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ARTICLE

Effect of the *N*-based ligands in copper complexes for depolymerisation of lignin

Jinhuo Dai,[a] Sepa Nanayakkara,[a] Thomas C. Lamb,[b] Andrew J. Clark,[b] Si-Xuan Guo,[a] Jie Zhang,[a] Antonio F. Patti,[a] and Kei Saito[*a]

Several organic soluble *N*-based ligands and their copper complexes were firstly investigated as catalysts to depolymerise organosolv lignin in the organic solvent, dimethylformamide (DMF) and an ionic liquid (1-ethyl-3-methylimidazolium xylenesulfonate, [emim][ABS]). The results of screening depolymerisation reactions in DMF and [emim][ABS] showed that all the copper-amine complexes catalysed lignin depolymerisation more efficiently in ionic liquids than in DMF. Among the seven types of ligands, copper complexes with two types of ligands ((*E*)-*N*-(pyridin-2-ylmethylene)aniline and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline depolymerised the lignin more efficiently than the others. These two copper complexes with *N*-based ligand were further studied to determine the most efficient conditions for the depolymerisation of the lignin. The most effective depolymerisation by conditions involved treatment at 180°C for 12 h in [emim][ABS]. Cyclic voltammetric studies were carried out to investigate the reversible potential associated with the copper centers of their complexes with these *N*-based ligands. The results suggest that two types of ligands have more positive reversible potentials than those of other copper complexes.

Introduction

Lignin, exists in the second cell wall of plants, and is well known as one of the most abundant renewable materials from the paper and pulp industry.[1-3] Lignin is also considered as a material with high commercial potential for producing fine chemicals. This biopolymer contains three types of primary phenylpropane units called monolignols and these creates fundamental units that combine in different ways to give various forms of the complex natural polymer known as lignin.[4-6] During the past few decades, lignin depolymerisation has become a research hotspot with many considerable methods reported, for example, depolymerisation using oxidation, reduction, biological methods and electrochemical methods.[7] The main challenge of the research is to selectively cleave different bonds in lignin in order to depolymerise lignin into fine chemicals with high value.[7]

The depolymerisation of lignin with several metallic catalysts has also been reported. However, there are drawbacks in most existing depolymerisation methods using metallic catalysts such as the need for high pressure and high temperature.[6] Pepper et al. investigated the catalytic ability of a number of catalysts, such as Raney Ni, Pd/C, Rh/C and Ru/C, on the hydrogenation of softwood lignin to produce monomeric products (dihydroconiferyl alcohol), however, this method required a pressure of 3.4 MPa with a temperature of 468K.[8] Koyama reported the hydrocracking of lignin model compounds by using Fe_2O_3-S, Fe_2O_3/Al_2O_2-S, and NiO-MoO_3-Al_2O_3 between 613 and 723 K.[9]

Some metal complexes with *N*-based ligands have been used for lignin oxidation and depolymerisation under a mild condition.[7] Metalloporphyrin complexes, such as trisodium tetra-4-sulfonatophthalocyanine iron(III), have been investigated to oxidize lignin.[10, 11] Zucca et al. also utilized immobilized Fe(III)-5,10,15,20-tetrakis(pentafluorophenyl)prophyrin on a pyridyl-functionalized poly(vinyl alcohol), to oxidize lignin model compounds at room temperature.[12] The drawbacks of these metalloporphyrins are that these catalyst complexes normally have a complicated structure and lack of recyclability and stability.[7] Metallosalen catalyst has also been used as a novel lignin oxidation and depolymerisation catalyst.[13] Drago et al. reported that Co(salen) complexes oxidised lignin model compounds rapidly with the presence of molecular oxygen to produce vanillin.[14]

Copper complexes with *N*-based ligand are well-known oxidation catalysts for 2,6-dimethylphenol(DMP) to form an engineering thermoplastic poly(2,6-dimethyl-1,4-phenylene oxide)(PPO) and also known as catalysts to depolymerise PPO. For example, PPO was first developed by using a copper-pyridine complex and its derivatives by the oxidative polymerisation of DMP.[15, 16] Some enzyme mimic complexes with *N*-based ligand are also applied for PPO polymerisation. Higashimura et al. studied the oxidative polymerisation of DMP catalysed by (1,4,7-triisopropyl-1,4,7-triazacyclononane)copper(II) to produce PPO.[17] We have studied the depolymerisation of PPO involving the redistribution mechanism to produce oligomeric PPO using a copper-pyridine complex.[18] This depolymerisation produced $M_n = 4.9 \times 10^2$ oligomeric PPO from PPO $M_n = 1.0 \times 10^4$.

