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## COMBINING LACCASE WITH CU(SALEN) CATALYSTS FOR OXIDATION OF KRAFT LIGNIN

*The transformation of kraft lignin using laccase with Cu(salen) catalysts was studied. The effect of the laccase/MCM – to – laccase/MCM + Cu(salen)/NaY ratio on the yields of monomeric aromatic chemicals (MACs) and the molecular weight (Mw) of kraft lignin was studied. The MACs yield decreased as the ratio increased, and the vanillin yield reached its highest value when the ratio of laccase was 50 wt % at a reaction temperature of 80 °C. The formation of MACs was enhanced by using a combination of laccase with Cu(salen) catalysts, while the formation of vanillin was dominant in the process. The formation of 4-hydroxy-3,5-dimethoxy benzaldehyde, 2-methoxy phenol, 4-hydroxy-3,5-dimethoxyphenyl ethanone, 4-hydroxy-3-methoxyphenyl ethanone, 4-hydroxy-3,5-dimethoxy benzoic acid, 4-hydroxy benzaldehyde, and 2-methoxy-4-vinylphenol was also found in this work. The effect of the reaction parameters on the MACs yield and the Mw of the kraft lignin was described, and the main reactions occurring in the kraft lignin were discussed.*

**Keywords:** kraft lignin, catalysis, combined catalysis, monomeric aromatic chemicals

### Introduction

Lignin is an aromatic polymer, which is synthesized during the secondary metabolism of plants, and after cellulose is the most abundant compound in nature. There are three phenylpropanoids depending on the degree of methoxylation: guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) respectively [Lu and Ralph 1997; Lupoi et al. 2015].

In order to develop useful applications such as the production of phenolic chemicals from lignin, various strategies have been employed for the depolymerisation and functionalisation of lignin [Mafakheri et al. 2014]. In

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recent years, some significant achievements, focusing on biomimetic catalysts (salen complexes) and enzymatic catalysts (laccase) have attracted considerable interest in the field of lignin oxidation as a consequence of the increasing desire for green and sustainable chemistry. Furthermore, a new approach to chemistry calls for innovative catalytic systems in the conversion of lignin into chemicals, such as the combination of biocatalysts as well as inorganic catalysts. However, the use of a combination especially of enzymatic- and inorganic catalysts can be complicated by the fact that they have different optimal conditions [Vennestrøm et al. 2010, Jindal and Sunoj 2014].

Inorganic catalysts have been extensively employed under harsh reaction conditions in chemical reactions. Chemical lignin transformation using inorganic catalysts, including catalytic reduction and catalytic oxidation, are extensively reported. The catalytic hydroconversion of a wheat straw soda lignin under  $H_2$  pressure over a supported NiMo sulfide catalyst, performed at  $350^\circ C$ , not only cleaved interlinkages but also functional groups (hydroxyl, carboxyl, methoxyl), thereby producing a mixture of phenols, aromatics, naphthenes and alkanes [Joffres et al. 2014]. A hydrosilane catalyst was employed for the reductive degradation of several lignin model compounds and lignins. Many of the functional groups, including alcohols, phenols, and  $\beta$ -O-4 and  $\alpha$ -O-4 ethers, were selectively cleaved by hydrosilanes [Zhang et al. 2014]. In contrast, many studies have used catalysts to oxidize lignin model compounds and lignin [Ma et al. 2015].  $LaFe_xMn_{1-x}O_3$  and  $La_{0.9}Sr_{0.1}MnO_3$  hollow nanospheres, used as catalysts in the presence of air at  $120^\circ C$  for the oxidation of lignin to produce vanillin, syringaldehyde, and p-hydroxybenzaldehyde, showed much better catalytic performance than traditional perovskite [Gao et al. 2013]. Vanadium catalysts were used to cleave the  $\beta$ -O-4 bond of dimeric lignin models, and as a result they were also effective in depolymerizing actual lignin-forming monophenolic chemicals [Chan et al. 2013]. There have been improvements in the oxidative depolymerization of lignin for heterogeneous catalysts as compared to homogeneous catalysts. The immobilization and hydrogenation of Cu(salen) complex could improve the transformation of kraft lignin to value-added monomers through catalysis [Zhou 2015]. In a recent study, a catalyst paper, Co(salen) paper, was used as a heterogeneous catalyst in the oxidation of kraft lignin using  $H_2O_2$  as an oxidant [Gao et al. 2015]. The process yielded 2.32 mg 2,6-dimethoxyphenol/kg, 3.80 mg vanillin/kg, and 2.63 mg syringaldehyde/kg, which were formed through oxidation, together with cleavage of the  $\beta$ -O-4 linkage.

