Rudie, A.W. and Hart, P.W., "Catalysis: A Potential Alternative to kraft Pulping. A Synthesis of the Literature", TAPPI PEERS, Tacoma, WA, September 14-17, 2014, Preprint 4-1.

Catalysis: A Potential Alternative to Kraft Pulping. A Synthesis of the Literature

Alan W. Rudie, Peter W. Hart

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, is indifferent to wood raw material and good at preserving the cellulose portion of the wood which is the part that provides strong fibers. Although an odiferous process, 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 there have been no new pulping processes discovered since the discovery of kraft pulping. Besides the minor adjustments like antrhraquinone or polysulfide, chlorine, chlorite and peracetic acid holopulping were discovered and evaluated decades ago. Various solvent pulping methods were discovered and evaluated in the 1980's and 1990's and this litany continues with ionic solvents, deep eutectic solvents and most recently protic ionic liquids. Where all of these alternative processes fail is process cost. The chemicals are too expensive and too hard to recover to use for commercial production of wood pulp. The premise of this review is that the only way to achieve better performance and a 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. This effort has reviewed the literature of existing pulping and delignification catalysts and proposes research areas of interest for more intensive experimental efforts.

Introduction

The kraft pulping process is a phenomenal industrial process which is indifferent to wood species, produces strong pulps, and because of the recovery of waste organics for energy and inorganics for regeneration of cooking liquor, has almost no waste.' The kraft process uses inexpensive chemicals, e.g. sodium hydrogen sulfide, sodium hydroxide or carbonate, sodium sulfate and lime. All of these chemicals are available for less than a quarter 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 the kraft pulping process 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 of these processes have failed. Several (but far from all) of these processes and their associated Achilles heels are listed below. 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) just does not have enough value to overcome the cost of the expensive chemicals. Mini-sulfite-sulfide pulping suffers from the lack of 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 suffers from corrosion problems. With over 100 years devoted to the problem of replacing the kraft pulping process and dozens of successful 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 miniscule.

There is a way around these constraints. The next pulping process will have to 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, anthraquinone is severely limited as a pulping catalyst. The number of cellulose end groups available to reduce the AQ to the delignification active anthrahydroquinone 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 anthraquinone. Without additional peeling and random cleavage reactions, there are enough reducing groups to treat just 0.041% of the ß-aryl ether bonds in the wood. Without alkaline peeling and random cellulose cleavage reactions, anthraquinone would be completely ineffective. But those are the two reactions the industry would like to prevent in order to obtain higher yields and stronger pulps. To generate an anthrahydroquinone to react with each ß-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 anthraquinone to provide more turnovers. To date, nothing has shown a significant benefit.[7,8] Part of the reason for a limited number of AQ turnovers may be due 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, the evidence is that under kraft pulping conditions, the sulfide reduces AQ to AHQ[14] and 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 critical 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 towards delignification catalysts for improving the enzyme saccharification of biomass.[21,22] Where the industry has clearly shown interest in the possibilities of pulping catalysts over the decades, it has never embraced the reality that this is the only logical approach that can improve on kraft processing in both cost and pulp quality.

Potential Catalytic Methods and Research Approaches:

There are at least three possible catalytic approaches towards pulping: oxidation, hydrolysis and reduction. Preliminary research has been performed on each of these methods. These studies may be used as a starting point to better define future research efforts in the area of catalytic pulping.

Oxidation

An oxidation based process can work using a stoichiometric oxidant: chlorine dioxide, peroxyacetic acid[2] and polyoxymetalates (POMs)[23] as examples, 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 the 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 suppressing it slightly. Of the metals evaluated, manganese was the only metal found to improve selectivity.[18]

Oxygen is an odd molecule by normal standards - it is 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. Where direct reactions of the oxygen triplet state with diamagnetic compounds is slow, the reactions with radicals (single unpaired electron) is 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), 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 electron 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 sodium chlorite and peroxyacetic acid based holopulping,[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. But in addition to nitrobenzene, 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 α-carbon of the lignin propane unit to a carboxylic acid. This reaction breaks the bond between the α (C1) and ß (C2) carbons and effectively cuts the lignin up 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 and 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^0 = 1.51-1.70 V depending on pH) and dichromate (E^0 = 1.33 V, acidic pH) are both regarded as strong oxidants. CuO is known as a weak oxidant (E^0 = 0.15-0.52 V). CuO also performs the Cα-β bond cleavage with a product distribution containing more aldehydes, but otherwise 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^0

