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SUPERCRITICAL CO₂ OXIDATION OF LIGNIN

Production of High Valued Added Products

In this work the use of supercrititical oxidation technologies are explored for fragmenting and converting lignins into high value low molecular weight chemicals and polycarboxylates that could be used as precursors to adhesives, plastics, detergents, metal chelants, polyurethane, antioxidant and other chemical industrial products.

Carbohydrates and lignin are amongst the most abundant organic compounds of the planet, representing a vast amount of biomass (in the range of hundreds of billions of tons). It is interesting to note that only 3% of this large resource is actually used by human beens. Despite the fact that a significant amount of recent research has been carried out aimed at augmenting the industrial use of readily available carbohydrates as organic raw materials [1-6], the systematic exploitation of this vast resource is still in its infancy. Our chemical industry needs to redevelop in a major way if it is interested in using biomass as its feedstock. Since environmental pressures are mounting and our dependence on fossil fuel becomes increasingly more questionable, the prevailing economic advantages for a petro-

chemically based economy will fade away within the next fifty years. This emphasizes the need for developing novel, environmentally benign processes aimed at converting our vast carbohydrate and lignin resources into useful products i.e, bulk and fine chemicals, monomers, polymers, solvents, packaging materials, pharmaceuticals etc.

Since lignin is a material that actually has a very little commercial utility, other than supplying the major source of energy in pulp mills, a number of significant opportunities exist at the light of the previous discussion. This article aims to present one environmentally friendly way that, when materialized, could create the foundations for a variety of new and useful chemicals and products from lignin streams that emerge from modern biomass/bio-energy saccharifi-

cation treatments. Such streams could be developed to indispensable commodities if novel ways of using lignin are developed. Lignin is structurally a highly intricate aromatic polymer composed of partly oxygenated phenylpropane units. Several interunit carbon-carbon and carbon-oxygen bonds are present in its structure and the relative abundance of these interunit linkages vary for different types of wood. To date many studies have been focused on the oxidative degradation of lignin aimed at producing useful low molecular weight aromatic compounds. These processes may be carried out by oxidation with nitroaromatics [7], using air in alkaline media [8], using ozone [9], electrochemical means [10], enzymes [11] or peroxide mediated by various metal ions [12]. Additional promising biomimetic degradation systems use dioxygen as the oxidant and various metal complexes as catalysts, with cobalt being one good example.

Drago *et al.* [13] have shown that dioxygen was able to oxidize isoeugenol to vanillin in good yields, using [bis(salicylidene-γ-imino-propyl)methylamine]cobalt(II), [Co(SMDPT)], as catalyst [13]; Bozell *et al.* has reported the oxidation of para-substituted phenolic compounds to benzoquinones using [N,N'-bis (salicylidene)ethane-1,2-diaminato]cobalt(II), [Co(salen)], as the catalyst [14, 15] while Haikarainen *et al.* has reported the aqueous oxidation of lignin model compounds using a similar water soluble cobalt compound as a catalyst to obtain vanillin and other biphenolic products [16].

Supercritical Fluids as Solvents for Chemical Reactions

When a gas such a carbon dioxide is subjected to high pressure and heated it changes its physical properties, becoming a supercritical fluid. In this state, it has the solvating power of a liquid and the diffusivity of a gas. In other words, it has properties of both a gas and a liquid. For $scCO_2$ the supercritical conditions are 31°C and 1,070 psi [18]. This means that supercritical fluids work extremely well as processing media for a wide variety of chemical, biological, and polymer extraction procedures. Another powerful aspect of supercritical fluids is their ability to precisely control which component(s) of a complex matrix are extracted and which ones remain behind [17]. This is accomplished via the precise control of several key parameters such as temperature, pressure, flow rates and processing time [19]. Because of higher diffusivity (faster mass transfer) of a supercritical fluid, compared to a liquid, extraction rates are generally much higher than the corresponding solid/liquid extraction systems [21]. Therefore, there are several advantages to using a supercritical fluid as a

solvent, including ease of solvent recovery, lower pressure drops, and lower mass-transfer resistance than liquids. Furthermore, and from a chemical perspective, there are additional advantages associated with the use of supercritical carbon dioxide ($scCO_2$). Supercritical fluids are of unique physical properties of can be exploited to control chemical reactivity. This is not possible with conventional solvents. $scCO_2$ has demonstrated reactivity modulations that arise from the effect of pressure and temperature. These reactivity modulations, which are actually governed by transition state theory, offer excellent opportunities for tuning and promoting reaction pathways occurring within complex substrates such as lignin.