We also reported the PPO depolymerisation mechanism as follows.[18] Under the oxidative conditions catalysed by copper complexes, two kinds of radicals (monomeric phenoxyl radical and polymeric phenoxyl radical) were generated. The redistribution was induced via a quinone ketal intermediate

[a.] *School of Chemistry, Monash University, Clayton, VIC 3800, Asutralia.*
 E-mail: Kei.Saito@monash.edu; Tel: +61-2-9905-4600;
 Fax: +61-3-9905-8501
[b.] *Department of Chemistry, University of Warwick, Gibbbet Hill, Coventry, CV4 7AL, UK.*

after the phenoxyl radical of PPO is attacked by the monomeric phenoxyl radical. Further study also showed that PPO can be depolymerised by copper-EDTA involving the redistribution mechanism in the ionic liquid ([emim][ABS]).[19]

Our group has applied this depolymerisation and demonstrated that lignin can be successfully depolymerised using copper-EDTA as catalyst in both water and ionic liquids (1-ethyl-3-methylimidazolium xylenesulfonate [emim][ABS] and 1-butyl-3-methylimidazolium methyl-sulfate [bmim][MeSO$_4$]), involving the redistribution mechanism under mild conditions (80°C, atmospheric pressure).[20]

Ionic liquids, because of their non-flammability, recyclability and non-volatility, have been widely used as a solvent for the organic reactions.[21, 22] Binder et al. demonstrated that ionic liquids are excellent solvents for processing woody biomass and lignin.[23] Kerstin et al. presented a method about oxidative depolymerisation of lignin in ionic liquid (1-ethyl-3-methylinidazolium trifluoromethanesulfonate [emim][CF$_3$SO$_3$]) using Mn(NO$_3$)$_2$ as a catalyst.[24] In their study, this catalyst system was shown to be an efficient reaction system as the conversion of lignin reached 66.3% after reacting for 24 h at a temperature of 100°C, however a pressure of 84 × 10^5 Pa air was required. Cox et al. reported using an acidic ionic liquid, 1-hexyl-3-methylimidazolium chloride (HMIMCl), as both solvent and catalyst for lignin depolymerisation.[25] In this method, lignin, extracted from oak wood, was depolymerised in HMIMCl and proceeds by a hydrolysis reaction with alkyl-aryl ether bond cleavage.

In this study, we have investigated several types of copper complexes with an *N*-based ligand for lignin depolymerisation involving the redistribution mechanism in DMF and an ionic liquid ([emim][ABS]). The *N*-based ligands showed below (Scheme 1) have been used to form copper complexes with copper halides and used as catalysts.