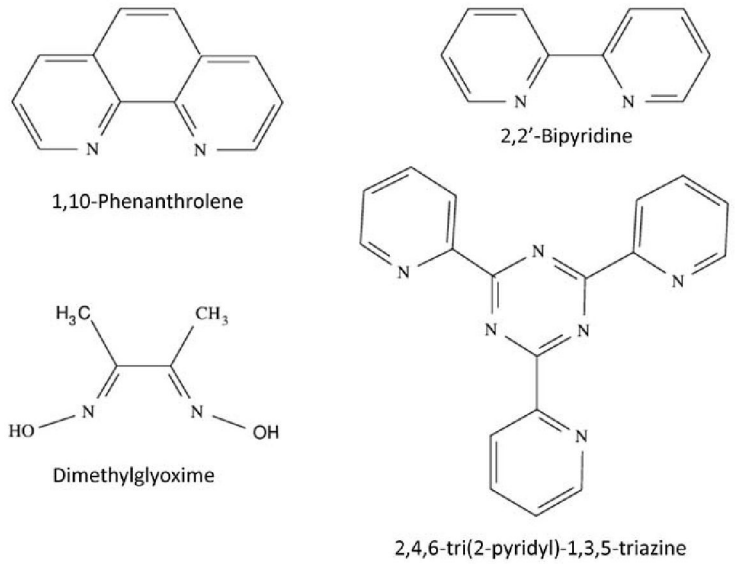
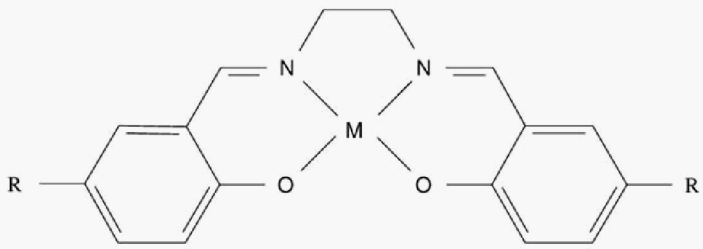


Figure 1. Several of the imines used in successful copper catalysts [44,50]

= 0.607 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] Where many accelerate delignification, most reduced selectivity as well.[39] Manganese, zinc and lanthanum all show improved selectivity under some conditions.[40]

It is important to understand that 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 radial stabilized by conjugation of the a-carbon and phenolic OH group. This leads to cleavage of the Cα - Cβ 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 C-α 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 issue 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 Fe, Mn and Co 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]



R = NMe_2, OMe, Me, H, Br, SO_3, NO_2

M = Mn, Co

Figure 2. Co and Mn salen complexes evaluated by Haikarainen[42]

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[44,47,48,49,50] (Figure 1) and metal Schiff Base compounds (salcomines) with cobalt and manganese (Figure 2 and Figure 3).[42,43] Using veratryl alcohol as the substrate, only the copper catalysts were active with the diamine ligands. 2,2'-bipyridine, 1,10-phenanthrolene,[50] 9,10-diaminophenantrene and 1,2-diamino cyclohexane[44] were the most active catalysts (Figure 1). In experiments with an unbleached softwood kraft pulp, the catalysts increased delignification from 37% to 53%, but the brown stock viscosity was reduced by nearly 50%.[49,50] Adding electron donating groups to the 4 and 4'

positions of bipyridine increased delignification and reduced the pulp viscosity loss marginally.[49] Catalyst activity was found to decreases 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:' up to 800 with bipyradine as the ligand.[50]

Several of the salen-based ligands (Figures 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 4-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_{z2} orbital from non-bonding 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_{z2} orbital and one remaining unpaired electron on the oxygen.[53,54,55] Under some conditions, this initial Co-O_2 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 complex 6 (Figure 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 a phenolic OH, and cobalt activation by bonding to the phenolate when using lignin model compounds containing the free phenol.[59]

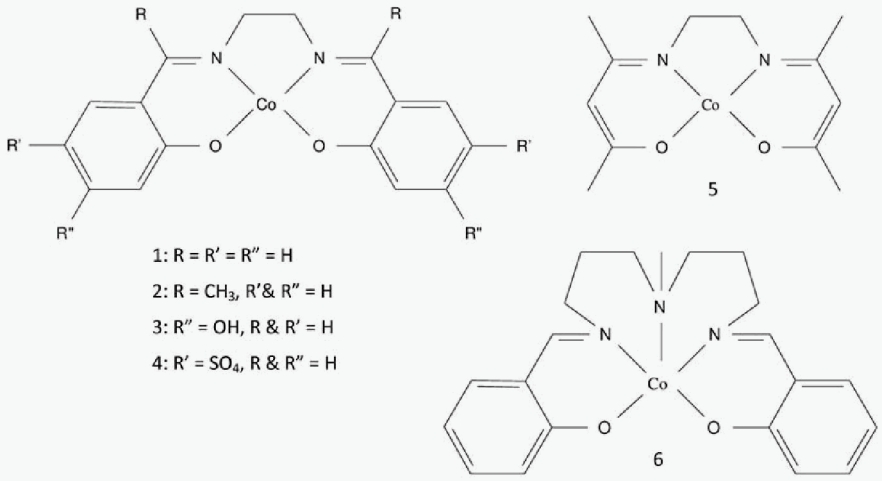


Figure 3. Additional salen compounds used with cobalt catalysts[43,58]

The coordination to the substrate by cobalt-salen complexes is both an advantage and disadvantage in terms of developing a catalytic system. The improved selectivity for delignification observed with Co-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 salcomine-like ligand and cobalt in solution is not strong enough to prevent cobalt oxide from precipitating under the alkaline conditions.