Over and above these unique properties, $scCO_2$ can also claim tunable solvating power. The high compressibility of the supercritical state gives substantial changes in density with small changes in pressure and temperature so that the solvating power of the fluid can be "tuned" [20]. More specifically, important solvent parameters of a supercritical fluid such as its viscosity, solubility parameter and dielectric constant can vary substantially with temperature and pressure. Such variations can provide unique opportunities for control of the kinetics of a chemical reaction. The enumerated properties of $scCO_2$ and of the critical state in general, impart supercritical fluids with the capacity to replace hazardous organic solvents while providing an ideal environment for the production of new materials. Additionally, carbon dioxide has the advantage of being nearly fully oxidized, nonflammable material, which facilitates the design of oxidation processes that are inherently safe to potential explosion hazards.

Previous efforts have focused at supercritical fluids as media for the liquefaction of wood [22] (using supercritical alcohol) and transformation of wood to liquid fuels [23] (using supercritical acetone and methanol). Other applications of $scCO_2$ include its use toward the determination of extractives in wood, pulp, paper, and pitch samples [23-27] as well as extraction of chlorinated phenols [25] and resins and fatty acids [26] from sediments collected downstream from a chlorine-bleaching pulp mill. Theoretical efforts to correlate and predict the solvating ability of $scCO_2$ have been proposed by York *et al.* [28]. In this effort the solubilities of nicotinic acid (NA) and *p*-acetoxyacetanilide were measured in $scCO_2$ at temperatures ranging from 35 to 75 °C and pressures varying from 100-200 bars. Using these data an attempt was made to create equations that could model the solubilities of these compounds at a variety of pressures and temperatures demonstrating the power of this approach [29].

Oxidation Chemistry in Supercritical and Expanded CO_2

In the area of oxidation chemistry, a novel work reported by Subramanian's group has shown that various phenols can be oxidized with dioxygen when catalyzed by the cobalt Schiff base, Co(salen) [30]. Cyclohexene was also shown to be oxidized under similar conditions when catalyzed by tetraphenylporphyrinato iron(III) chloride, in CO_2-expanded CH_3CN. These reactions were shown to proceed with impressive catalytic turnover frequencies, conversions, and selectivities. Subramanian's group has demonstrated that there are several advantages of conducting oxidations in homogeneous CO_2-expanded reaction mixtures including higher oxygen miscibility, compared to neat organic solvents. In addition CO_2-expanded reaction mixtures allow for transition metal catalysts to be solubilized without modification (i.e., fluorination) increasing catalyst solubility by about one to two orders of magnitude. In general, it has been shown that by conducting an organic chemical reaction in $scCO_2$, as opposed to an organic solvent, a number of processes has demonstrated significant changes in the chemo, regio-, or stereo-selectivity of the reaction [26] with major environmental sustainability advantages [31]. Reactions as diverse as ring-opening metathesis polymerization and ring-closing olefin metatheses using well-defined metal catalysts have been carried out in $scCO_2$ [32]. Supercritical carbon dioxide was shown to be a versatile reaction medium for use with molybdenum alkylidene complexes, ruthenium carbenes and N-heterocyclic carbene ligands exhibiting similar catalytic efficiencies to chlorinated organic solvents [32]. This effort aims at coupling recent advances in supercritical and catalytic science with a systematic exploration of simple and selective reaction pathways on lignin toward products which have broad industrial application profiles with our biomass resources as the feedstock.
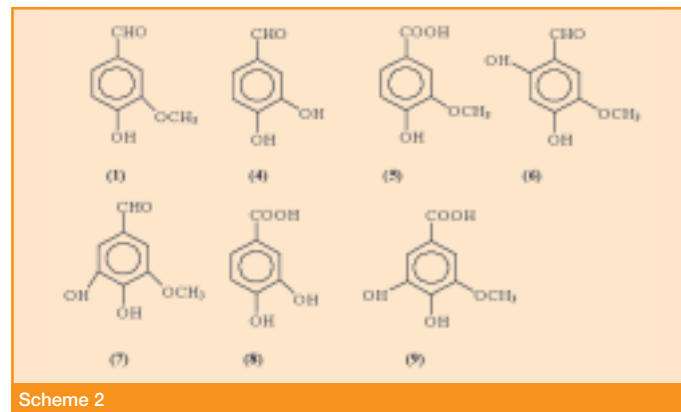
Results and Discussion
Oxidation of Model Compounds