Enzymatic catalysis has always attracted great attention due to its high catalytic ability and selectivity, but generally it is performed under mild reaction conditions as the enzyme easily deactivates in harsh reaction conditions [Dashtban et al. 2010]. However, in principle enzymatic properties might be improved by protein engineering, resulting in an increase in the possible combinations with chemical catalysts. Moreover, enzyme stability, and under

various conditions sometimes even enzyme activity, might also be improved via immobilization strategies [Garcia-Galan et al. 2012]. For instance, laccase immobilized on the magnetic silica nanoparticles exhibited a higher thermal stability, storage stability and operational stability than free laccase in catalyzing guaiacol as a phenolic lignin model compound [Hu et al. 2015].

While combining enzymatic with chemical catalysis seems to be required in order to deal with the efficient conversion of kraft lignin to fine chemicals due to the complex mechanism of lignin degradation and the limited effects with single catalysts, the use of chemoenzymatic catalysis in one reactor would provide several advantages over conventional processes, such as process intensification, shorter reaction time, higher product yield, less material consumption and the isolation of the reaction products. There is an increasing overlap between the operating conditions of enzymes and chemical catalysts as enzymatic thermostability is now increasing and new chemical catalyst design is moving towards operating under milder conditions [Lee et al. 2014]. Cañas and Camarero [2010] indicated that vanillin or aceto vanillone formed in the chemical oxidation of lignin may act as laccase mediators. Therefore, it is possible to use laccase in combination with chemical catalysts in the transformation of kraft lignin.

This study was hence mainly concerned with the oxidation of kraft lignin using laccase with Cu(salen) catalysis. Spectroscopic methods were used to describe the structural information from the spectra and to provide an insight into reaction interpretation. This may represent a new approach in the field of lignin conversion.

## Experimental methods

### Chemicals

Benzene, ethanol, sodium hydroxide, 1,4-dioxane, chloroform, pyridine, acetic acid, sulfuric acid, tetrahydrofuran, acetic anhydride, acetone, ethyl acetate, n-hexane, anhydrous sodium sulfate, a NaY molecular sieve (surface area, 584 m<sup>2</sup>/g; pore size 2.2 nm), and a MCM-41 molecular sieve (surface area, 1052 m<sup>2</sup>/g; pore size 4.8 nm) were purchased from Sinopharm Chemical Reagent Co. Ltd. (China). The following reagents were obtained from Sigma-Aldrich: guaiacol (99.0%), cyclohexanol (99.0%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (95%), CDCl<sub>3</sub> (99.8% atom D), and DMSO-d<sub>6</sub> (99.9% atom D). Laccase was supplied by Novozymes (recombinant laccase from *Bacillus pumilus*, 22.3 U/mg). All the chemicals were analytical grade and were used as received unless stated otherwise. The deionized water produced was used throughout the whole procedure.

## Kraft lignin

The kraft lignin was obtained from a pulp mill (China), which cooked eucalyptus (*E. urophylla* × *E. grandis*) with a high pulp yield (~60%) using a modified kraft method with NaOH and Na<sub>2</sub>S. The crude kraft lignin was purified by refluxing in 80% dioxane containing 0.05 M HCl in a nitrogen atmosphere. The kraft lignin contained 90.70% Klason lignin, 7.30% acid soluble lignin, 0.81% carbohydrate as determined by Klason hydrolysis, and 0.84% ash as determined by burning in a muffle at 575°C. The weight-average molecular weight (Mw) was 3021 as determined by Waters 2695 GPC gel permeation chromatography.

## Catalyst

Cu(salen) was synthesized and immobilized onto NaY via the impregnation method (Cu(salen)/NaY) [Zhang and Zhou 2012].

Laccase was immobilized into MCM-41 using a typical procedure. 0.1 g MCM-41 was suspended in 5 ml phosphate buffer (0.1 M) containing 6.0 mg laccase, followed by vibration in an orbital shaker for 12 h. The solid was separated using centrifugation, washed with a buffer solution, and vacuum-dried at a low temperature (Laccase/MCM).

## Catalytic experiments

The kraft lignin oxidation using laccase with Cu(salen) catalysis was carried out in a sealed vial and air was used as an oxidant. A typical trial was performed on the kraft lignin (100 mg) using laccase/MCM with Cu(salen)/NaY. Laccase/MCM and Cu(salen)/NaY were also tested for comparison. The amount of catalyst used amounted to 10 wt% to the dry weight of kraft lignin and an acetonitrile/THF mixture (100 ml, 10:1) was employed to dissolve the kraft lignin in the typical trial. The mixture was left to stand for 24 h. The catalyst was then separated, washed and finally dried for reuse in a vacuum oven at 40°C. The Partial liquid phase was vacuum-dried for FTIR and THz analysis. The content of the monomeric aromatic compounds (MACs) from the kraft lignin in the liquid phase was quantitatively determined using GC and GC-MS. Each compound was identified using a GC-MS database and by comparing them to the authentic chemicals.