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 there are few chemical reductions that occur during pulping. The reducing potential of the cooking medium is however regarded as significant[60] and reducing sugars are proposed to participate in delignification reactions.[61] There is considerable research on lignin hydrogenations using Raney nickel, in situ precipitated nickel and other standard chemical hydrogenation catalysts.[62,63,64] Among these are a few using homogeneous catalysts, for example dicobalt octacarbonyl.[20,65] As with pulping, the hydrogenation processes are largely hydrolysis reactions with the catalytic hydrogenation doing little more than stabilizing phenols.[66] A problem with a chemical reducing approach is that water is very limited as a solvent for reducing processes. At potentials more reducing than $E^o = 0$ 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.[67] When hydrogenations have been applied to mechanical pulps, some hydrogenation of the aromatic rings was observed, but there was no significant evidence of delignification.[68]

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

Hydrolysis

Since both acid sulfite and alkaline pulping (soda and kraft) are basically hydrolysis reactions, this approach has appeal. Hydrolysis reactions are already catalyzed - acid in the case of sulfite and hydroxide in the case of soda. The process cleaves the ß-aryl ether bond, adding a proton from water to one fragment and 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 H^+. The strongest base active in water is OH-. A reason why kraft pulping conditions are faster and more effective than soda is that SH^- is thought to be a better nucleophile at the cooking temperature than is OH^-.[69]

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 NaSH, 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.[70] The reaction is referred to as an oxidative addition in that after the insertion, both of the organic fragments are regarded as negatively charged and the transition metal formally oxidized by two electrons. In the catalytic process, another molecule also coordinated to the metal then inserts itself between the M-CH_2R bond releasing that fragment to the solvent. Often, that other molecule is a 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 saclomine 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 non-aqueous 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 ß-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 α-OH oxidized to a ketone, and γ-OH and ß-phenolate both leaving with reduction of Cß and Cγ 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 ether, but rather an internal redox rearangment of the two parts of the lignin model dimer.

Comments and Recommendations

Most transition metal homogeneous catalysts have specialized 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. It is important to note the many common

and commercially successful catalysts tend not to have intricate or detailed organic ligands. For example, tris-triphenylphosphine Rhodium chloride, the common homogenous hydrogenation catalyst, has a relatively simple ligand structure. Although the ligands are critical 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 an active metal redox catalyst[23,71] 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/bleaching environment. These become a recovery problem in that not only is very effective 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 in order to reactivate the metal cluster. Efforts to develop catalytically active POMs that can handle many turn-over 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 lignin-like 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, 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,[72] 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-α secondary alcohols, to ketones, and the ketones to benzoic acids, skipping the phenolic and benzoic radicals of the existing processes. This is going to require a shift to different metals. Two-electron transitions are more common in the second and third row transition metal series, and the ability to undergo two single-electron oxidations or reductions in air and/or aqueous conditions is far more common in the early elements in the first row transition metals.

Conclusions

The objective of this paper is to summarize research on catalytic methods that can oxidize, reduce, or hydrolyze lignin and to advance research interest in this area. The existing pulping

processes have withstood an assault by a century of chemistry. When the kraft process was developed, the chemical nature of glucose and cellulose was not known (1 891) and the basic nature of lignin did not yield to analysis for another half century. The inspired piece of chemistry that lead 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 anthraquinone 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 assessable orbital was highlighted. It has also been noted that many homogenious catalysts do not rely upon complicated organic ligands. Finally, the importance of the number and rate of catalytic turnovers rather than the inherent cost of the catalyst has been identified as a critical factor in developing an economical pulping method.
Developing an economic rival to the kraft pulping process is critical 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 the incremental improvements, or is the industry committed to a better future?

References:

1. Clayton, D.W., The chemistry of Alkaline Pulping in The Pulping of Wood, R.G. McDonald and J.N. Franklin editors, Pulp and Paper Manufacture, Volume I The Pulping of Wood, McGraw-Hill, New York, 1969, pp347-438.
2. Leopold, B., Chemical composition and physical properties of wood fibers I. Preparation of holocellulose fibers from loblolly pinewood, Tappi j., 44(3): 230-240(1961).
3. Holton, H., Soda additive softwood pulping: a major new process, Pulp and Paper Canada, T218-T223(1977).
4. Donnni, G.P., Blain, T.J., Holton, H.H. and Kutney, G.W., 300 alkaline pulping additives: structure-activity relationships, J. Pulp and Paper Science, TR134-140(1983).
5. Simard, G.L., Genco, J.M. and Henriksson, K.E., The effect of reducing agents on anthraquinone pulping, Tappi J., 62(5): 91-92(1979).
6. Irvine, G.M., Nelson, P.J. and Gniel, G.M., Studies on soda-anthraquinone pulping. Part 3. Soda-AQ pulping of Pinus Radiata wood in the presence of reducing agents, Appita, 40(3): 189-192(1987).
7. Gierer, J., Lindberg, O. and Noren, I., Alkaline delignification in the presence of anthraquinone/ anthrahydroquinone, Holzforschung, 33: 213(1979).
8. Landucci, L.L., Quinones in alkaline pulping, characterization of an anthrahydroquinone-quinone methide intermediate, Tappi, 63(7): 95-99(1980).

