, its dissolution and removal from the matrix can increase this amount to over 70 % [38]. Even residual lignin in woody biomass after fractionation exhibits as much as 25 % free phenols [39]. Accordingly, catalyst development focusing on selective transformation of substituted phenols would more accurately model the structure of lignin as an isolated source of renewable carbon. To address this problem, we are employing oxidation of *para*-substituted phenolics with Co-Schiff base complexes and oxygen that is applicable to the arenes composing biorefinery lignin [40].

Cobalt-Schiff base complexes have been extensively used to catalyze oxygen activation in the oxidation of phenols [41–44]. However, the use of these complexes for the oxidation of *p*-substituted phenols as models of catalytic conversion of lignin within the biorefinery has not been widely studied. We reported that O_2 in the presence of various Co-Schiff base catalysts [e.g., Co(salen), Fig. 4] and pyridine in MeOH at room temperature converted several *p*-substituted lignin models into 2,6-dimethoxybenzoquinone (DMBQ) in high yield. The proposed mechanism of the transformation is shown in Fig. 5.

Co(salen) coordinates an axial ligand (L, typically pyridine) and then adds O_2 to form a catalytically active Co-superoxo adduct (reaction II). The axial ligand is required for effective catalyst reactivity, as Co(salen) itself binds O_2 poorly [45]. Subsequently, the superoxo adduct abstracts a phenolic hydrogen from the substrate (reaction III) resulting in a phenoxy radical, which combines with a second equivalent of the superoxo adduct (reaction IV). The final step (reaction V) results in the formation of the quinone oxidation product and formaldehyde.

More recent work reveals that reaction yield is also influenced by the presence of different coordinating bases (Table 3). We anticipated that stronger donors (e.g., those bearing methyl groups) would afford higher yields of DMBQ by enhancing reaction II and increasing the amount of catalytically active superoxo complex in solution. Using syringyl alcohol as a model of the S units in lignin, we observed that the yield of quinone shows a slight correlation with the pK_a of the imidazole's conjugate acid. Exceptions were noted in those cases where an inactive bis-imidazole Co complex that cannot bind oxygen forms (for example, using Im and 1-MeIm in a 10:1 ligand/catalyst [*L*/*C*] ratio) [46]. Thus, at a lower *L*/*C* ratio of 1:1, the yield of DMBQ increases significantly in the presence of 1-MeIm as a ligand. As the donor ability of the imidazole ligand increases, the dioxygen affinity of the Co complex and its ability to abstract a hydrogen atom from the starting phenol also increases.

However, the yield of DMBQ plateaued as the donor ability of the imidazole increased, both at a 1:1 and a 10:1 *L*/*C* ratio. Computational evaluation of these complexes provided additional insight as to the mechanism of oxidation [47]. Examination of the geometry of the superoxo complexes formed in reaction II revealed that they adopt an "umbrella" conformation upon binding of the imidazole ligand, distorting the salen ligand from planarity, consistent with previous X-ray analyses [48, 49]. Figure 6 shows the minimized structure for the Co(salen)/2,4-dimethylimidazole complex with oxygen, where the angle of the salen ligand is measured at 145.15°. Depending on the imidazole ligand added, this angle varied between 145° and 171°.

We suggest that the stronger donor ability of the substituted imidazoles and the resulting ligand distortion are counterbalancing effects on the reactivity of Co(salen)/imidazole/O_2 complexes. Strongly donating ligands promote binding of Co(salen) complexes to O_2 by raising the energy of the Co dz^2 orbital, promoting transfer of an electron to the O_2 [50]. However, attempting to use sterically hindered donors to