In addition, control trials, in which the catalysts were absent, were performed under identical conditions for examining catalysts

$$\text{Yield of MACs (\%)} = \frac{\text{Total weight of various MAC}}{\text{Weight of kraft lignin}} \times 100$$

### Characterization of kraft lignin

For the THz analysis, a standard THz time-domain transmission spectrometer was used (fig. 1). The experimental equipment consisted of two pieces. A Tai Mai femtosecond laser as a pump and light source was purchased from Spectra-Physics Ltd. (United States). The central wavelength of the laser was 800 nm, the pulse width amounted to 90 fs and the repetition rate was 80 MHz. The second important piece of equipment was the Z-2 THz time-domain spectroscopic analysis system, provided by Zomega Ltd. (United States). The system consisted of a Z-2 THz time-domain spectrometer, a lock-in amplifier and a data acquisition system. In this study, pellets made from the kraft lignin measuring 0.8 mm thick  $\times$  12 mm in diameter were used for the THz measurements. A THz spectrum of the sample was obtained at a frequency range of 0.2~1.5 THz by comparing the frequency content of the transmitted THz pulse with a reference spectrum.

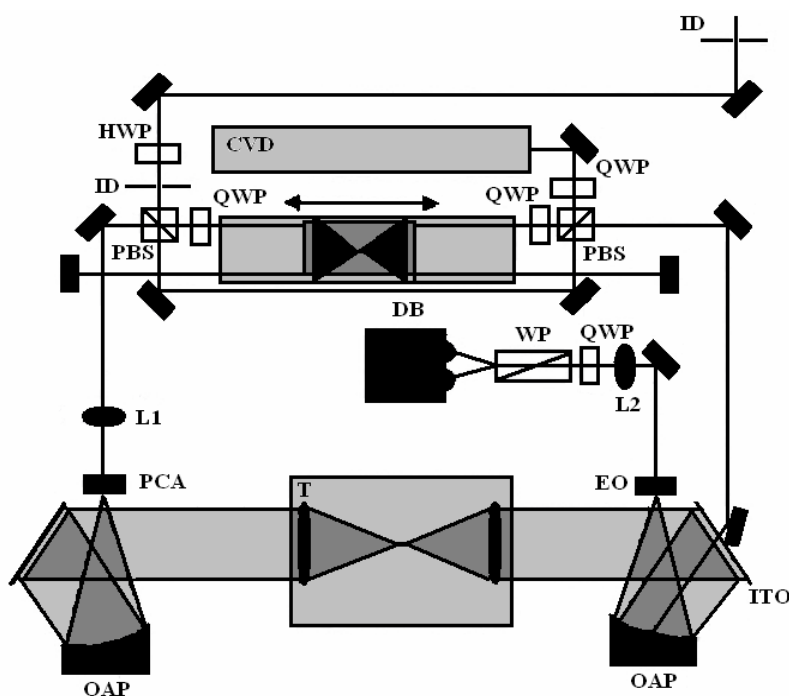


Fig. 1. Schematic setup for THz time-domain spectroscopy: HWP – half wave plate, PBS – polarization beam splitter, PCA – photoconductive antenna, QWP – quarter wave plate, OAP – off-axis parabolic mirror, WP – wollaston prism, DB – balance detector, EO – electro-optic crystal

FTIR analyses were carried out on KBr pellets using a 800 Nicolet FTIR spectrometer. The spectra were obtained within a spectral range of 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

The molecular weight of the kraft lignin was determined using Waters 2695 GPC gel permeation chromatography with a differential refractive index detector using tetrahydrofuran (THF) as the eluent (1.00 mL/min).

## Results and discussion

### Comparison between the effect of combined and single catalysts of laccase/MCM, Cu(salen)/NaY on the degradation of kraft lignin

Chemoenzymatic catalysis using laccase/MCM + Cu(salen)/NaY was comparatively investigated in terms of the yield of MACs and the  $M_w$  of the kraft lignin. As shown in figure 2a, in the chemoenzymatic catalysis using laccase/MCM + Cu(salen)/NaY, the MACs yield increased from 0.28% to 3.63% as the reaction worked from 2 h to 18 h, increasing to 3.81% at the reaction time of 24 h. In contrast, the  $M_w$  of the kraft lignin decreased as the MACs yield increased as the reaction proceeded. Unlike catalytic experiments, a slight decrease in molecular weight was observed in the control experiments, where the degradation products were not observed by GC-MS. It was desirable that the degradation of the kraft lignin using laccase with Cu(salen) catalysis led smoothly to the production of MACs in comparison, as shown by the relation between the MACs yield and the molecular weight of the kraft lignin (fig. 2b).