9. Kondo, R. and McCarthy, J.L., Condensation of lignins with coniferyl alcohol in alkaline aqueous solutions, J. Wood Chemistry and Technology, 5(1): 37-52(1985).
10. Brogdon, B.N. and Dimmel, D.R., Fundamental studies of relative delignification efficiencies (I): conventional pulping systems, J. Wood Chemistry and Technology, 16(3):261-283(1996).
11. Fleming, B.I., Kubes, G.J., MacLead, J.M. and Bolker, H.I., Polarographic analysis of soda-anthraquinone pulping liquor, Tappi, 62(7): 55-58(1979).
12. Dimmel, D.R. and Shepard, D., The alkaline reactions of some simple quinonemethide-anthrahydroquinone adducts, J. Wood Chemistry and Technology, 2(1): 73-95(1982).
13. Algar, W.H., Farrington, A., Jessup, B., Nelson, P.F. and Vanderhoek, N., The mechanism of soda-quinone pulping, Appita 33(1): 33-37(1979).
14. Revenga, J.A., Rodriguez, F. and Tijero, J., Reduction constant of anthraquinone in kraft pulping liquor, J. Pulp and paper Science, 21(3): 104-109(1995).
15. Crestini, C., Crucianelli, M., Orlandi, M. and Saladino, R., Oxidative strategies in lignin chemistry: a new environmental friendly approach for the functionalization of lignin and lignocellulosic fibers, Catalysis Today, 156: 8-12(2010).
16. Hage, R. and Lienke, A., Application of transition-metal catalysts to textile and wood-pulp bleaching, Angewandte Chemie, 45: 206-222(2006).
17. Fullerton, T.J. and Ahern, S.P., Salcomine as a catalyst for oxygen delignification, TAPPI J., 61(12) 37-39(1978).
18. Landucci, L.L. and Sanyer, N., Influence of transition metals in oxygen pulping, Tappi, 58(2): 60-63(1975).
19. Popova, N., Bogolitsyn, K., Kosheleva, A. and Shulgina, E., The catalytic oxidation of the lignin model compounds, 12th International Symposium on Wood and Pulping Chemistry, Volume 11, PP 47-48 (2003).
20. Nahum, L., Delignification of wood by hydrogenation in the presence of dicobalt octacarbonyl, I & EC Product Research and Development, 4(2): 71-74(1965).
21. Son, S. and Toste, F.D., Non-oxidative vanadium catalyzed C-O bond cleavage: Application to degradation of lignin model compounds, Angewandte Chemie, Int. Ed., 49: 3791-3794(2010).
22. Hanson, S.K., Wu, R. and Silks, L.A., C-C or C-O bond cleavage in a phenolic lignin model compound: selectivity depends on vanadium catalyst, Angewandte Chemei, Int. Ed., 51: 3410-3413(2012).
23. Weinstock, I.A., Atalla, R.H., Reiner, R.S., Houtman, C.J. and Hill, C.L., Selective transition metal catalysis of oxygen delignification using water-soluble salts of polyoxometalate (POM) anions, Holzforschung, 52(3): 304-310(1998).
24. Ericsson, B., Lindgren, B.O. and Theander, O., Factors influencing the carbohydrate degradation under oxygen-alkali bleaching, Svensk Paperstidning, 74(22): 757-765(1971)
25. McClosky, J.T., Sinkey, J.D. and Thompson, N.S., Catalytic influence of iron and magnesium ions in oxygen bleaching reactions, Tappi, 58(2): 56-59(1975).
26. Lamberts, J.J.M. and Neckers, D.C., Rose Bengal derivatives as singlet oxygen sensitizers, Tetrahedron, 41(11): 2183-2190(1985).
27. DeRosa, M.C. and Crutchley, R.J., Photosensitized singlet oxygen and its applications, Coordination Chemistry Reviews, 233-234: 351-371(2002).
28. Watkins, A.R., quenching of electronically excited states by the free radical tetramethylpiperidine nitroxide, Chemical Physics Letters, 29(4): 526-528(1974).

29. Kuzmin, V.A. and Tatikolov, A.S., Energy transfer in the course of triplet state quenching of aromatic hydrocarbons by nitroxyl radicals, Chemical Physics Letters, 53(3): 606-610(1978).
30. Drago, R.S. and Corden, B.B., Spin-pairing model of dioxygen binding and its application to various transition-metal systems as well as hemoglobin cooperativity, Accounts of Chemical Research, 13: 353-360(1980).
31. Nishimi, T., Kamachi, T., kato, K., Kato, T. and Yoshizawa, K., Mechanistic study on the production of hydrogen peroxide in the anthraquinone process, European Journal of Organic Chemistry, (22): 4113-4120(2011).
32. Tasman, J.E. and Berzins, V., The permanganate consumption of pulp materials, TAPPI J., 40(9): 695-699(1957).
33. Lapierre, C., Determining lignin structure by chemical degradation, Chapter 2 in Lignin and Lignans, C. Heitner, D.R. Dimmel and J.A. Schmidt editors, CRC Press, Boca Raton, 2010, pp: 11-48.
34. Chang, H.M., and Allan, G.G., Oxidation, Chapter 11 in Lignins: Occurrence, Formation, Structure, and Reactions, Sarkanen, K.V., and Ludwig, C.H. (eds). New York: Wiley Interscience, pp. 433-485 (1971).
35. Garves, K., Degradation and oxidation of cellulose in acidic potassium permanganate solutions, Holzforschung, 51: 526-237(1997).
36. Rapson, W.H., The role of pH in bleaching pulp, TAPPI 39(5): 284-295(1956).
37. Pearl, I.A. and Beyer, D.L., Studies on lignin related products, the oxidation of fermented sulfite spent liquor with cupric oxide under pressure, TAPPI J., 33(11):544-548(1950).
38. Pearl, I.A., Beyer, D.L. and Whitney, D., Studies on the chemistry of aspenwood XV Further studies on the oxidation of lignosulfonates with alkaline cupric and silver oxides, Tappi J., 44(7): 479-484(1961).
39. Abrahamsson, K. and Samuelson, O., Oxygen alkali cooking of wood meal, Part 111. Influence of oxygen pressure, carbon dioxide and metal compounds, Svensk Papperstidning, 13: 480-485(1973).
40. Abrahamsson, K. and Samuelson, O., Oxygen alkali cooking of wood meal, Part V. Influence of metal compounds and soaking in acid, Svensk Papperstidning, (4): 135-140(1975.
41. Perng, Y.S., Oloman, C.W., Watson, P.A. and James, B.R., Catalytic oxygen bleaching of wood pulp with metal porphyrin and phthalocyanine complexes, Tappi J., 77(11): 119-125(1994).
42. Haikarainen, A., Metal-salen catalysts in the oxidation of lignin model compounds, Academic Dissertation, Department of Chemistry, University of Helsinki, 2005.
43. Kervinen, K., Studies on veratryl alcohol oxidation catalyzed by Co(salen) type complxes and molecular oxygen in aqueous solution, Department of Chemistry, University of Helsinki, 2005.
44. Korpi, H., Copper di-imine complexes: Structures and catalytic activity in the oxidation of alcohols by dioxygen, Thesis, Department of Chemistry, University of Helsinki, 2005.
45. Hanson, S.K., Baker, R.T., Gordon, J.C., Scott, B.L. and Thorn, D.L., Aerobic oxidation of lignin models using a base metal vanadium catalyst, Inorganic Chemistry, 49: 5611-5618(2010).