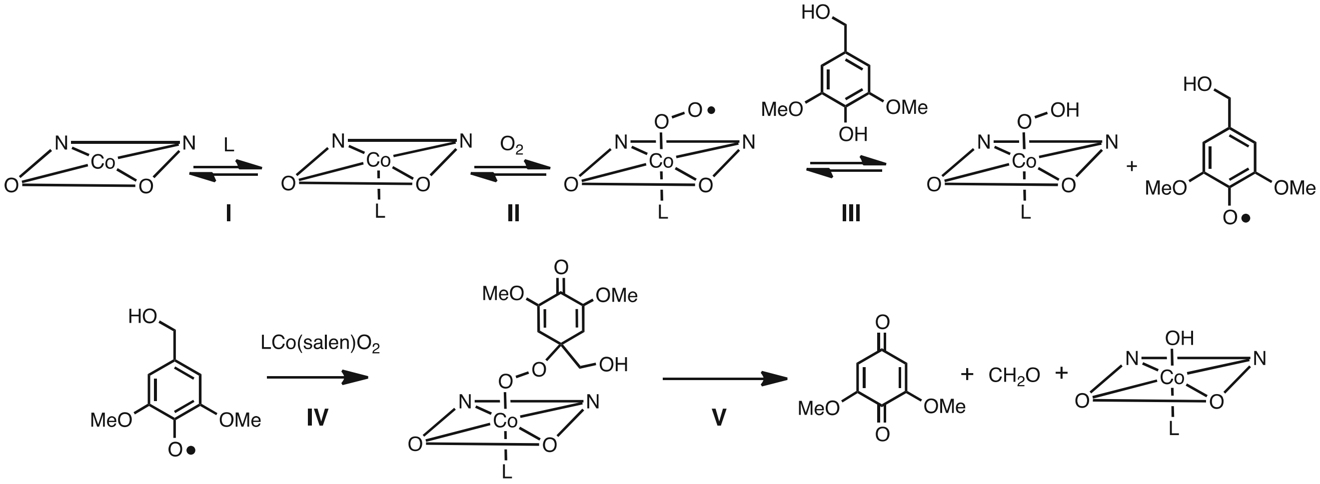
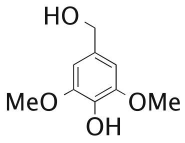
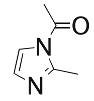
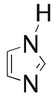
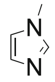
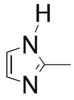
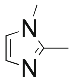
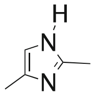


Fig. 5 Mechanism for the Co-Schiff base catalyzed oxidation of *p*-substituted phenols to benzoquinones

Table 3 Influence of imidazole ligands on the yield of DMBQ from Co(salen)-catalyzed oxidation of syringyl alcohol

Substrate	Added imidazole	Conjugate acid pK_a[a]	DMBQ yield (%,10:1 L:C)	DMBQ yield (%, 1:1 L:C)
 **3**		5.03[b]	30	31
	 Im	7.00	<5	5[c]
	 1-MeIm	7.33	29	69
	 2-MeIm	7.85	67	63
	 1,2-diMeIm	8.00	72	65
	 2,4-diMeIm	8.52[d]	71	67

achieve that improved binding distorts the salen, reducing electron donation from the ligand and minimizing the effect of the external ligand that might otherwise be expected. The result is that ligands showing higher donor ability do not have a significantly better effect on yield than poorer donors [9].

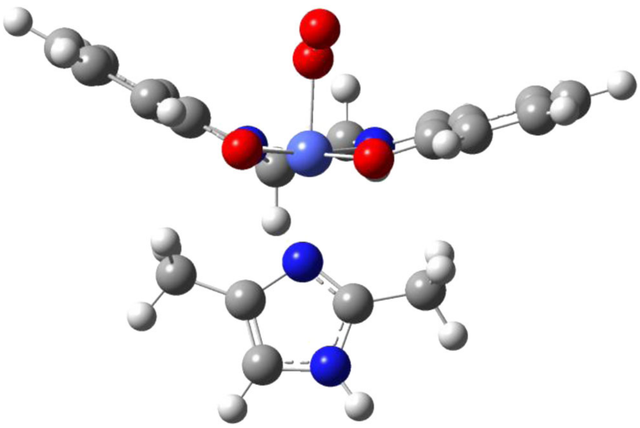


Fig. 6 Calculated minimum energy structure for Co(salen)/2,4-dimethylimidazole complex with O_2

Oxidation of compounds modeling lignin's G units proceeded in much lower yield. However, the effective use of lignin within the integrated biorefinery will require that all primary structural units in lignin can be converted to HVOs. We found that the yield of quinone from the oxidation of G models is strongly affected by the presence of sterically hindered aliphatic nitrogen bases, e.g., the yield of benzoquinone from the oxidation of vanillyl alcohol was improved from 21 to 51 % upon the addition of diisopropylethylamine (DIPEA). Importantly, this improvement was realized without compromising the already high yield observed for the oxidation of S models. Mechanistically, we suggest that the presence of the hindered base promotes partial deprotonation of the phenol substrate, affording a phenoxide anion that is more readily oxidized by the Co(salen)/O_2 complex.

