

# *Catalysis—a potential alternative to kraft pulping*

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**ABSTRACT:** A thorough analysis of the kraft pulping process makes it obvious why it has dominated for over a century as an industrial process with no replacement in sight. It uses low-cost raw materials; collects and regenerates over 90% of the chemicals needed in the process; and is indifferent to wood raw material and good at preserving the cellulose portion of the wood, the part that provides strong fibers. Although the process is odiferous, extremely capital intensive, and very poor at preserving hemicellulose yield, no alternatives have been able to replace it for process cost and product quality. There is a misconception that no new pulping processes have been discovered since the discovery of kraft pulping. Besides the minor adjustments—such as anthraquinone or polysulfide—chlorine, chlorite, and peracetic acid holopulping were discovered and evaluated decades ago. Various solvent pulping methods were discovered and evaluated in the 1980s and 1990s. This work continues with ionic solvents, deep eutectic solvents, and most recently protic ionic liquids. Where all these alternative processes fail is process cost. The chemicals are too expensive and too difficult to recover for use in a commercial process to produce wood pulp. The premise of this review is that the only way to achieve better performance and lower cost than the existing kraft pulping process will be a process using a catalyst to control and direct the reactions. With a high enough reaction rate and a sufficiently high number of turnovers, even an expensive catalyst can still be low cost. We reviewed the literature of existing pulping and delignification catalysts and propose research areas of interest for more intensive experimental efforts.

**Application:** This paper summarizes the research on catalytic methods that could lead to viable, cost-effective alternatives to kraft pulping.

**K**raft pulping is a phenomenal industrial process that is indifferent to wood species, produces strong pulps, and has almost no waste because of the recovery of waste organics for energy and inorganics for regeneration of cooking liquor [1]. The kraft process uses inexpensive chemicals (e.g., sodium hydrogen sulfide, sodium hydroxide or carbonate, sodium sulfate, and lime). All these chemicals are available for less than USD 0.25 per pound; lime is available for just pennies per pound. The high percentage of pulping chemicals recovered and the low cost of the makeup chemicals make kraft pulping inexpensive to operate. When looking for alternatives to the kraft process, it is imperative to keep this low cost aspect in mind or the new process will be guaranteed to fail, at least as an industrial replacement for the kraft process.

Over the last half-century, several alternative pulping processes have been developed. All these processes have failed. Several (but far from all) of these processes and their associated Achilles heels are mentioned here. Holopulping with chlorine, chlorine dioxide (sodium chlorite), and peroxyacetic acid [2] all use too much of a too-expensive chemical. Pulp yield (the major advantage of holopulping) does not have enough value to overcome the cost of the

expensive chemicals. Minisulfite-sulfide pulping lacks ability to inexpensively generate the sodium sulfite. Alkaline sulfite anthraquinone methanol (ASAM) and solvent pulping require complex and expensive solvent recovery processes, higher-pressure-rated digesters, and explosion-proof motors and controls. Polysulfide requires a difficult regeneration process and also has corrosion problems. With more than 100 years devoted to the problem of replacing the kraft pulping process and dozens of delignification processes that failed at the ultimate goal of being more cost-effective than kraft pulping, hopes for a lower-cost process with a more direct delignification are minuscule.

The way around these constraints is that the next pulping process must be catalytic. If a chemical performs a catalytic function and can provide sufficient turnovers, the expense of the catalyst is no longer a large factor. A catalyst-based process could achieve the selectivity of holopulping without the huge cost of bleaching chemicals currently used as stoichiometric reagents in holopulping processes. This idea has been validated by the one well-documented pulping catalyst, anthraquinone (AQ) [3,4]. Anthraquinone accelerates pulping and reduces the frequency of condensation reactions where lignin fragments form new