Some of these ligands, such as 1,1,4,7,7-pentamethyldiethylenetriamine (**L1**), tris(2-pyridylmethyl)amine (**L2**)[26], and tris(2-Pyridylmethyl)amine (**L3**)
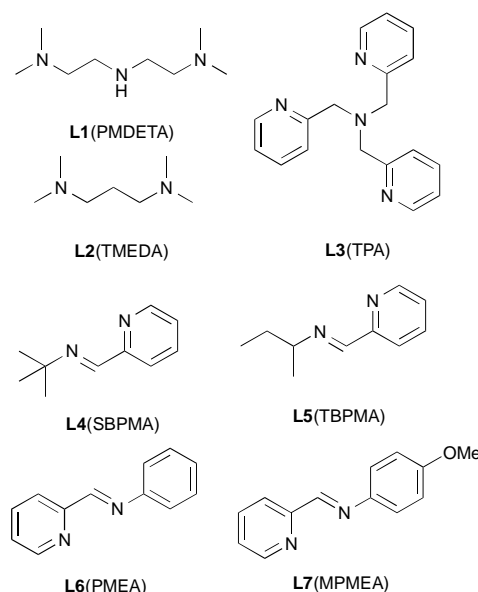
Scheme 1 *N*-based ligands: **L1**: *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA); **L2**: *N,N,N',N'*-Tetramethylenediamine (TMEDA); **L3**: Tris (2-Pyridylmethyl)amine (TPA); **L4**: (*E*)-*N*-sec-butyl-1-(pyridin-2-yl)methanimine (SBPMA); **L5**: (*E*)-*N*-tert-butyl-1-(pyridin-2-yl)methanimine (TBPMA); **L6**: (*E*)-*N*-(pyridin-2-ylmethylene)aniline (PMEA); **L7**: (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline (MPMEA).

are commercially available and others are easy to synthesize and relatively stable.

Initial screening studies with different copper complexes with *N*-based ligand in DMF and IL were carried out to select the most efficient *N*-based ligands for lignin depolymerisation.
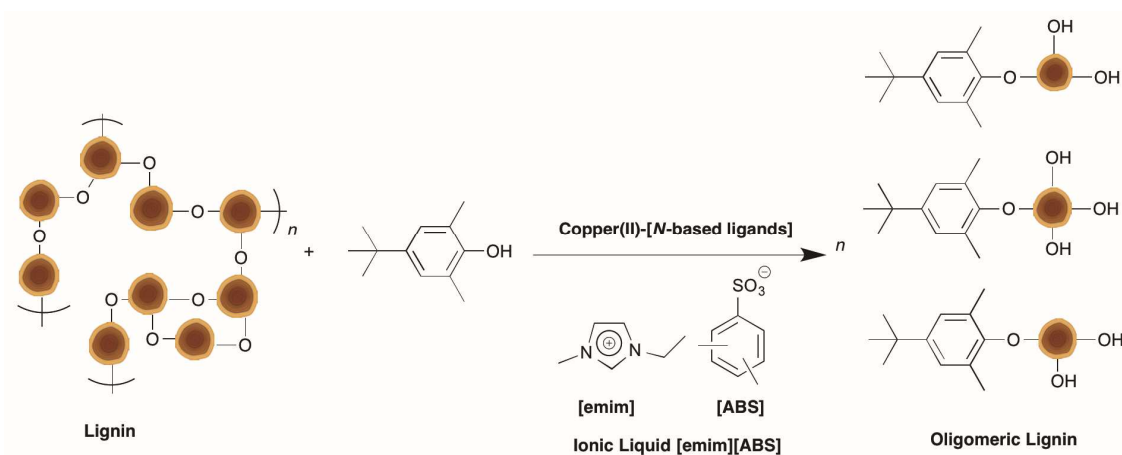
Scheme 2 Schematic representation of proposed lignin depolymerisation mechanism.

On the basis of these results, ligands (E)-N-(pyridin-2-ylmethylene)aniline (**L6**) and (E)-4-methoxy-N-(pyridin-2-ylmethylene)aniline (**L7**) were selected for further study. The novelty of this research lies in using several types of copper complexes with the N-based ligand as catalysts for lignin depolymerisation in organic solvents and an ionic liquid.

Results and discussion

In this study, organosolv lignin was selected as a lignin for depolymerisation research. This organosolv lignin was isolated by removing the low molecular weight fraction by stirring in methanol for 2h to dissolve the low molecular weight fraction as we previously reported.[20] Organosolv lignin was stirred in methanol for 2 h to dissolve the low molecular weight fraction. The methanol insoluble fraction, which was high molecular weight lignin, was filtered and dried. This part of lignin was defined as M-lignin used for all the depolymerisation reactions. The molecular weight and polydispersity of M-lignin was measured by GPC to give M_n = 12,500 and Đ (M_w/ M_n) = 1.86.