46. Hanson, S.K., Baker, R.T., Gordon, J.C., Scott, B.L., Silks, L.A. and Thorn, D.L., Mechanism of alcohol oxidation by dipicolinate vanadium (V): Unexpected role of pyridine, J. American Chemical Society, 132: 17804-17816(2010).
47. Lahtinen, P., Korpi, H., Haavisto, E., Leskelä, M., and Repo, T., Parallel screening of homogenious copper catalysts for the oxidation of benzylic alcohols with molecular oxygen in aqueous solutions, J. Combinatorial Chemistry, 6: 967-973(2004).
48. Lahtinen, P., Lankinen, E., Leskelä, M., and Repo, T., Insight into copper oxidation catalysts: Kinetics, catalytic active species and their deactivation, Applied Catalysis A, 295: 177-184(2005).
49. Korpi, H., Sippola, V., Filpponen, I., Sipilä, J., Krause, O., Leskelä, M., and Repo, T., Copper-2,2'-bipyridines: Catalytic performance and structures in aqueous solutions, Applied Catalysis A, 302: 250-256(2006).
50. Korpi, H., Lahtinen, P., Sippola, V., Krause, O., Leskelä, M. and Repo, T., An efficient method to investigate metal-ligand combinations for oxygen bleaching, Applied Catalysis A, 268: 199-206(2004).
51. Calvin, M., Bailes, R.H. and Wilmarth, W.K., The oxygen carrying synthetic chelate compounds, J. American Chemical Society, 68: 2254-2256(1946).
52. Crumbliss, A.L. and Basolo, F., Monomeric oxygen adducts of N,N'-ethylene-bis(acety1acetoniminato)ligand cobalt(II). Preparation and Properties, J. American Chemical Society, 92(1): 55-60(1970).
53. Brown, l.D. and Raymond, K.N., A σ-bonded dioxygen adduct of the pentacyanocobalt(II) anion. Crystal structure of [N(C2H5)4]3[Co(CN)5(O2)]·5H2O, Inorganic Chemistry, 14(11): 2595–2601(1975).
54. Henrici-Olive, G. and Olive, S., Activation of molecular oxygen, Angewante Chemi International Edition, 13: 29-38(1974)
55. Dedieu, A., Rohmer, M.M. and Veillard, A., Binding of dioxygen to metal complexes. The oxygen adduct of Co(acacen), J. American Chemical Society, 98(19): 5789-5800(1976).
56. Zombeck, A., Drago, R.S., Corden, B.B. and Gauly, J.H., Activation of molecular oxygen. Mechanistic studies of the oxidation of hindered phenols with cobalt-dioxygen complexes, J. American Chemical Society, 103(25): 7580-7585(1981).
57. Kervinen, K., Lahtinen, P., Repo, T., Svahn, M. and Leskelä, M., The effect of reaction conditions on the oxidation of veratryl alcohol catalyzed by cobalt salen-complexes, Catalysis Today, 75: 183-188(2002).
58. Kervinen, K., Korpi, H., Mesu, J.G., Soulimani, F., Repo, T., Rieger, B., Leskelä, M. and Weckhuysen, B.M., Mechanistic insights into the oxidation of veratryl alcohol with Co(salen) and oxygen in aqueous media: an in situ spectroscopic study, European J. Inorganic Chemistry, (2005): 2591-2599(2005).
59. Bozell, J.J., Hames, B.R. and Dimmel, D.R., Cobalt-Shiff base complex catalyzed oxidation of para-substituted phenolics. Preparation of benzoquinones, J Organic Chemistry, 60(8): 2398-2404(1995)
60. Kubes, G.J., Fleming, B.I., MacLeod, J.M. and Bolker, H.I., Sulfur-free delignification, Redox potentials and pulping rates of soda amine liquors, Tappi, 61 (8): 46-50(1978).
61. Fullerton, T.J. and Wilkins, A.L., The mechanism of cleavage of -ether bonds in lignin model compounds by reducing sugars, J.Wood Chemistry and Technology, 5(2): 189-201(1985).