and irreversible carbon-carbon bonds with other aromatic groups in lignin [5,6]. Unfortunately, AQ is severely limited as a pulping catalyst. The number of cellulose end groups available to reduce the AQ to the delignification-active anthrahydroquinone (AHQ) form is very limited, and the reaction mechanism results in the loss of much of the AQ with relatively few catalytic turnovers. For a 0.1% AQ charge on wood, there are enough end groups at the start of the cook to reduce and activate just 6% of the applied AQ. Without additional peeling and random cleavage reactions, there are enough reducing groups to treat just 0.041% of the  $\beta$ -aryl ether bonds in the wood. Without alkaline peeling and random cellulose cleavage reactions, AQ would be completely ineffective. However, those are the two reactions the industry would like to prevent so as to obtain higher yields and stronger pulps. To generate an AHQ to react with each  $\beta$ -aryl ether bond in lignin requires 11% of the starting wood mass as peeled sugars. This reliance on reducing sugars is a limiting factor in the number of turnovers AQ can perform, drastically limiting the impact on accelerating lignin removal.

Several scientists have looked for alternative stoichiometric reducing chemicals that could be added with AQ to provide more turnovers. To date, nothing has shown a significant benefit [7,8]. The limited number of AQ turnovers may be due in part to an addition product with lignin quinone methides [9,10]. The addition adduct has the potential to rearrange to more stable products that do not release the AQ back into the pulping solution [11,12]. Efforts to recover AQ from black liquor have confirmed that very little survives the pulping process [13], and this may be at least one reason why the addition of stoichiometric reducing chemicals is not particularly effective [7,8]. In fact, evidence suggests that under kraft pulping conditions, the sulfide reduces AQ to AHQ [14]; yet kraft AQ pulping shows no greater efficacy than soda pulping with AQ. It is the reactivity of AHQ with lignin that is process limiting. In this, AQ also validates the second of the two key ideas—sufficient turnovers are required to minimize catalyst cost. With AQ, the most limiting aspect appears to be reaction rate, with a secondary issue of catalyst degradation.

There has been significant scientific interest in the possibility of other delignification catalysts, and several reviews on this topic have been published [15,16]. Cobalt salcomine [17] and various aquo-ion transition metals have been tested as oxygen delignification catalysts [18,19]. Dicobalt octacarbonyl and various rhodium compounds have been evaluated as homogeneous hydrogenation catalysts [20]. Recently, scientific interest has shifted toward delignification catalysts for improving the enzyme saccharification of biomass [21,22]. Although the industry has clearly shown interest in the possibilities of pulping catalysts over the decades, it has never embraced the reality that catalysis is the only logical approach that can improve on kraft processing in both cost and pulp quality.

## Potential catalytic methods and research approaches

At least three catalytic approaches toward pulping are possible: oxidation, hydrolysis, and reduction. Preliminary research performed on each of these methods may be used as a starting point to better define future research on catalytic pulping.

### Oxidation

An oxidation-based process can work using a stoichiometric oxidant (e.g., chlorine dioxide, peroxyacetic acid [2], and polyoxymetalates [23]), or the oxidation process can be catalyst driven using a less-reactive stoichiometric oxidant. The lowest cost, most readily available, and certainly powerful enough oxidant to drive this reaction is molecular oxygen. Fundamentally, a catalyst designed to oxidize lignin using molecular oxygen needs to activate the oxygen and control the oxidation reaction with lignin to avoid unwanted competing reactions.

The role of trace transition metals on the rate and outcome of oxygen delignification was discovered early in the development of the process [18,24,25]. Early effort was largely dedicated to reducing carbohydrate degradation during oxygen delignification and understanding the role of magnesium salts in preserving pulp viscosity. Ericsson et al. noted that an acid wash to remove trace transition metals in the pulp prior to oxygen delignification had little impact on the delignification rate, but reduced cellulose degradation [24]. Landucci and Sanyer demonstrated that by adding transition metals, both delignification and cellulose degradation could be accelerated. Copper and manganese almost doubled the rate of delignification, and cobalt and iron suppressed it slightly. Of the metals evaluated, manganese was the only metal found to improve selectivity [18].