In our initial efforts to ensure three model compounds, namely (Scheme 1): vanillin, 3,4-dimethoxybenzylalcohol and 3,3'-
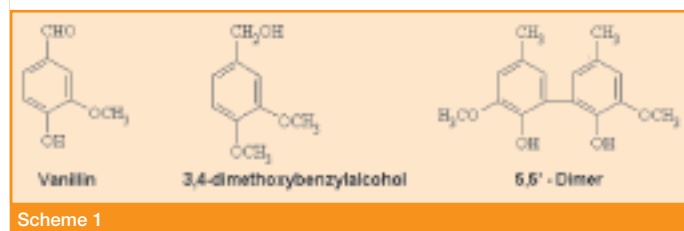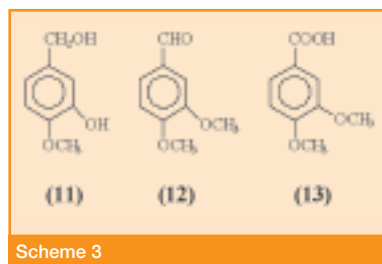
Scheme 1

dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (5-5' dimer) were subjected to oxidation in $scCO_2$, using 30% aqueous hydrogen peroxide as the oxidant in total absence of alkali. The molar ratio of model compounds (and latter lignin) to peroxide was 1/1. At 80 °C and under the $scCO_2$ peroxide oxidation conditions, vanillin (1) yielded six different products which are indicative (not surprisingly) of aldehydic oxidation products (5), (8), (9), hydroxylation insertion chemistry on the aromatic ring (6), (7) and demethylation reactions (4), (8) (Scheme 2).

However by lowering the temperature to 31 °C only products (5), (6) and (7) were detected, pointing to the facility of the hydroxylation and aldehydic oxidation reactions as opposed to the demethylation reactions.

Our efforts to further understand this novel solvent system toward aromatic oxidations prompted an examination of the same chemistry under totally aqueous conditions. Vanillin was found to be significantly less reactive under totally aqueous conditions at 80 °C (1 hour) since only traces of products (5), (6), (7), and (9) were detected. Interestingly, the $scCO_2$ peroxide oxidation of 3,4-dimethoxybenzyl alcohol at 80 °C yielded the demethylation product (11), and the two simple oxidation products of the alcohol i.e. aldehyde (12) and acid (13) (Scheme 3). Reactions with the same etherified model, under totally aqueous conditions, yielded only traces of products (11) to (13) in a manner similar to the chemistry observed for vanillin. However, the most significant aspect of our findings relies on the fact that peroxide induced oxidations in $scCO_2$ did not require the creation of the precursor phenoxy anion since no alkali was used during our experiments. In addition, no radical coupling products were detected, signifying a novel, relatively clean and predictable product distribution in $scCO_2$.

Recent work in our laboratory has addressed the issue of abundance and reactivity of dibenzodioxocins in softwood lignins [36].

Scheme 2

Scheme 3

Scheme 4 - Products obtained from the peroxide promoted oxidation of 3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (5-5' dimer) in scCO$_2$, at 80 °C, 1,070 psi, for one hour. The total amount of starting material remaining was found to be about 50%

Since these structures are present in softwoods in significant amounts (about 4-5 per 100 C9 units) [36], they release stoichiometric amounts of 5,5'-biphenolic moieties once the wood is pulped with alkali or hydrosulfide anions or even acids [36]. Other aspects of our work has shown that such 5,5'-biphenolic moieties are rather resistant to oxidation [39-41].

Consequently, it was thought pertinent to examine the reactivity of such a model compound, i.e. 3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (5-5' dimer) toward peroxide oxidation in scCO$_2$ in total absence of alkali. To our surprise the oxidation reaction in scCO$_2$ carried out at 80 °C and at 1,070 psi, yielded the array of products depicted in Scheme 1 with about 50% of the stating material being eliminated. The obtained product distribution is indicative of C-C fragmentation processes occurring along the 5-5' bond (products 15, 16), demethylation reactions (17), ring opening reactions (18), hydroxylation reactions (19) and side chain oxidation reactions (20), (21) (Scheme 4).

In an effort to further validate the significance of these findings we carried similar oxidation experiments in purified (metal free) water in a glass reactor for the same time and temperature (1 hour at 80 °C at atmospheric pressure), always in total absence of alkali. Our analyses showed unaltered starting material to be present in the reaction mixture with undetectable amounts of any of the products found when the reaction was conducted under the scCO$_2$ conditions enumerated above.

It is also of extreme significance to note that when the same compound was oxidized with peroxide under aqueous conditions in the presence of alkali, the following products were detected and quantified [42].