62. Sobolev, I. and Schuerch, C., Alkaline hydrogenation pulping, TAPPI 41(10): 545-551(1958).
63. Snajberk, K. and Zavarin, E., Hydrogenolysis of white fir lignin using metallic nickel catalysts generated in situ, Tappi, 53(8): 1507-1509(1970).
64. Pepper, J.M. and Rahman, M.D., Lignin and related compounds. XI Selective degradation of aspen poplar lignin by catalytic hydrogenolysis, Cellulose Chemistry and Technology, 21: 233-239(1987).
65. Bolker, H. I. and C. M. Li (1973), Delignification of wood by hydrogenolysis with a soluble catalyst, Canadian Wood Chemistry Symposium (Chem. Inst. Can./CPPA, Chateau Frontenac), Extended Abstrs. Vol. 4, pp. 39-41.
66. Schultz, T.P. The attempted depolymerization of HCl lignin by catalytic hydrogenolysis, J Wood Chemistry and Technology, 2(1): 33-46(1982).
67. Hu, T.Q. James, B.R. and Lee, C.-L. Towards inhibition of yellowing of mechanical pulp. Part I: Catalytic hydrogenation of lignin model compounds under mild conditions, J. Pulp and Paper Science, 23(4): J153-J156(1997). Ibid., Part II, 23(5): J200-J205(1997).
68. Hu, T.Q., James, B.R., and Wang, Y., Towards inhibition of yellowing of mechanical pulp. Part 111: Hydrogenation of milled wood lignin, J. Pulp and Paper Science, 25(9): 312-317(1998).
69. Smith, D.A. and Dimmel, D.R., Electron transfer reactions in pulping systems (IX): reactions of syringyl alcohol with pulping reagents, J wood Chemistry and Technology, 14(2):297-313(1994).
70. Cotton, F.A., and Wilkinson, G., Advanced Inorganic Chemistry, 3rd ed. John Wiley and Sons, New York, 1972, Chapter 24: Organometallic compounds in homogeneous catalytic reactions, pp: 770-800.
71. Weinstock, I.A., Atalla, R.H., Reiner, R.S., Moen, M.A., Hammel, K.E., Houtman, C.J., Hill, C.L. and Harrup, M.K., A new environmentally benign technology for transforming wood pulp into paper, engineering polyoxometalates as catalysts for multiple processes, J. Molecular Catalysis, 116: 59-84(1997).
72. Landucci, L.L., Electrochemical behavior of catalysts for phenoxy radical generation, TAPPI 62(4): 71-74(1979).

CATALYSIS
A POTENTIAL ALTERNATIVE TO KRAFT PULPING

Alan Rudie

Peter Hart

A review of the literature relevant to catalyzed pulping conducted for the Advanced Pulping committee of Agenda 2020 Technology Alliance.

1978

- When I started with International Paper Company in 1978, kraft was king.
  - You could smell a kraft mill before you could see it.
  - A new mill cost half a billion or more in new capital.
  - They had just completed countercurrent washing schemes to reduce effluent and were in the process of corroding away their bleach plants.
  - They were evaluating alternative pulping methods including solvents and oxygen pulping.

2014

Nothing has changed.

Ok – the corrosion thing is a bit better under control.

2050

- If we do not want to be able to reuse these slides in 2050, we had better look at:
  - What has gone wrong (if this is not a failure in R&D what is?)
  - How can we fix it
  - How best to focus scarce R&D resources to improve the odds of having a new commercial system in place by 2050

WHAT DID WE DO?

- Solvents:
  - MSAQ, ASAM, Methanol (Ethanol)-SO_2,
  - Organosolve, AICell, AEM
- Ionic Solvents
  - If inexpensive solvents fail, maybe expensive solvents will succeed?
- BioPulping
  - Fungi do a pretty crude job of degrading lignin
- Holopulping: chlorine, chlorine dioxide (acid chlorite), peracetic acid

WHY THEY FAIL

- The fundamental problem with solvent methods is that lignin is a cross linked polymer.
  - Additive chemicals (AQ, HSO_3^-) do break lignin bonds but adds the expense of the chemicals to the cost of solvent recovery.
- The fundamental problem with stoichiometric reactive chemicals is that sodium hydroxide and sodium sulfide are inexpensive and recoverable.

HOW IS WHAT WE DID WRONG

- It was not wrong, but in hind sight, it was not right.
- What do we really want:
  - Low operating cost
  - High strength
  - High yield
  - Agnostic towards species and harvest condition.

SOME OTHER THINGS WE SHOULD WANT

- Lower capital costs
- Less need for bleaching
- Capability of pulping softwoods and hardwoods together
- Ability to size the pulp mill to the paper mill and reduce wood transportation distances
- Reduced water needs

DECISION PROCESS: COSTS

- Can stoichiometric chemicals be low enough costs?
  - Not as low as NaOH and NaHS
  - For example, using peroxide as oxidant requires three peroxides to cleave the Ca-CP bond and oxidize each fragment to a carboxylic acid. About 13% hydrogen peroxide on wood.
- Can solvent methods be low cost?
  - Capital and operating costs to recover chemicals is expensive.
  - In kraft, the active chemicals are 20% of the mass of the wood, in solvents, the wood is 20% of the mass of the solvent. If kraft recovery is expensive, the recovery problem is 25 times bigger.
- Can biopulping work?
  - Not with existing organisms/enzymes.

THE GOAL: HOW DO WE

Achieve the selectivity of holopulping with the operating cost structure of kraft.