Overall, the optimal degradation of kraft lignin could be achieved when the reaction was performed at 80°C for 18 h, where the MACs yields obtained in the catalysis using laccase/MCM + Cu(salen)/NaY, Cu(salen)/NaY, and laccase/MCM were 3.63%, 2.15%, and 1.06%, respectively. The higher yield of MACs and lower  $M_w$  of the kraft lignin obtained in the chemoenzymatic catalysis than in the single catalysis indicated that the degradation of the kraft lignin was favoured in chemoenzymatic catalysis, possibly due to the synergistic effect of the unique properties of the enzyme as well as biomimetic catalyst [Gregor et al. 2012], which implied that more ether linkages in the kraft lignin were broken via chemoenzymatic catalysis. This was observed in the terahertz spectra (fig. 3) in which the 49.8  $\text{cm}^{-1}$  and 57.6  $\text{cm}^{-1}$  vibrations were the characteristic absorption peaks of the  $\beta$ -O-4 linkage [Su et al. 2015]. The kraft lignin sample employed in this paper was prepared by cooking under mild conditions and should have still contained a fair number of  $\beta$ -O-4 bonds. The intensity of  $\beta$ -O-4 linkage in the kraft lignin in the terahertz spectra decreased from the laccase/MCM treatment to the Cu(salen)/NaY treatment and to the laccase/MCM + Cu(salen)/NaY treatment. On the other hand, the FTIR analysis confirmed that the intensity of the carbonyl group in the kraft lignin in the FTIR spectra was enhanced with the laccase/MCM + Cu(salen)/NaY catalysis, as shown in figure 3.

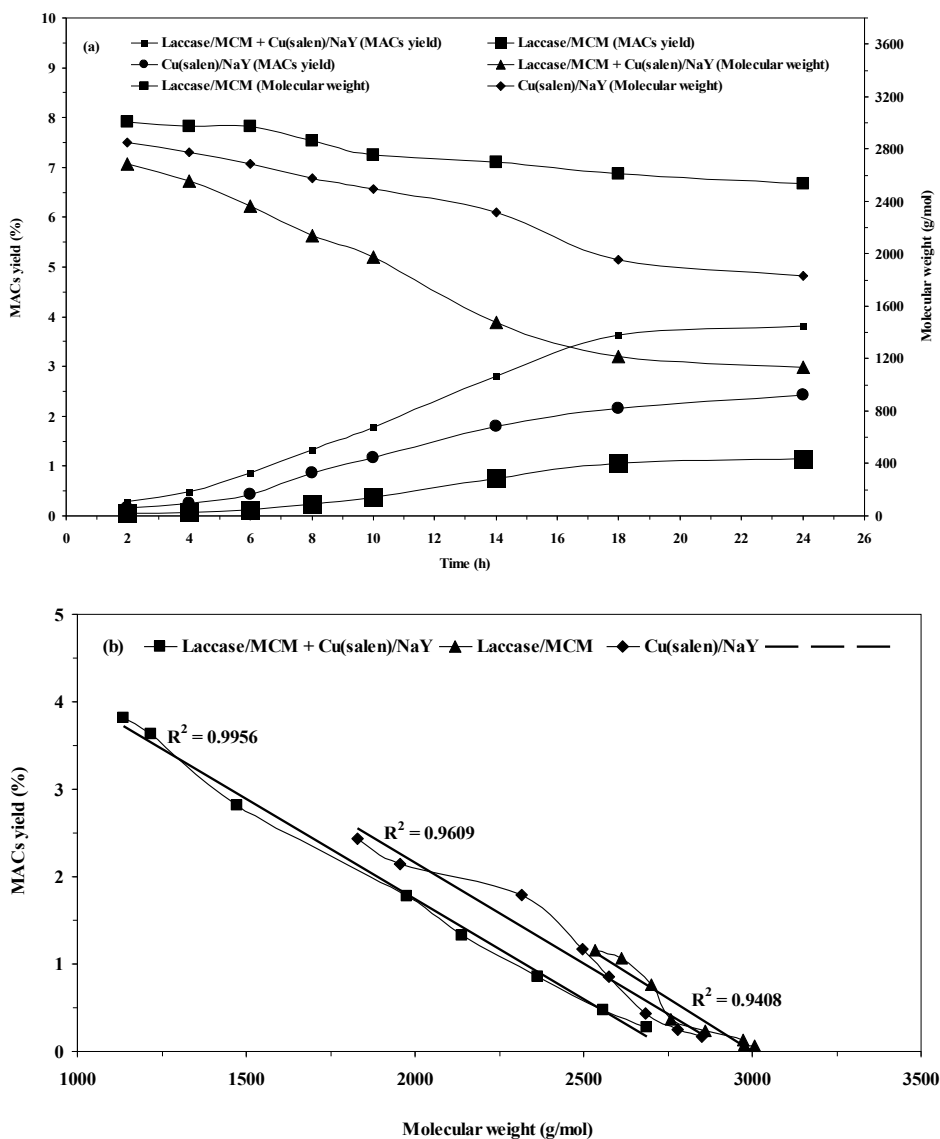
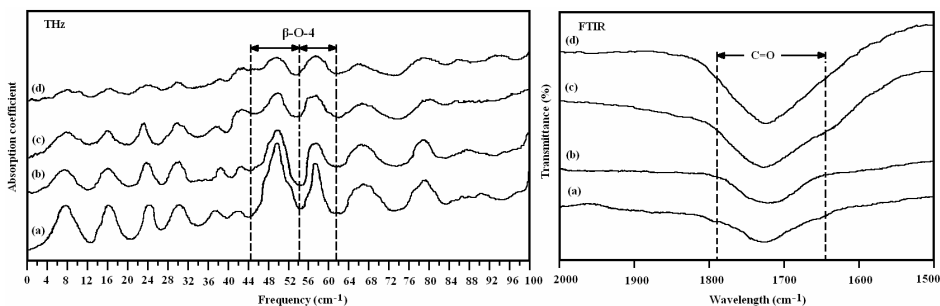
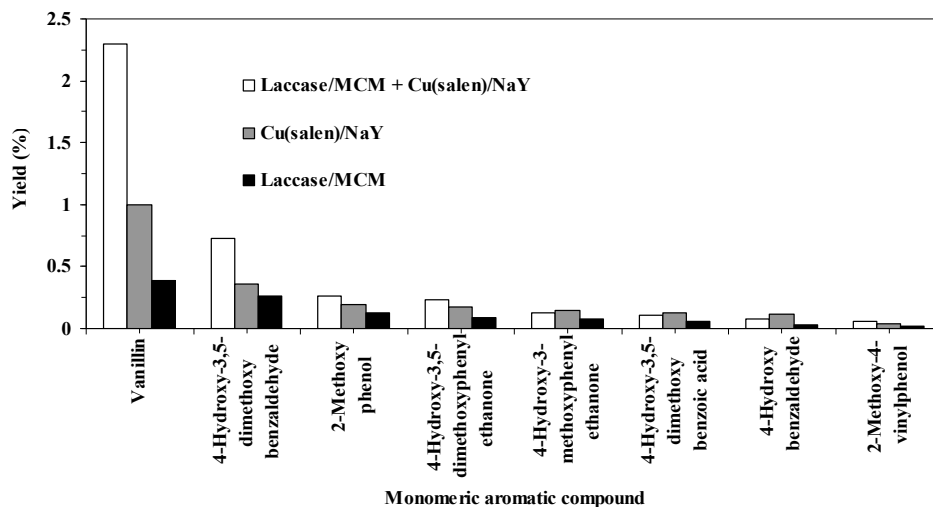