Screen depolymerisation of lignin in DMF and [emim][ABS]

Initial attempts to depolymerise lignin were conducted in separate experiments, using the [emim][ABS] and DMF with the seven N-based ligands (Scheme 2). DMF was chosen to enable solubilisation of the N-based ligands, monomer (TBDMP) and M-lignin. It was thought that the solubility enhanced the depolymerisation efficiency by making the solution of lignin, monomer and catalysts homogeneous. Screening reactions were carried out in DMF and [emim][ABS] at the temperatures of 120°C and 180°C separately. All the screening reactions were carried out in these two solvents using 4-tert-butyl-2,6-dimethyl-phenol (TBDMP) as additives and Cu(I)/N-based ligands as catalysts under oxygen flow. These reactions were performed for 6 hours based on the result of previous research for lignin depolymerisation in water with copper-EDTA.[20] TBDMP was selected as a phenol additive under the conditions as it could not polymerise due to the tert-butyl group on para-position in the redistribution process. Samples of every reaction were collected and the molecular weight of each sample was measured by GPC (Fig. 1, Fig. 2). As for the initial samples, the high molecular weight peak, of which the retention time is around 14 min, is M-lignin and the low molecular weight peak with the retention time of 16.8 min is TBDMP.

Table 1 summarizes the molecular weight and polydispersity changes of M-lignin in the 6 h depolymerisation reaction conditions using copper complexes with different N-based ligands.

Fig.1. GPC chromatograms of depolymerisation of M-lignin in DMF with copper complexes with different N-based ligands.

After 6 h, the depolymerisation of M-lignin was observed as the molecular weight of all samples decreased (Table 1). The M_n became smaller than the initial M_n of the M-lignin (M_n = 12,500), and the polydispersity became larger than Đ of the initial M-lignin (M_w/ M_n = 1.86). This indicated all these copper complexes with N-based ligand could catalyse lignin depolymerisation with TBDMP involving the redistribution mechanism. Moreover, the GPC data (Table 1) showed the M_n of all the depolymerised lignin with different copper complexes is smaller for reactions conducted in [emim][ABS], compared with those conducted in DMF. This demonstrated that lignin