- Use inexpensive stoichiometric chemicals but achieve selective lignin reactions.
- Operate in water.
  - Lowest cost solvent
  - Do not need explosion proof equipment

CATALYSTS

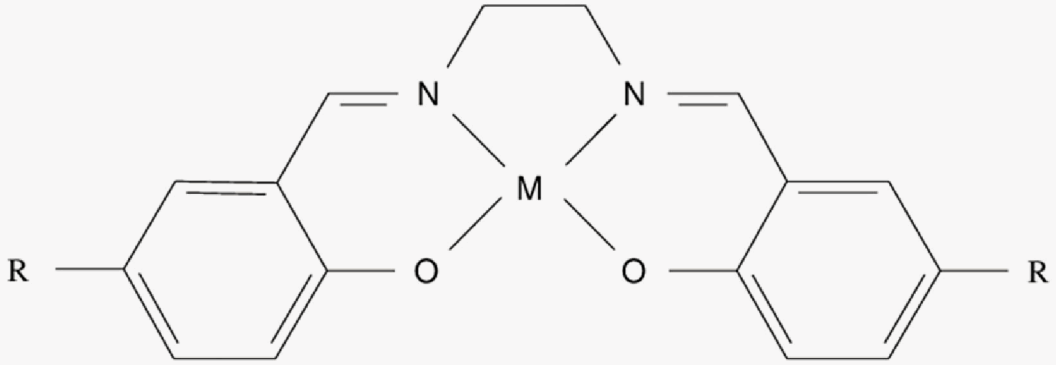
- Catalysts are processes that:
  - Use a stoichiometric chemical more selectively than it can be used in bulk reactions.
  - Work by lowering the activation energy for desirable reactions.
  - Are not consumed in the reaction

PULPING CATALYSTS?
YES, WE ALREADY HAVE SOME

- Anthraquinone
- Acid (in sulfite pulping)
- Caustic (in kraft and soda pulping)

- To function on an insoluble substrate, the catalyst must be soluble (homogeneous).

SOME KNOWN CATALYSTS: COBALT SALCOMINE



R = NMe_2, OMe, Me, H, Br, SO_3, NO_2

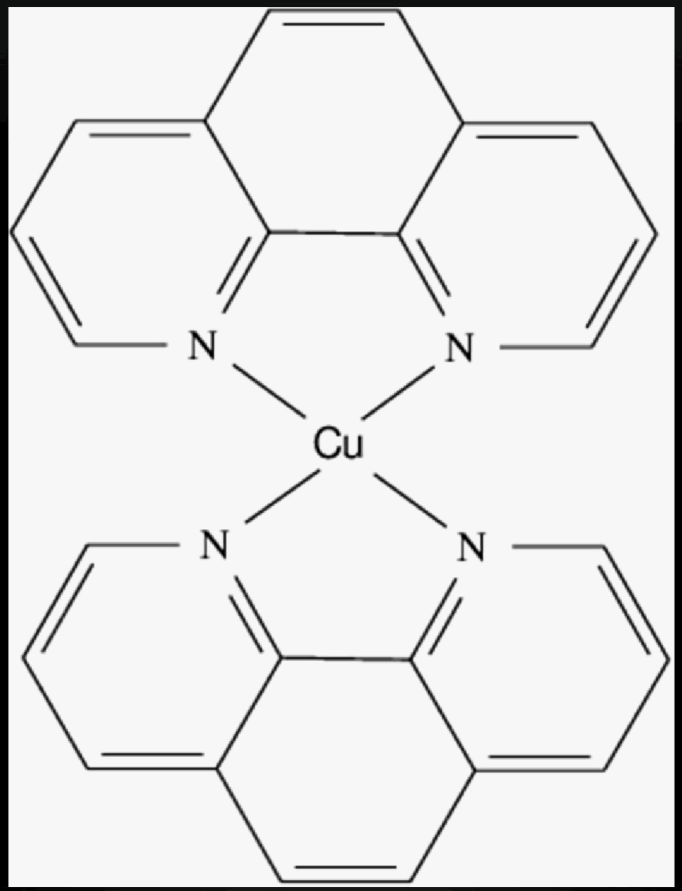
M = Mn, Co

Initially, Fullerton and Ahern, TAPPI J., 61(12): 37-39(1978).

COBALT SALCOMINE

- Activates oxygen
  - Reversible reaction,
- Some model compound reactions require the alcoholic oxygen on C-a to bond to the Cobalt.
- Reactivity is not high and turnovers are low
- Decomposition is reversal of formation – loss of metal to hydrolysis and low solubility, followed by reversal of the hydrazone

COPPER AMINES



Germer, 10th ISWPC, pp428-431(1999).

COPPER AMINES

- Activate oxygen
- Does not seem to require bond to form to lignin
- Selectivity is not great (about the same as un-catalyzed)
- Turnovers are better than Cobalt, but still not high
- Decomposition appears to be reversal of the complex formation and precipitation of copper at the high pH.

METALS USED IN LIGNIN ANALYSIS

- Cupric oxide
  Cobalt oxide
  Silver Oxide
  Mercuric oxide
  Permanganate
  Vanadium oxide
  Dichromate
  Nickel

  All oxidize lignin breaking the bond between C-a and C-ß to produce a benzoic acid or aldehyde.

  These metal oxides do not activate oxygen

THE METAL OXIDES

- Selectivity of permanganate is similar to chlorine and hypochlorite.
- Since most of these metals do not react rapidly with oxygen, they need another oxidant as the primary oxidant – possibly peroxide, possibly Co-salcomine or Copper amines.
- Reactions need to be acidic or neutral pH to keep the metals in solution.