Fig. 2. MACs yield and Mw of kraft lignin: a – effect of reaction time, b – relation between MACs yield and molecular weight of kraft lignin. Reaction temperature: 80°C; laccase/MCM-to-Cu(salen)/NaY ratio 1:1 (wt %)

The yield of various monomeric aromatic compounds obtained under various catalyses at 80°C for 18 h was quantitatively determined and is shown in figure 4. In all the cases, vanillin was the most abundant compound among the analysed MACs, and its yield, based on the dry weight of the kraft lignin, ranged



**Fig. 3. β-O-4 linkage (THz spectra) and carbonyl group (FTIR) in kraft lignin: a – kraft lignin, b – kraft lignin after treatment with laccase/MCM, c – kraft lignin after treatment with Cu(salen)/NaY, d – kraft lignin after treatment with laccase/MCM + Cu(salen)/NaY. Reaction temperature: 80°C; reaction time: 18 h; laccase/MCM-to-Cu(salen)/NaY ratio 1:1 (wt %)**



**Fig. 4. Effect of different catalysts on yield of monomeric aromatic compounds**

from 0.39% to 2.30%. The yield of vanillin was clearly higher (2.30%) in the catalytic oxidation by laccase/MCM + Cu(salen)/NaY than the yield in several other oxidation processes of kraft lignin under similar reaction conditions. Chan et al. [2013] obtained a yield of 0.78% for vanillin, which was released by the vanadium-catalyzed degradation of dioxasolv-lignin at 80°C for 24 h. 4-Hydroxy-3,5-dimethoxy benzaldehyde was also abundant in the MACs, while 2-methoxy phenol, 4-hydroxy-3,5-dimethoxyphenyl ethanone, 4-hydroxy-3-methoxyphenyl ethanone, 4-hydroxy-3,5-dimethoxy benzoic acid, 4-hydroxy benzaldehyde, and 2-methoxy-4-vinylphenol were relatively abundant. The yield of various monomeric aromatic compounds increased as the catalytic power increased from laccase/MCM to Cu(salen)/NaY and to laccase/MCM + Cu(salen)/NaY.