Oxygen is an odd molecule by normal standards—its technically a diradical with two unpaired electrons [26,27]. This is referred to as a triplet state, where the lowest energy configuration has both electrons in either a spin up or spin down state. Symmetry rules dictate that reaction with another substance cannot change the net spin state, requiring the reacted molecule or atom to end up in a triplet state with the oxygen reversing that transition. Direct transition to the singlet state is forbidden by spin, symmetry, and parity rules. But once in the singlet state, oxygen is free to react as long as it has enough oxidizing potential to drive the reaction. If the substance will burn, oxygen has enough oxidizing potential to drive that reaction.

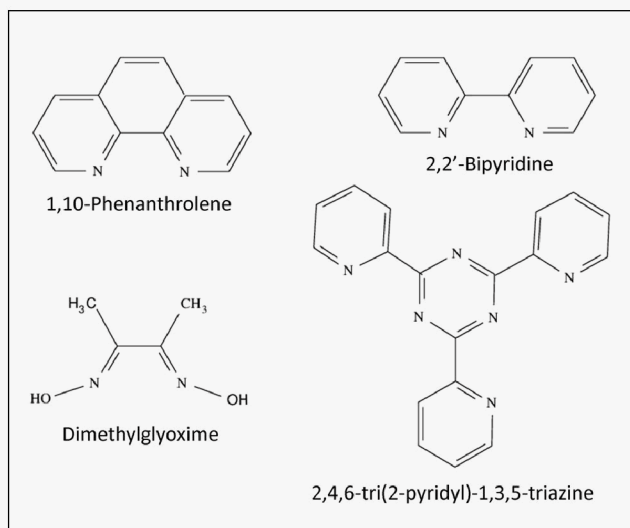
Transition metals catalyze oxygen reactions because they often have unpaired electrons and accessible oxidation states. These features relieve some of the kinetic barriers to reaction of oxygen. Whereas direct reactions of the oxygen triplet state with diamagnetic compounds are slow, reactions with radicals (single unpaired electron) are quite rapid [28,29], and the unpaired electrons in transition metals can serve this purpose. The most reactive metals—Cu(II), Co(II), Fe(III), and

Mn(II)—all have an odd number of electrons. Square planar Cu(II) and square pyramidal Co(II) compounds both have a single unpaired electron in an exposed orbital. The two radicals, the unpaired electrons on the metal, and the triplet state oxygen react or quench, giving a complex where the metal and oxygen each supply one electron to form a bond. For these compounds, the metal is oxidized by one electron and the oxygen is reduced by one electron to superoxide ( $M^+-O_2^-$ ) with the oxygen remaining bonded to the metal [30]. There are organic molecules that react with oxygen as well. Photochemical activation of rose bengal is commonly used to generate singlet oxygen [26,27], and hydroquinones can react directly with oxygen to produce peroxide and a quinone [31].

The use of metal oxidizing chemicals for wood and pulp delignification is a standard research process, with the most common example being the permanganate-based kappa number test [32]. Less commonly used oxidative pulping methods are holopulping based on sodium chlorite and peroxyacetic acid [2] and nitrobenzene oxidation for lignin fragmentation and analysis [33]. The nitrobenzene lignin fragmentation is a noteworthy example. This is performed in a stoichiometric mode with excess oxidant. In addition to nitrobenzene, however, multiple metals, including potassium permanganate, cupric oxide, sodium dichromate, mercuric oxide, silver oxide, cobalt oxide, vanadium, and nickel [34] all perform the same reaction—oxidizing the  $\alpha$ -carbon of the lignin propane unit to a carboxylic acid. This reaction breaks the bond between the  $\alpha$  (C1) and  $\beta$  (C2) carbons and effectively cuts the lignin into monomers, dimers, and trimers. The resulting benzoic acid functional group provides lignin fragments that are soluble at neutral pH. Of these available oxidants, permanganate has been evaluated as a potential bleaching chemical; although reported to be hard on cellulose [35], the viscosity loss was less than experienced with chlorine and hypochlorite [36].