Table 1 The M_n and Đ of depolymerised samples from screening reaction

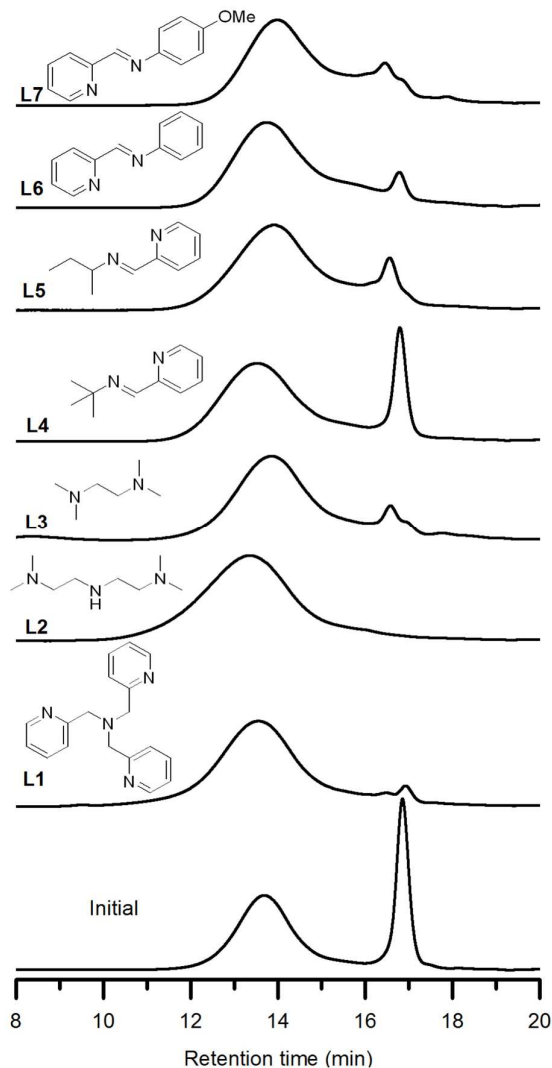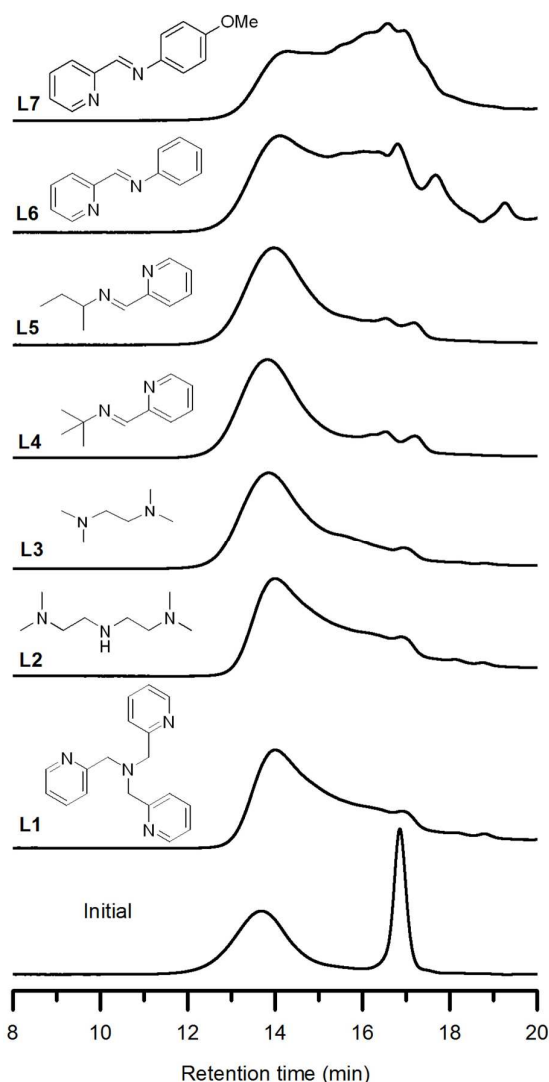| Ligands	In DMF		In [emim][ABS]	
	M_n (g/mol)	Đ (M_w/M_n)	M_n(g/mol)	Đ(M_w/M_n)
L1	11,500	3.6	6,000	2.5
L2	11,300	3.4	5,000	2.7
L3	7,000	3.0	5,000	3.2
L4	7,100	5.9	5,700	2.4
L5	8,400	3.4	6,200	2.5
L6	5,600	3.6	2,500	3.2
L7	5,200	2.6	2,500	2.4

Fig. 2. GPC chromatograms of depolymerisation of M-lignin in [emim][ABS] with copper complexes with different *N*-based ligands.

From the results from the above screening reactions, these two *N*-based ligands were selected and several depolymerisation reactions were carried out in [emim][ABS] with L6 and L7 with different reaction times in order to find the optimum lignin depolymerisation conditions using these two *N*-based ligands and also to investigate the difference between these two ligands as described below.

Depolymerisation of lignin in [emim][ABS] with L6 and L7

Two extended reactions were carried out with different reaction times in [emim][ABS] with the copper complexes, **L6** and **L7**.

These two reactions were undertaken over 48 h with samples collected at the following reaction times: 3 h, 6 h, 9 h, 12 h, 18 h, 24 h, 36 h, 48 h. Samples from the different reaction times were subjected to GPC to give M_n and $Đ$ (M_w/ M_n). The GPC chromatograms of depolymerised lignin are shown below (Fig. 3).

Within 3 h of reaction time, the peaks of M-lignin and TBDMP showed a molecular weight decrease from about 12,000 to about 10,000 and the $Đ$ increased from 1.8 to 1.9. After 6 h, the average molecular weight of M-lignin was reduced to M_n = 3,900, with a higher $Đ$ (M_w/ M_n = 2.09).