### Effect of reaction temperature on MACs and Mw of kraft lignin

The reaction temperature allows for a change in the catalytic reaction, especially the enzymatic reaction [Mohammadalia et al. 2012; Decaneto et al. 2015]. To determine the optimal reaction temperature of the catalytic degradation of kraft lignin, the effect of the reaction temperature on the MACs yield and the Mw of the kraft lignin was therefore investigated. Figure 5 shows changes in the MACs yield and the Mw of the kraft lignin at all the reaction temperatures. The MACs yield increased as the reaction temperature increased from 20°C to 80°C but decreased with a further increase in the temperature, suggesting that the temperature of 80°C was suitable not only for the chemical but also for the enzymatic catalysis in the chemoenzymatic oxidation of the kraft lignin. In addition, the Mw of the kraft lignin generally showed the opposite trend to the MACs yield, and the slow trend of the Mw of the kraft lignin at higher reaction temperatures indicated that the repolymerization may have occurred to the kraft lignin. Other studies have shown similar results in the further reaction of lignin [Li et al. 2007; Toledano et al. 2014].

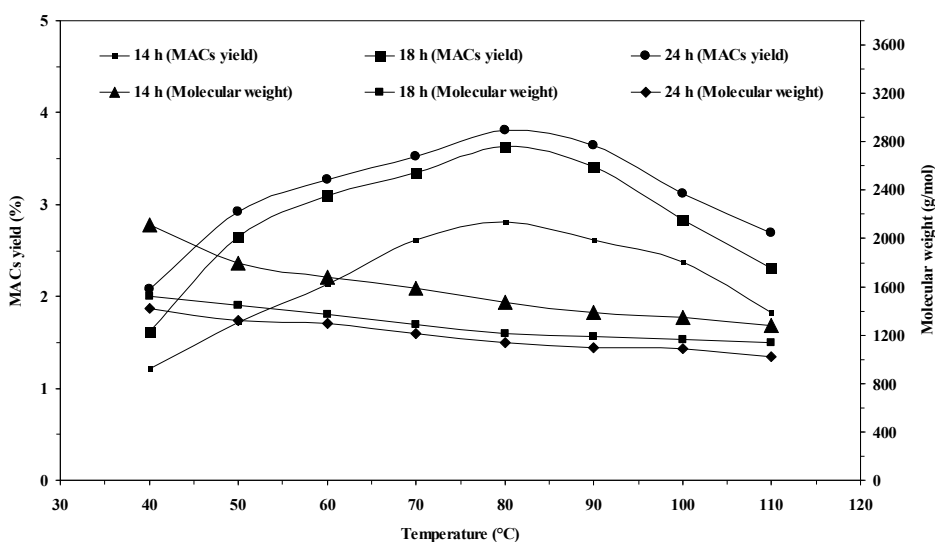


Fig. 5. Effect of reaction temperature on MACs yield and Mw of kraft lignin. Laccase/MCM-to-Cu(salen)/NaY ratio, 1:1 (wt %)

### Effect of laccase/MCM – to – laccase/MCM + Cu(salen)/NaY ratio on MACs and Mw of kraft lignin

The ratio between the two catalysts used in the catalytic reaction had an important effect on the reaction rate [Liu et al. 2010]. The effect of the laccase ratio from 0% to 100% on the yield of MACs produced at 14 h, 18 h and 24 h is shown fig. 6. At all times, the MACs yield decreased slowly as the laccase ratio

increased from 0% to 50%, and it decreased drastically with a further increase in the laccase ratio. In contrast, the Mw of the kraft lignin increased as the laccase ratio increased from 0% to 100%, which was due to weak enzymatic catalysis as compared to chemical catalysis [Sabuzi et al. 2015]. Although the decrease in the MACs yield was generally not desirable because it caused a decrease in the efficiency of MACs production, the combination of laccase and Cu(salen) may be the best option due to the specificity of the laccase in terms of the vanillin yield [Moilanen et al. 2011], which was found to be the highest at a laccase ratio of 50 wt %, as shown in figure 6.