Most recently, we have synthesized a series of unsymmetrical Co complexes that incorporate a hindered aliphatic base within the Schiff base ligand and that show excellent performance in the oxidation of both S and G lignin models (Fig. 7 and Table 4) [51].

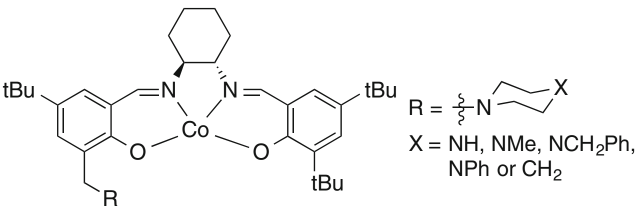
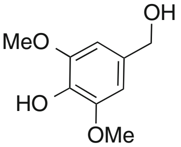
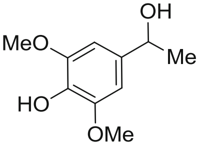
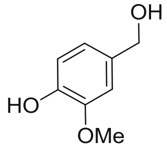
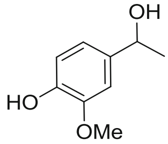
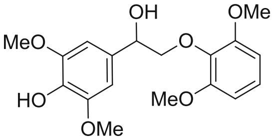
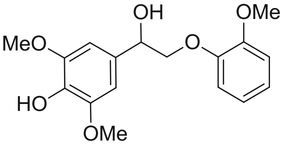
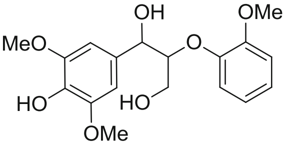
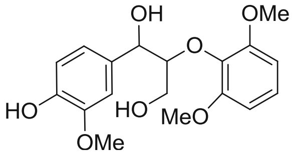


Fig. 7 New unsymmetrical Co-Schiff base catalysts for oxidation of lignin and lignin models

Each of the new catalysts convert syringyl derivatives (entries 1 and 2) into DMBQ in good to very good yield with the N-benzyl catalyst (X = NCH_2Ph) showing the highest reactivity, affording DMBQ in 74 % yield after only 1 h (entry 1) and comparable yields in 16 h with as little as 2 % catalyst. Conversion of the starting alcohol to the corresponding aldehyde is observed as a side product in some reactions. Moreover, the catalysts exhibit significantly higher reactivity than Co(salen). Interestingly, these oxidations do not require the addition of an external axial ligand for Co, and indeed, addition of pyridine to the oxidation led to low yields of DMBQ and recovery of much of the starting material. The increased effectiveness of the N-benzyl system as a catalyst was demonstrated by the oxidation of the G models vanillyl alcohol and α-methyl vanillyl alcohol to the corresponding monomethoxybenzoquinone (MMBQ) in 83 and 51 % yield, respectively (entries 3 and 4). Moreover, several phenolic lignin models containing both S and G subunits linked through a β-aryl ether bond are converted to the

Table 4 Oxidation of lignin model monomers and dimers using unsymmetrical N-benzyl catalyst

entry	substrate	*t*(h)	**MMBQ**(%)	**DMBQ**(%)	**aldehyde**(%)
1		1		74	19
2		16	-	72	11
3		16	83	-	-
4		24	51	-	22
5		16	-	81	traces
6		16	17	86	traces
7		48	21	64	traces
8		48	0	10	0