The depolymerisation reaction was continued for 12 h, and the average molecular weight decreased to M_n = 2,000 with a $Đ$ of M_w/ M_n = 2.63. The depolymerisation was continued for 48 h but the molecular weight remained at about 2000 after 12 h, which indicated the best reaction time for depolymerisation with L6 was up to 12 h. This result showed it was difficult to completely depolymerise lignin even using TBDMP as additive, one reason being that the redistribution mechanism involved is an equilibrium reaction[27-29] and the low molecular weight part of depolymerised lignin can be repolymerised simultaneously with the depolymerisation.

could be depolymerised more efficiently in [emim][ABS] with all these different copper-amine complexes compared with DMF. The reason could be that the ligands were more readily soluble in [emim][ABS] other than in DMF.

When comparing all the depolymerisation reactions, the M_n and $Đ$ (M_w/ M_n) of depolymerised lignin were different to each other. This demonstrated that copper complexes with different *N*-based ligand showed the different catalytic ability for depolymerisation. Among all these ligands, the molecular weight of depolymerised lignin from **L6** and **L7** was lower than that of other ligands in these screening reactions and **L6** and **L7** were considered to be more efficient than other ligands.
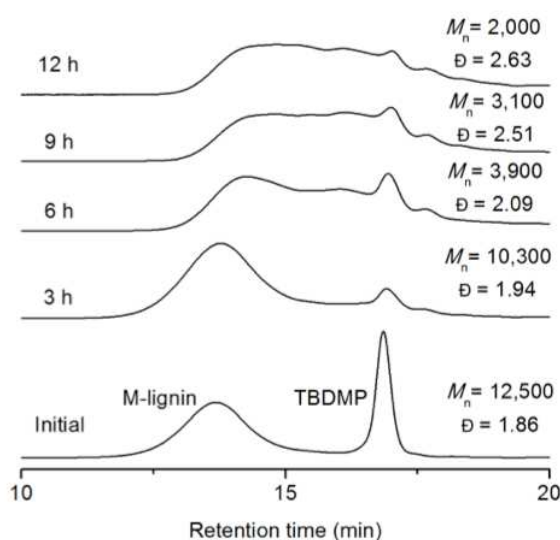

Fig. 3. GPC chromatograms of depolymerised M-lignin in [emim][ABS] using copper-**L6** with different reaction times.
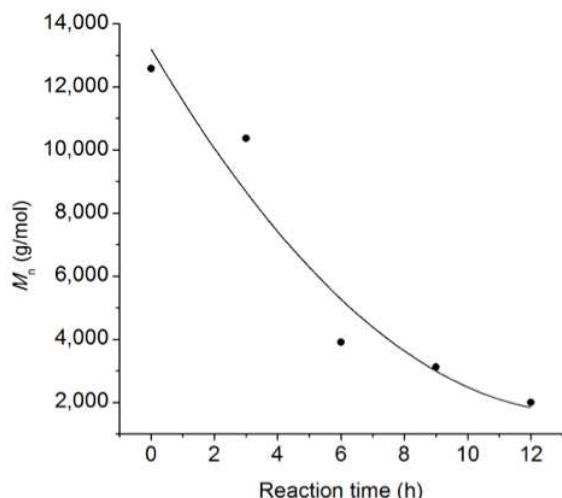
Fig. 4. M_n of samples from different reaction time of lignin depolymerisation with copper-**L6**.
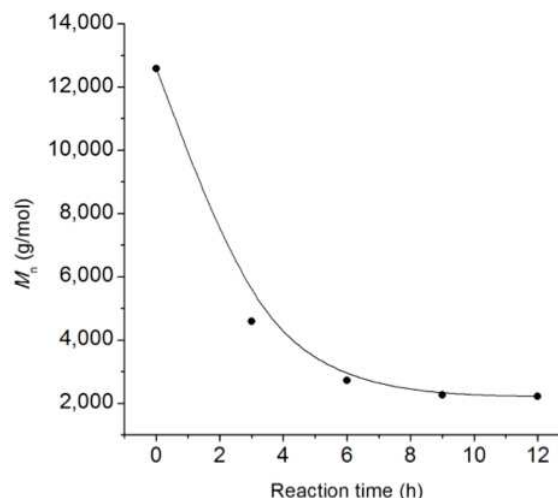