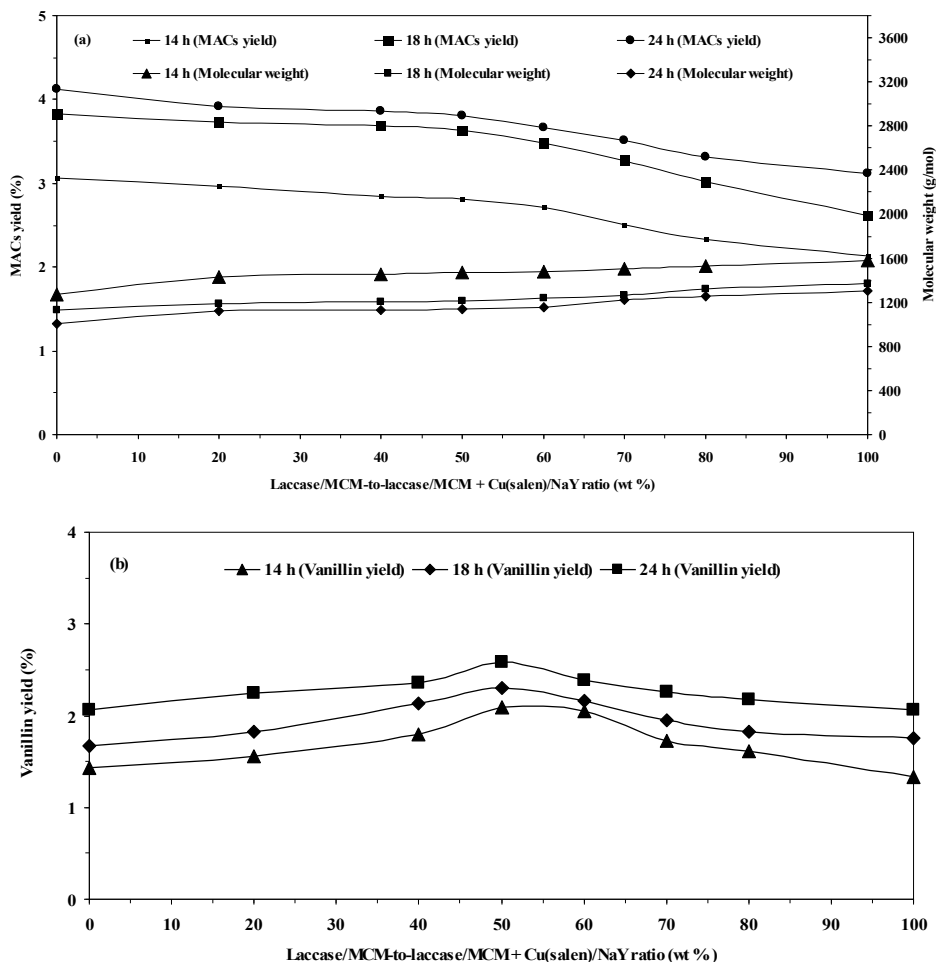


Fig. 6. Effect of laccase/MCM-to-laccase/MCM + Cu(salen)/NaY ratio (wt %) on MACs yield and Mw of kraft lignin. Reaction temperature, 80 °C

## Conclusions

The kraft lignin was successfully transformed to MACs using laccase with Cu(salen) catalysis in one-pot. The MACs yield was dependent on the laccase ratio and reaction parameters. The vanillin yield was the highest when the laccase ratio was 50 wt % at a reaction temperature of 80°C. The spectra obtained by THz and FTIR confirmed that the combination of laccase with Cu(salen) enhanced the cleavage of the  $\beta$ -O-4 linkage and the oxidation of side-chains in the kraft lignin.

There remain, however, some factors which cannot be fully explained, therefore prompting the need for further research in the future. The increase in the MACs yield and decrease in the molecular weight of the kraft lignin observed in the reaction with laccase/MCM and Cu(salen)/NaY does not necessarily mean that the degradation of the kraft lignin was favoured. For instance, in the reaction with laccase/MCM only or Cu(salen)/NaY only a specific portion of the kraft lignin sample may be selectively degraded to reaction products other than the MACs detected in this paper.

## References

- Cañas A.I., Camarero S.** [2010]: Laccases and their natural mediators: biotechnological tools for sustainable eco-friendly processes. *Biotechnology Advances* 28: 694-705
- Chan J.M.W., Bauer S., Sorek H., Sreekumar S., Wang K., Toste F.D.** [2013]: Studies on the Vanadium-catalyzed nonoxidative depolymerization of *Miscanthus giganteus*-derived lignin. *ACS Catalysis* 3: 1369-1377
- Dashtban M., Schraft H., Syed T.A., Qin W.** [2010]: Fungal biodegradation and enzymatic modification of lignin. *Journal of Biochemistry and Molecular Biology* 1: 36-50
- Decaneto E., Suladze S., Rosin C., Havenith M., Lubitz W., Winter R.** [2015]: Pressure and temperature effects on the activity and structure of the catalytic domain of human MT1-MMP. *Biophysical Journal* 109: 2371-2381
- Gao P., Li C., Wang H., Wang X., Wang A.** [2013]: Perovskite hollow nanospheres for the catalytic wet air oxidation of lignin. *Chinese Journal of Catalysis* 34: 1811-1815
- Gao T.-T., Zhou X.-F., Zhu Z.-L.** [2015]: Catalytic conversion of kraft lignin using paper-like Co(salen) as an effective catalyst. *Drewno* 58: 79-91
- Garcia-Galan C., Berenguer-Murcia A., Fernandez-Lafuente R., Rodrigues R.C.** [2012]: Potential of different enzyme immobilization strategies to improve enzyme performance. *Advanced Synthesis and Catalysis* 43: 2885-2904
- Gregor C.A., Hommes G., Schäffer A., Corvini P.F.-X.** [2012]: Multi-catalysis reactions: new prospects and challenges of biotechnology to valorize lignin. *Applied Microbiology and Biotechnology* 95: 1115-1134
- Hu J., Yuan B., Zhang Y., Guo M.** [2015]: Immobilization of laccase on magnetic silica nanoparticles and its application in the oxidation of guaiacol, a phenolic lignin model compound. *RSC Advances* 5: 99439-99447
- Jindal G., Sunoj R.B.** [2014]. Mechanistic insights on cooperative asymmetric multicatalysis using chiral counterions. *Journal of Organic Chemistry* 79: 7600-7606
- Joffres B., Lorentz C., Vidalie M., Laurenti D., Quoineaud A.-A., Charon N., Daudin A., Quignard A., Geantet C.** [2014]. Catalytic hydroconversion of a wheat straw soda