The surprising thing about this list is the wide range in oxidation potential of the active metals. Permanganate ( $E^\circ = 1.51\text{--}1.70\text{ V}$ , depending on pH) and dichromate ( $E^\circ = 1.33\text{ V}$ , acidic pH) are both regarded as strong oxidants. Cupric oxide is known as a weak oxidant ( $E^\circ = 0.15\text{--}0.52\text{ V}$ ); it also performs the  $\alpha$ - $\beta$  bond cleavage with a product distribution containing more aldehydes, but otherwise is similar to stronger oxidants. After treatments, approximately 50% of the lignin in a sulfite liquor was extractable as monomeric phenols [37,38]. Silver oxide ( $E^\circ = 0.607\text{ V}$ ) gives almost identical results [38]. Cobalt, copper, iron, vanadium [39], manganese, zinc, and lanthanum have all been evaluated as metal additives in bicarbonate-oxygen pulping [40]. Whereas many metals accelerate delignification, most reduce selectivity as well [39]. Manganese, zinc, and lanthanum all show improved selectivity under some conditions [40].

Many of these reactions do not proceed all the way to the benzoic acid product and give other byproducts of lignin. The reaction is thought to proceed through a single electron oxidation that produces a phenolic radical stabilized by

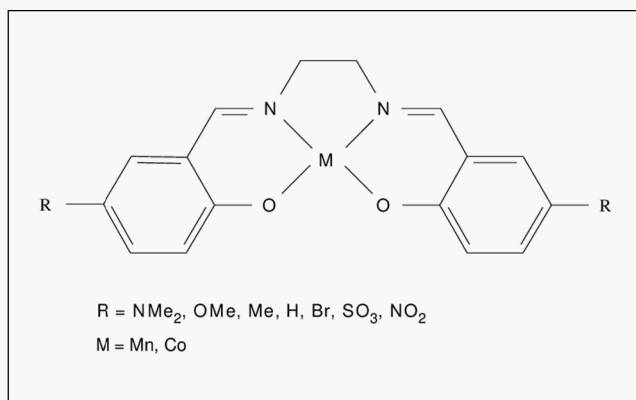


1. Several of the imines used in successful copper catalysts.

conjugation of the  $\alpha$ -carbon and phenolic OH group. This leads to cleavage of the  $\alpha$ - $\beta$  bond, with the starting phenolic forming an aldehyde and the radical transferred to the cleaved fragment. An alternative reaction is also observed. The lignin radical is oxidized by a second metal, converting  $\alpha$  to a ketone as a stable intermediate. In addition to the variable oxidation paths provided by this type of single-electron oxidation, condensation reactions to carbohydrates or other lignin fragments are possible. The key point is that this represents a fairly simple reaction path initiated by many different transition metals and potentially accessible by a catalytic approach.

Because trace metals were inferred as important to oxygen delignification and are commonly used as oxidation catalysts, there have been many papers evaluating metal complexes as catalysts for oxygen delignification. Cobalt salcomine [17] and a group of porphyrin compounds using iron, manganese, and cobalt as active metals [41] were tested. Recently, cobalt and manganese salcomine, cobalt and manganese with other Schiff base ligands [42,43], and copper dinitrogen compounds [44] have been evaluated as possible pulping or bleaching catalysts using lignin model compounds and also in oxygen delignification reactions on wood pulp. Similar vanadium (IV) complexes have been tested as well [45,46].

Noteworthy in this regard are projects funded by TEKAS as part of the SEKAVA project. These included an evaluation of copper, cobalt, iron, and manganese diamine complexes [44, 47-50] (Fig. 1) and metal Schiff Base compounds (salcomines) with cobalt and manganese (Figs. 2 and 3) [42,43]. Using veratryl alcohol as the substrate, only the copper catalysts were active with the diamine ligands. The most active catalysts were 2,2'-bipyridine, 1,10-phenanthroline [50], 9,10-diaminophenanthrene, and 1,2-diaminocyclohexane [44] (Fig. 1). In experiments with an unbleached softwood kraft pulp, the catalysts increased delignification from 37%–53%, but the brownstock viscosity was reduced by nearly