Fig. 6. M_n of samples from different reaction time of lignin depolymerisation with copper-**L7**.
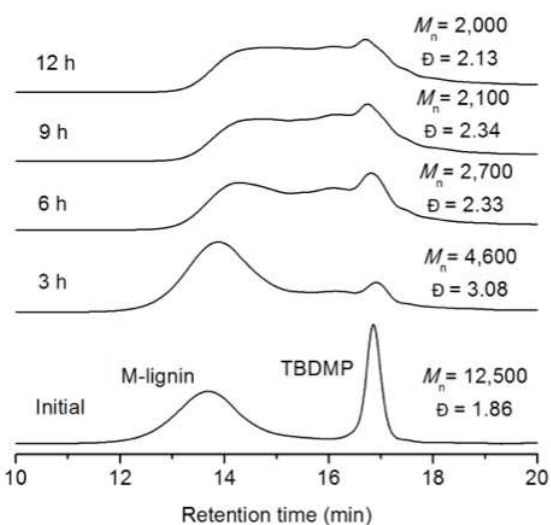

Fig. 5. GPC chromatograms of depolymerisation of M-lignin in [emim][ABS] using copper-**L7** with different reaction times.

Further depolymerisation of lignin using the copper-**L7** complex with TBDMP was carried out. All the samples of depolymerised lignin obtained from different reaction times were analysed by GPC to determine the M_n and Đ (Fig. 5). Within 3 h of reaction time, the average molecular weight of lignin decreased from M_n = 12,500 to M_n = 4,500 with Đ increasing from M_w/ M_n = 1.86 to M_w/ M_n = 3.08. This indicated depolymerisation of the mixture with copper-L7 complex resulted in a significant molecular weight decrease within 3 h of reaction time. After 6 h, the average molecular weight was reduced to M_n = 2,700 with Đ (M_w/ M_n) = 2.33. The depolymerisation reaction was carried out for 48 h but there was no significant decrease in

molecular weight after 9 h, with the molecular weight remaining around M_n = 2,000 (Fig. 6). This reaction showed a similar result to the depolymerisation using the copper-L6 complex. The M-lignin was not completely depolymerised by the copper-**L7** complex as the low molecular weight oligomers can repolymerise concurrently with depolymerisation. Based on the results of these depolymerisation reactions, the best reaction time for **L7** was found to be 9 h.

In summary, the GPC chromatogram of the lignin depolymerisation in Fig. 3 showed that lignin could be depolymerised into oligomers with average molecular weight at about M_n =2,000 in [emim][ABS] using copper-**L6** and copper-**L7** complex within 12 h and 9 h, respectively. Comparing the results of the depolymerisation catalysed by the copper-L6 complex with that of the copper-**L7** complex, the copper-**L7** complex could catalyse lignin depolymerisation more efficiently. These copper complexes were used as a catalyst to generate radicals on phenols to perform the depolymerisation process. The hypothesis for this result is that the reversible potential of copper-**L7** complex could be more positive than that of copper-**L6** complex. The reversible potentials of different copper complexes are known to change due to the structure of coordinated ligand and different N-based ligands in copper complexes can affect the radical generation rate that can affect the lignin depolymerisation rate.[29-31]

Electrochemical Measurements

In the depolymerisation reactions, Cu(I)Cl was added to coordinate with different ligands to form copper complexes, in which the Cu$^+$ center was then oxidized to Cu^{2+} under air flow. Cyclic voltammetric measurements were carried out to determine the reversible potentials of the copper centers of the copper complexes with different N-based ligands. This part of work aimed to study if the differences in the reversible potentials of copper complexes could correlate to the different depolymerising ability of copper complexes with each ligand in [emim][ABS]. The Cu$^{+/2+}$ redox processes associated with the copper complexes are shown in Fig. 7. At a more negative potential region, the reduction of Cu$^+$ to metallic Cu is evident since