- lignin: Characterization of the products and the lignin residue. *Applied Catalysis B-Environmental* 145: 167-176
- Lee C.W., Wang H.J., Hwang J.K., Tseng C.P.** [2014]: Protein thermal stability enhancement by designing salt bridges: A combined computational and experimental study. *PLOS ONE* 9, e112751
- Li J., Henriksson G., Gellerstedt G.** [2007]. Lignin depolymerization/repolymerization and its critical role for delignification of aspen wood by steam explosion. *Bioresource Technology* 98: 3061-3068
- Liu J., Xu J., Zhao Z., Duan A., Jiang G., Jing Y.** [2010]: A novel four-way combining catalysts for simultaneous removal of exhaust pollutants from diesel engine. *Journal of Environmental Sciences* 22: 1104-1109
- Lu F., Ralph J.** [1997]: Derivatization followed by reductive cleavage (DFRC method), a new method for lignin analysis: protocol for analysis of DFRC monomers. *Journal of Agricultural and Food Chemistry* 45: 2590-2592
- Lupoi J.S., Singh S., Parthasarathi R., Simmons B.A., Henry R.J.** [2015]: Recent innovations in analytical methods for the qualitative and quantitative assessment of lignin. *Renewable and Sustainable Energy Reviews* 49: 871-906
- Mafakheri F., Nasiri F.** [2014]: Modeling of biomass-to-energy supply chain operations: Applications, challenges and research directions. *Energy Policy* 67: 116-126
- Ma R., Xu Y., Zhang X.** [2015]: Catalytic oxidation of biorefinery lignin to value-added chemicals to support sustainable biofuel production. *ChemSusChem* 8: 24-51
- Mohammadalia E.-N., Sheikhdavoodi M.J., Almassi M., Kruse A., Bahrami H.** [2012]: Effect of reaction temperature and type of catalyst on hydrogen production in supercritical water gasification of biomass. *Iranica Journal of Energy and Environment* 3: 202-209
- Moilanen U., Kellock M., Galkin S., Viikari L.** [2011]: The laccase-catalyzed modification of lignin for enzymatic hydrolysis. *Enzyme and Microbial Technology* 49: 492-498
- Sabuzi F., Churakova E., Galloni P., Wever R., Hollmann F., Barbara F., Conte V.** [2015]: Thymol bromination – A comparison between enzymatic and chemical catalysis. *European Journal of Inorganic Chemistry* 2015: 3519-3525
- Su T.-F., Huang R., Su Y.-Q., Zhao G.-Z., Wu D.-Y., Wang J.-A., Gong C.-R., Xu C.-H.** [2015]: Vibrational spectra of guaiacylglycerol- $\beta$ -guaiacyl ether: Experiment and theory. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy* 139: 456-463
- Toledano A., Serrano L., Labidi J.** [2014]: Improving base catalyzed lignin depolymerization by avoiding lignin repolymerization. *Fuel* 116: 617-624
- Vennestrøm P.N.R., Christensen C.H., Pedersen S., Grunwaldt J.-D., Woodley J.M.** [2010]: Next-generation catalysis for renewables: Combining enzymatic with inorganic heterogeneous catalysis for bulk chemical production. *ChemCatChem* 2: 249-258
- Zhang J., Chen Y., Brook M.A.** [2014]: Reductive degradation of lignin and model compounds by hydrosilanes. *Acs Sustainable Chemistry and Engineering* 2: 1983-1991
- Zhang N., Zhou X.-F.** [2012]: Salen copper (II) complex encapsulated in Y zeolite: An effective heterogeneous catalyst for TCF pulp bleaching using peracetic acid. *Journal of Molecular Catalysis A-Chemical* 365: 66-72
- Zhou X.-F.** [2015]: Catalytic oxidation and conversion of kraft lignin into phenolic products using zeolite-encapsulated Cu(II) [H<sub>4</sub>]salen and [H<sub>2</sub>]salen complexes. *Environmental Progress & Sustainable Energy* 34: 1120-1128

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