The product distribution of Scheme 5 is indicative of a more elaborate set of oxidations reactions. Under aqueous alkali peroxide conditions, phenolate
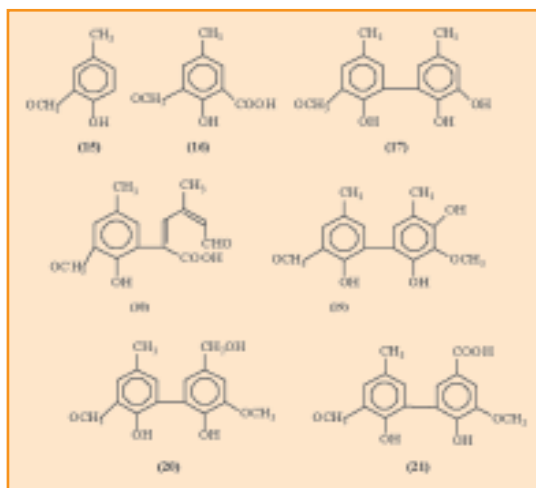
anions are transformed into phenoxyl radicals followed by hydroxyl and superoxide radical attack on the aromatic ring eventually creating dioxetane intermediates that lead to further fragmentation and ring opening reactions [43-44].

Therefore, based on our model compound studies it may be concluded that in phenolic model structures, when subjected to aqueous alkaline peroxide oxidative degradation, a complex product distribution and an extensive breakdown of the aromatic character occur. This is not the case, however, when these molecules are subjected to peroxide induced oxidations in scCO$_2$ in the absence of alkali.

In an effort to further probe the characteristics of unmodified and uncatalyzed oxidations in scCO$_2$, we carried out quantitative yield measurements with the 5-5' biphenolic compound (3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol). After oxidation for one hour under scCO$_2$ conditions (in total absence of alkali) we determined the amount of starting material as a function of temperature and CO$_2$ pressure.

The data of Figure 1 demonstrates that temperature and pressure play a very important role in defining the oxidative degradation of 3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol. Up to a temperature of 80 °C the amount of starting material is reduced almost monotonically at the three pressures examined. Beyond this temperature, however, a significant increase in the rate of its elimination is observed causing its near quantitative oxidation at temperatures above 150 °C and elevated pressures.

Oxidation of Residual Kraft Lignin

In our efforts to further understand the potential of peroxide induced oxidation chemistry in scCO$_2$ we isolated Residual Kraft Lignin (RKL) from softwood using a high yield procedure recently developed at our laboratory [45, 46]. The RKL lignin was then oxidized in accordance with the experimental protocol previous-
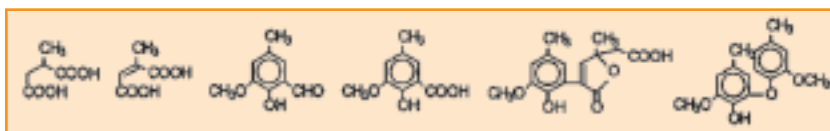
Scheme 5 - Products obtained from the aqueous alkaline peroxide oxidation of 3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol (5-5' dimer) at 80 °C under atmospheric pressure for one hour. Total amount of starting material remaining was found to be 56% [42]
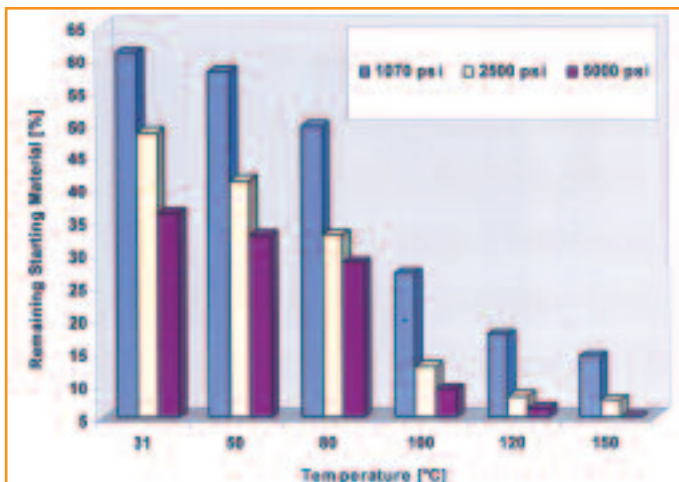
Fig. 1 - A plot of the amount of starting material (3,3'-dimethoxy-5,5'-dimethyl-[1,1'-biphenyl]-2,2'-diol) as a function of temperature and pressure for peroxide induced oxidation under scCO$_2$ conditions at 80 °C and at 1,070 psi, for one hour

ly described. Two series of oxidations were carried out. Namely: an oxidation using one mole of peroxide per mole of lignin C9 unit in purified (metal free) water under reflux at 80 °C and atmospheric pressure (denoted as RKL in H$_2$O$_2$ in Figure 2). In addition, an identical oxidation was carried out under scCO$_2$ conditions (denoted in Figure 2 as RKL in H$_2$O$_2$/scCO$_2$). After the reactions, the RKL lignin was freeze dried and then subjected to phosphitylation followed by quantitative ^{31}P functional group analyses [47-49].