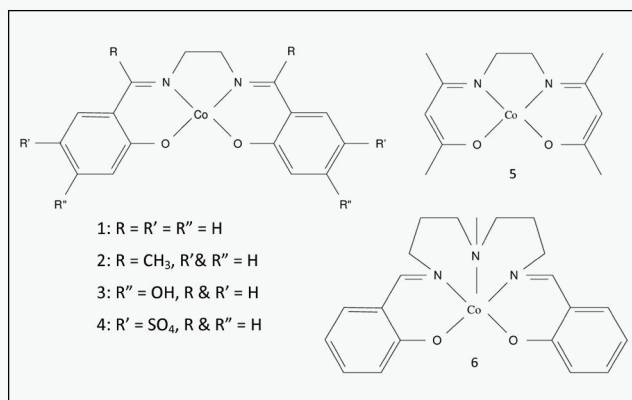
**2. Cobalt and manganese salen complexes evaluated by Haikarainen [42].**

50% [49,50]. Adding electron-donating groups to the 4 and 4' positions of bipyridine increased delignification and marginally improved the pulp viscosity [49]. Catalyst activity was found to decrease during the reaction, and Lahtinen et al. concluded this was due to a condensation reaction between veratraldehyde and the amine ligand; turnovers (moles of veratryl alcohol oxidized per mole of catalyst) ranged from 20 to 90 using 1,2-diamino cyclohexane as the ligand [48] and up to 800 with bipyridine as the ligand [50].

Several of the salen-based ligands (Figs. 2 and 3) were also active oxidation catalysts, primarily with cobalt as the active metal. These cobalt-salcomine complexes are well known and one of the most studied systems for coordinating oxygen [51,52]. The salen ligand produces a square planar complex with cobalt. This generally does not bond with oxygen, but addition of a fifth coordination site, often from added pyridine, converts the complex from four-coordinate square planar to a five-coordinate square pyramid. The addition of two more shared electrons and the fifth bond site in an axial position shifts the d<sub>z2</sub> orbital from nonbonding with a pair of electrons to antibonding with a single electron. Reaction with oxygen results in a six-coordinate octahedral complex with spin pairing [30] in the d<sub>z2</sub> orbital and one remaining unpaired electron on the oxygen [53-55]. Under some conditions, this initial Co-O<sub>2</sub> complex bonds with a second cobalt-salen molecule to give a dimer with a peroxide-like bridge.

The standard mechanistic hypothesis has been the five-coordinate model and compound 6 (Fig. 3) has been commonly used in experimental work [56]. However, compound 6 was found to be inactive by Kervinen et al. [57], leading to a proposed mechanism where the veratryl alcohol occupies this axial site [58]. However, there is evidence for different mechanisms with different lignin model compounds: cobalt activation by a fifth ligand for compounds without the phenolic OH, and cobalt activation by bonding to the phenolate when using lignin model compounds containing the free phenol [59].

The coordination to the substrate by cobalt-salen com-



**3. Additional salen compounds used with cobalt catalysts.**

plexes is both an advantage and disadvantage in terms of developing a catalytic system. The improved selectivity for delignification observed with cobalt-salen catalysts is probably due to this direct coordination. When oxidizing lignin in wood or unbleached wood pulp, there is not a single type of lignin monomer for the catalyst to bind to and only about 10% of the monomers have a free phenol. The laboratory work with lignin model monomers shows very different activity and different ideal conditions for the different monomers. The reaction with free phenols also requires the reactions to be performed at high pH for the phenolate to bond to the cobalt. But high pH is itself a problem. The equilibrium between cobalt coordinated to the salcominelike ligand and cobalt in solution is not strong enough to prevent cobalt oxide from precipitating under the alkaline conditions.