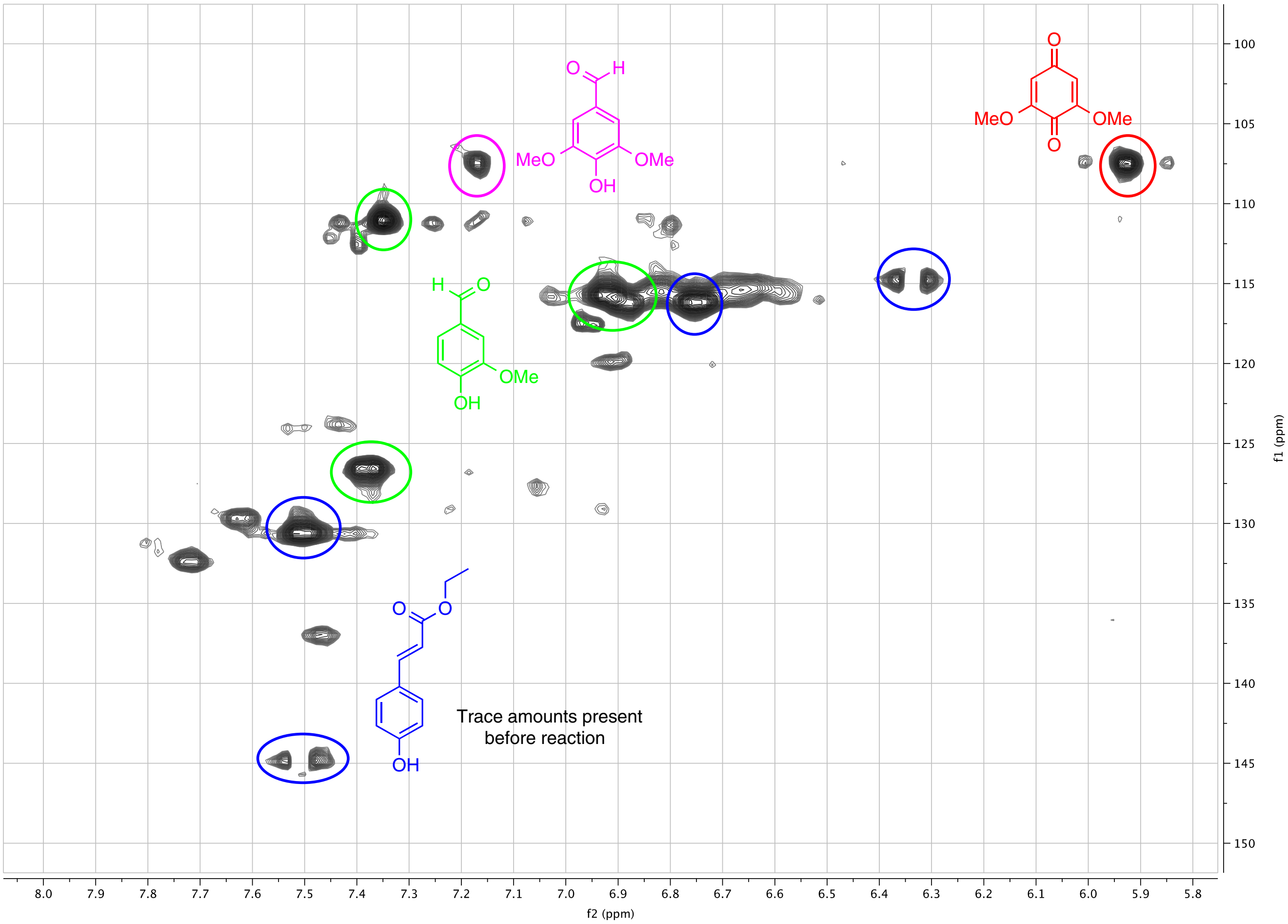


Fig. 8 Typical 2D HMQC spectrum of lignin oxidation products

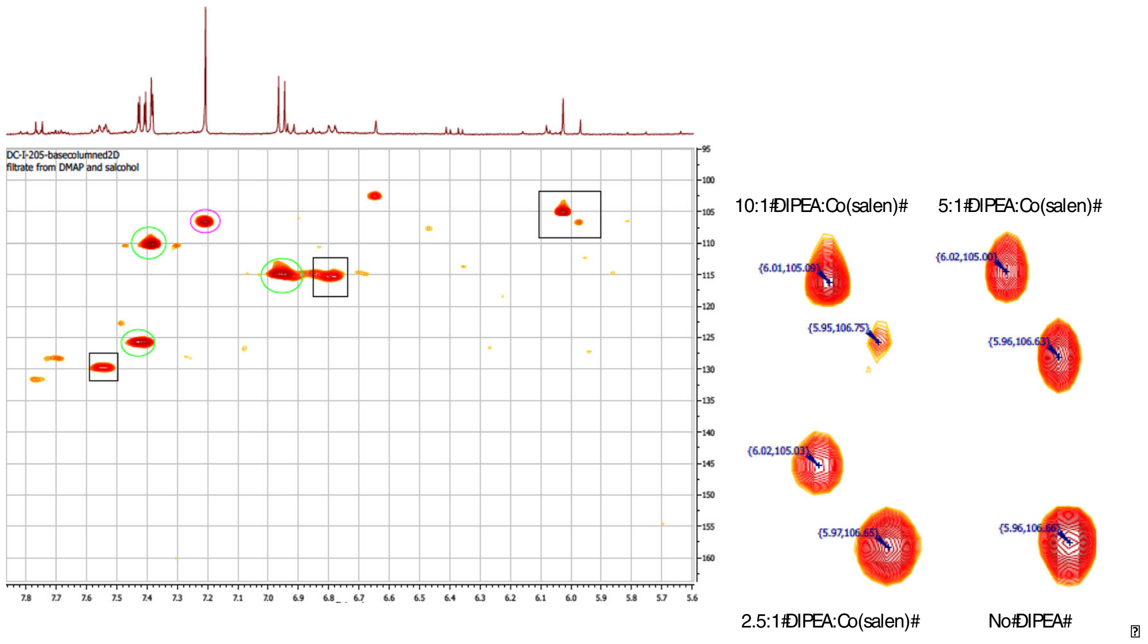


Fig. 9 Organosolv lignin oxidation in the presence of DIPEA

corresponding benzoquinones. Models bearing two S substructures were converted to two equivalents of DMBQ in 81 % yield (entry 5), and compounds incorporating both S and G subunits also gave high DMBQ yields (entries 6 and 7). More moderate yields of quinone were observed for the G residue of these dimers. Interestingly, placing the S residue of an S, G model dimer as the β-substituent led to much lower yields of quinone product (entry 8). The current research is examining the impact of moving the bound aliphatic base to different locations within the salen ligand.

Collectively, these results demonstrate approaches potentially able to convert both of the primary structural units available in biorefinery lignin streams to benzoquinones as examples of HVOs. We have applied these processes to lignin isolated by our organosolv fractionation process. Using O_2 in the presence of Co(salen) and DIPEA, HMQC analysis revealed that the main products from the oxidation of switchgrass organosolv lignin were vanillin, DMBQ, and syringaldehyde. Preliminary results from the oxidation of poplar organosolv lignin using the newer catalysts show the same products. While the yield of low molecular weight product has remained low for the samples tested to date, it is comparable to typical yields for related lignin oxidations [52]. Figure 8 shows a typical NMR spectrum of the products isolated after lignin oxidation. The formation of DMBQ is in line with model studies [40] that show the selective conversion of the aromatic functionality. The addition of an aliphatic base such as DIPEA produces significant changes in the identity of the products of the reaction (Fig. 9). As the amount of DIPEA is increased, the amount of DMBQ is reduced and replaced by the presence of a new structurally similar material. This new material is also observed with the newer catalysts that include a hindered base as part of the salen ligand. Preliminary results from mass spectrometry suggest that this product is 2,5-dimethoxybenzoquinone that could arise from the conversion of G units in the lignin to MMBQ followed by Michael addition of methanol solvent during the oxidation. We are continuing to investigate these processes and will report results in future publications.

Conclusions

The ability to integrate production of biobased chemicals with the production of biofuels will play a critical role in development of an integrated biorefinery. Our research has revealed that organosolv fractionation of biomass can serve as a source of high-quality lignin. Further, this lignin can be converted to low molecular weight aromatics. The current yield of these processes is low, but ongoing work in our laboratories is examining methodology to extend the lifetime of oxidation catalysts and expand the number of substructural units able to be converted by these processes.

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