OXYGEN ALKALI COOKING

Abrahamsson and Samuelson looked at the impact of trace metals on oxygen-bicarbonate cooking of wood meal.

- Mn, Zn and Lanthanum improved reaction rate and selectivity under some conditions

  Time to a target kappa was reduced about 40%
- Fe, Co, Cu, reduced selectivity
- Selectivity differences suggest the reaction is not just outer sphere electron transfer producing a phenoxy radical.

OTHER METALS

- Vanadium complexes and methyltrioxylrhenium have also been used to oxidize lignin-like molecules
  - Both operate in solvents – not water
  - $Re(CH_3)O_3$ uses peroxide as primary oxidant.
  - Vanadium is primarily being considered for biorefiney pretreatment.

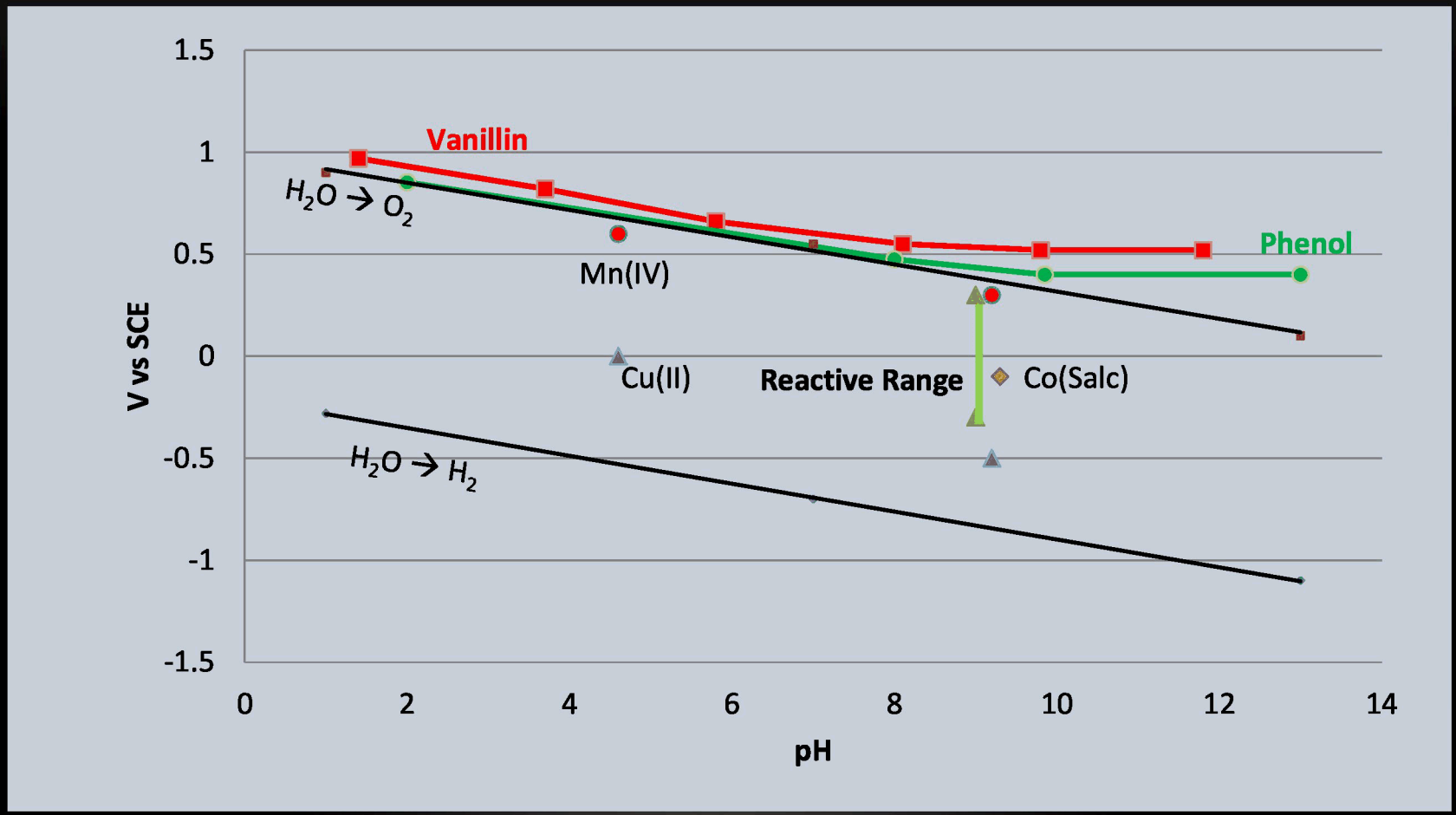
THINGS TO THINK ABOUT

- Nearly all transition metals are insoluble under alkaline conditions.
  - This means simple metal salts will be minimally functional (reaction of two insoluble substances) and if in a complex, it will decompose to insoluble metal oxide.

  None of the known catalysts appear to be a functional lead.
- The process requires two distinct steps
  - Activation of oxygen
  - Oxidation of a lignin phenol

  It may require different metal complexes

ELECTROCHEMISTRY OF LIGNIN MODELS



CONCLUSION

- The reason for doing this is not that any of the existing work has shown promising results

  If the companies have anything better – something they have not already tried – go for it.

  Continuing to operate as we have has not been productive. If a better pulping process is really something we want, we have to change how we approach the research.

  Metal catalysts could also turn out to just be a dream. But cost wise – it can work. Cost wise – most of the alternatives cannot.