The biorefinery interest in obtaining higher value out of lignin has generated considerable interest in catalysis capable of breaking bonds in the lignin left over from enzymatic saccharification and kraft black liquor. Bozell et al. have combined experimental efforts with molecular orbital calculations to understand the effect of manipulating the electron withdrawing character of the fifth ligand in cobalt(salen) using a series of substituted imidazoles [60]. They used the same approach to evaluate the impact of bulky groups attached to the ligand [61] on oxidation of lignin models. Chiang et al. added electron withdrawing and electron donating functional groups to the ligand and evaluated the impact on radical initiated polymerizations [62]. This effort includes considerable characterization of complexes including cyclic voltammetry (redox potential) X-ray photoelectron spectroscopy (binding energy) and electron paramagnetic resonance (electronic shielding of the unpaired electron). Pui et al. added various halogens to the salen ligand and reported the impact on catalytic oxidation of di-*t*-butylphenol [64]. A limitation of these efforts is that the experimental oxidations were carried out in organic solvents and may not apply directly to a commercial system where water is likely to be the solvent or at least present during the oxidation process.

### Reductive cleavage

Although most existing commercial pulping processes, including soda, sulfite, and kraft pulping, are conducted in a chemically reductive environment, the reactive chemistry of the processes are hydrolysis and dehydrolysis reactions and few chemical reductions occur during pulping. The reducing potential of the cooking medium is, however, regarded as significant [64], and reducing sugars are proposed to participate in delignification reactions [65]. There is considerable research on lignin hydrogenations using Raney nickel, in situ precipitated nickel, and other standard chemical hydrogenation catalysts [66-68]. Among these are a few using homogeneous catalysts (e.g., dicobalt octacarbonyl) [20,69]. As with pulping, the hydrogenation processes are largely hydrolysis reactions with the catalytic hydrogenation doing little more than stabilizing phenols [70]. A problem with a chemical reducing approach is that water is very limiting as a solvent for reducing processes. At potentials more reducing than  $E^\circ = 0$  V, proton reduction to dihydrogen becomes a competing reaction. Given the numbers of alcohol functional groups on carbohydrates as well as lignin, this is probably also a practical limit for chemically reducing lignin.

Results of catalytic hydrogenation of mechanical pulps have been reported by Hu and James. Using lignin model compounds and a number of traditional rhodium- and ruthenium-based hydrogenation catalysts, they found preferential hydrogenation of double bonds and aromatic groups before reducing aldehydes and ketones [71,72]. When hydrogenations have been applied to mechanical pulps, some hydrogenation of the aromatic rings was observed, but there was no significant evidence of delignification [73].

Hydrogenation of lignin has been combined with autohydrolysis, but because both lignin and carbohydrates are sensitive to hydrolysis reactions, the outcomes are limited by the effectiveness and selectivity of the autohydrolysis. Whereas the possibility for catalytic reducing processes still exists, there is little precedent to work with metals assisting reductive cleavage.

### Hydrolysis

Because both acid sulfite and alkaline pulping (soda and kraft) are basically hydrolysis reactions, this approach has appeal. Hydrolysis reactions are already catalyzed—acidin the case of sulfite and hydroxide in the case of soda. The process cleaves the p-aryl ether bond, adding a proton from water to one fragment and  $\text{OH}^-$  to the other. The acid or base is conserved, and the stoichiometric reagent is water. It needs to be recognized that the strongest acid available in a protic environment is  $\text{H}^+$ . The strongest base active in water is  $\text{OH}^-$ . Kraft pulping conditions are faster and more effective than soda because  $\text{SH}^-$  is thought to be a better nucleophile at the cooking temperature than is  $\text{OH}^-$  [74].

A small molecule approach to hydrolysis catalysis could focus on a stronger base, which would require something other than water as the reaction medium, or stronger

nucleophiles than sulfide. A limiting factor to this approach is that a strong nucleophile is more likely to function as a stoichiometric reagent and is unlikely to be lower cost than sodium hydrosulfide, or compatible with the recovery process. Considering a catalyzed approach, this type of insertion reaction, where a metal ion first bonds to exposed electrons on the substrate and then inserts itself into a bond, is common in transition metal homogeneous catalysis [75]. The reaction is referred to as an oxidative addition; that is, after the insertion both of the organic fragments are regarded as negatively charged and the transition metal is formally oxidized by two electrons. In the catalytic process, another molecule also coordinated to the metal then inserts itself between the M-CH<sub>2</sub>R bond, releasing that fragment to the solvent. Often, that other molecule is hydrogen (hydrogenation) or carbon monoxide (hydroformylation). When the hydride ion then migrates to an attached organic molecule, the reductive elimination occurs and the catalyst returns to the initial state. This process, oxidative addition, reductive elimination, is well documented for homogeneous hydrogenation and hydroformylation catalysts.