Since no alkali was used in any of these experiments the RKL was not soluble in the aqueous medium and a limited amount of oxidation occurred. This is evidenced by the minor increase in the -COOH and the simultaneous minor decrease of the condensed and total phenolic OH contents (see RKL in H$_2$O$_2$ bars in Figure 2). By simply changing the reaction medium from water to CO$_2$ at its critical point a very significant degree of oxidation was obtained. The amount of -COOH groups are seen to at least double with the concomitant decrease of the condensed and phenolic -OH groups (see RKL in H$_2$O$_2$/scCO$_2$ bars in Figure 2).

Despite that fact that the examined scCO$_2$ peroxide promoted reaction conditions have not been optimized, no co-solvents have been used and the reactions have not been catalyzed in any way, some very significant changes in the structure of RKL lignin have occurred that require immediate attention in order to be fully explored.

Conclusions

Overall the data of our study demonstrates that a very significant scientific and technological potential exists in further understanding and exploring a variety of salient features of this chemistry. Our study has demonstrated that:
- scCO$_2$ oxidation conditions proceed in a way that is rather different to their aqueous counterparts;
- aromatic compounds, such as 5-5' biphenols, which are relatively stable under aqueous oxidative conditions, can be readily oxidized under scCO$_2$ peroxide promoted oxidation conditions in total absence of alkali;
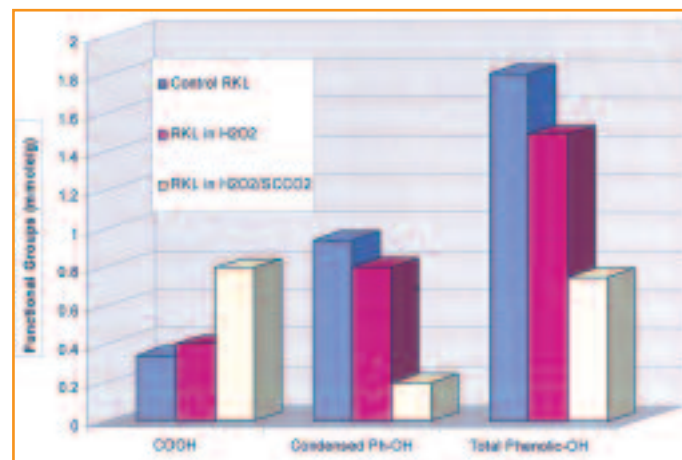- the product distributions under scCO$_2$ oxidation conditions seem

Fig. 2 - Functional group development in softwood Residual Kraft Lignin (RKL) for oxidations carried under aqueous peroxide (RKL in H$_2$O$_2$) and scCO$_2$ peroxide promoted reaction conditions at 80 °C and at 1,070 psi, for one hour. One mole of H$_2$O$_2$ was used per mole of lignin (assuming mol. Wt. of repeat unit for lignin 186 g/mol)

Ossidazione supercritica di lignina per la produzione di materiali ad alto valore aggiunto

ABSTRACT

In questo lavoro si esplora l'uso delle tecnologie di ossidazione supercritica nella frammentazione e conversione di lignine in materiali a basso peso molecolare e policarbossilati utilizzabili come precursori per la produzione di adesivi, materiali plastici, detergenti, chelanti, antiossidanti ed altri. Il lavoro ha dimostrato che è possibile ossidare lignina residua kraft in CO$_2$ supercritica in totale assenza di alcali. Ciò offre interessanti prospettive in particolare per lo sviluppo di nuove tecnologie di frammentazione ambientalmente sostenibili.
Ciò aggiunge un valore ai flussi industriali di lignina che sono correntemente sottoutilizzati e necessitano di nuovi mercati.

to be simpler than those that are formed under aqueous conditions in the presence of alkali;

- otherwise difficult to oxidize, residual kraft lignin is seen to be readily oxidized with peroxide in $scCO_2$, selectively inducing the formation of large amounts of carboxylic acids on its surface via the elimination of phenolic moieties;

- it is very likely that $scCO_2$ could readily offer a novel, environmentally benign technology platform that may allow the efficient production of highly functional molecules and polycarboxylates from lignin, useful to a variety of industries.

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