Although oxidative insertion is a common mechanism for transition metal reactions with organic compounds, it is not a common reaction with ethers, which would be the most useful reaction for delignification. In considering the oxidative insertion process, the metal would need to insert into either the H-OR, HO-R, or RO-R bond. Most metals in aqueous or protic environments are surrounded by water molecules and have no inclination to insert into an alcohol or ether. The cobalt salcomine process is proposed to bond to the O- of a lignin phenolate, but the pH must be high enough for the phenolate ion to exist [58]. Switching to nonaqueous conditions improves the chances for this type of insertion. Vanadium bonded to a primary alkoxide is part of the mechanism proposed for cleavage of a common  $\beta$ -aryl ether model using vanadium as the catalyst [21,45]. Although this catalyst is similar to other oxidation catalysts evaluated for biorefinery pretreatment, the products did not show oxidation of the benzyl OH group. Instead, the product amounted to a rearrangement of the phenylpropane with the  $\alpha$ -OH oxidized to a ketone, and  $\gamma$ -OH and  $\beta$ -phenolate both leaving with reduction of C $\beta$  and C $\gamma$  to an olefin. Hanson et al. evaluated the reaction and found that relatively minor changes in the ligand surrounding the vanadium are responsible for the different reaction paths. These reactions were all carried out under alkaline conditions and in organic solvents, acetonitrile, dimethyl sulfoxide, or pyridine [22,45]. It is not technically an insertion because the alkaline conditions have removed the proton from the alcohol in advance of coordination to the vanadium and not technically a hydrolysis either, but rather an internal redox rearrangement of the two parts of the lignin model dimer.

## COMMENTS AND RECOMMENDATIONS

Most transition metal homogeneous catalysts have special-



ized organic ligands around them, molecules that help adjust the redox potential of the metal to a range most suitable for the reaction of interest. The ligand may also limit or direct the orientation of reactive molecules to control reaction paths to a desired outcome. The cobalt salcomine catalyst is a noted example of a transition metal catalyst with organic ligands [17], and the more recent vanadium catalysts have used similar complexes [21,22]. Porphyrins are another example of an organic complex used to stabilize and activate metal cations in redox reactions. Of note, many common and commercially successful catalysts do not require intricate or detailed organic ligands. For example, tris-triphenylphosphine rhodium chloride, the common homogeneous hydrogenation catalyst, has a relatively simple ligand structure. Although the ligands are crucial to function, they primarily adjust the redox potential and electron density at the metal so that it will bond, in the case of olefin hydrogenation, to the olefins and hydrogen.

Transition metal oxidation catalysts with organic ligands are a problem. Organic materials are all sensitive to oxidation, and the ligands bound to transition metals are no exception. They not only need to be robust to the metal in an oxidized state, they also need to avoid reacting with the partially reduced oxygen radical or peroxide product of the initial oxidation. Noteworthy in this regard is that the salcomine catalysts did become ineffective after relatively few cycles, but the primary decomposition was hydrolysis of the ligand back to the original aldehyde and amine used to prepare it, not oxidation to an inert form.

The effort on oxidations using polyoxometalates is an example of using an oxidized inorganic structure to provide the surrounding ligand for a metal redox catalyst [23,76] rather than an oxidatively sensitive organic molecule. This method has its own limitations, among them the huge deadload mass of the bulky inorganic structure and the cost of the tungsten-molybdenum metal-oxide clusters. The cluster is also a very good chelating chemical and tends to collect any trace metals in the pulping or bleaching environment. These become a recovery problem; not only is very thorough chemical recovery needed to mitigate the cost of the metal cluster, but methods to remove trace metals found in wood and corroded from the process are required to reactivate the metal cluster. Efforts to develop catalytically active polyoxymetalates that can handle many turnover cycles and might not warrant recovery are well directed.

Of the three possible catalytic approaches discussed, the oxidative approach appears to be the most likely to succeed. It also has the best leads in several viable candidate compounds known to oxidize ligninlike organic molecules and in some cases even accelerate oxygen delignification reactions. The high pH they need to be effective presents a problem in catalyst stability. The copper-based systems and possibly also the cobalt salcomines are free-radical, single-electron transfer processes and that will limit selectivity. Processes that can transfer two electrons will convert oxygen

directly to peroxide, and peroxide directly to water, thus avoiding the possibility of other radical chain reactions. There is evidence in the initial work by Landucci that manganese tends to transfer two electrons at once [77], but work with manganese catalyst has not shown notable activity. With a catalyst that transfers two electrons at the same potential, lignin fragments will go directly from **C- $\alpha$**  secondary alcohols to ketones, and the ketones to benzoic acids, thus skipping the phenolic and benzoic radicals of the existing processes. This will require a shift to different metals. Two-electron transitions (at the same potential) are more common in the second- and third-row transition metals. Transition metals with three oxidation states that are all stable in water are more common in the early elements in each row of the transition metals. The search for potential catalysts must continue to look beyond cobalt and copper.

## CONCLUSIONS

The existing pulping processes have withstood an assault by a century of chemistry. When the kraft process was developed (1891), the chemical nature of glucose and cellulose was not known and the basic nature of lignin did not yield to analysis for another half-century. The inspired piece of chemistry that led to the kraft process was the recognition of periodicity in the chemical elements and the formation of the periodic table of the elements. Sodium sulfide would behave like sodium hydroxide but could be produced in a furnace and did not require a lime cycle to regenerate. In spite of the limited understanding of the chemistry when it was discovered, the kraft process has become the predominant pulping process and has held that position for a half-century. With current understandings of lignin and carbohydrate structures, and with modern chemical methods, an economical catalytic pulping process could be developed.

Several catalytic pathways have been discovered and discussed in this work. The cobalt- and copper-based oxidation catalysts have been well researched, and their limitation in turnover and selectivity do not appear to be readily improved by simple changes in the complexes. The limiting issues of AQ chemistry have also been touched upon. Potential pitfalls associated with operating metal-based catalytic systems in aqueous and aqueous-alkaline solutions have also been identified. The high reactivity of oxygen with metals containing a single electron in an accessible orbital was highlighted. It has also been noted that many homogeneous catalysts do not rely upon complicated organic ligands. Finally, the number and rate of catalytic turnovers, rather than the inherent cost of the catalyst, have been identified as key factors in developing an economical pulping method.

Developing an economic rival to the kraft pulping process is important to the survival of the paper industry. The pulping industry currently collects value from less than 50% of its starting material and struggles to control the odor of reduced-sulfur compounds. Fifty years of process development and optimization has produced an industry that is an engineer's dream

and an MBA's nightmare. Is it going to be 50 more years of incremental improvements, or is the industry committed to a better future? **TJ**

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## ABOUT THE AUTHORS

I (Rudie) was asked to do this review by the Agenda 2020 Technology Alliance NextGen Pulping Committee. It is one of my areas of interest. I am trained as an inorganic chemist and since I started working in the industry, I have thought inorganic catalysts were the pulping process of the future. This was one of the first opportunities to advance the idea of catalyzed pulping.

While doing this literature review, I discovered there is more research than I had anticipated. Most importantly, there has been a considerable recent effort in Finland in this area. Although there is no material for mills to use directly, people need to manage research. They might want to ask why 100 years of research has not provided a replacement for the kraft process.

They might also want to ask why industry and academia have not succeeded in this task. The industry's Focus on development work and short-term gains is not providing an alternative to the capital, operating, and environmental costs of the kraft process.

The USDA Forest Service R&D is conducting a theoretical (molecular modelling, molecular orbital theory) evaluation of some of the known catalysts.

Also underway is a literature review of the metal oxide stoichiometric catalysts to determine if that process has potential as a mechanism for an oxidative pulping catalyst.



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