Table 2 E_m of copper complexes with different ligands vs. Fc$^{0/+}$

Ligands	L1	L2	L3	L4	L5	L6	L7
E_m / mV	-695	-523	-760	-210	-320	-193	-152
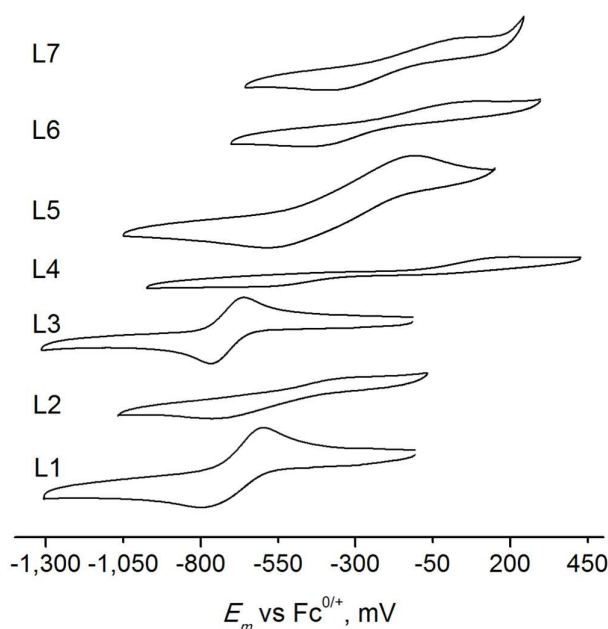
Fig. 7. Cyclic voltammograms of copper complexes with different ligands.

a characteristic copper stripping peak was observed in the reverse anodic sweep (results not shown).

The E_m (reversible potential) values (taken as the average of the reduction and oxidation peak potentials) of copper complexes with different ligands vs. Fc$^{0/+}$ are shown in Table 2. The copper centers of different copper complexes with different *N*-based ligands show different E_m values. The E_m values (Table 2) of copper-**L6** and copper-**L7** are more positive than those with other ligands, indicating that they are stronger oxidizing agents than other copper complexes coordinating with other ligands. Based on the depolymerisation mechanism, this result could explain why copper-**L6** and copper-**L7** more efficiently depolymerise lignin compared to the other ligands. The reversible potential of copper-**L7** is more positive than that of copper-**L6**, which is consistent with the fact that copper-**L7** is the best copper complex for lignin depolymerisation involving the redistribution mechanism among the seven ligands.

Experimental

Materials

Organosolv lignin, DMP, Cu(I)Cl, sodium dodecyl sulfate (SDS), 1-ethyl-3-methylimidazolium chloride, PMDETA, TMEDA, TPA, dicholormethane (DCM), 2-pridinecarboxaldehyde, aniline, p-anisidine, were purchased from Sigma-Aldrich. Hydrochloric acid (32%) was obtained from Ajax Finechem. High purity oxygen purchased from Air Liquid Australia was used for experiments that required oxygen gas. Dimethyl formamide (DMF), for gel permeation chromatography (GPC) analysis, Chloroform (CDCl$_3$), deuterium oxide (D$_2$O), and methanol were purchased from Merck. All reagents were used as purchased from the supplier without any further purification.

Measurements

^{1}H NMR spectra were recorded on a Bruker DRK-400 spectrometer operating at 400 MHz as solutions in CDCl$_3$ and D$_2$O. The molecular weight of isolated lignin and depolymerised samples were measured by GPC performed on a Tosoh EcosHLC-8320 Gel Permeation Chromatograph equipped with both refractive index (RI) and ultraviolet (UV) detectors (UV detection, λ = 280 nm) using Tosoh alpha 4000 and 2000 columns. DMF(with 10mM LiBr) was used as mobile phase with a flow rate of 1.0mL/min.UV detector in GPC chromatograms set at 280 nm was used to analyze all the depolymerised samples and isolated lignin. Calibration curves were obtained using polystyrene standards.

Synthesis of 4-*Tert-butyl*-2,6-dimethylphenol (TBDMP)

TBDMP was prepared from DMP by following the reported literature procedure.[26] v_{max} (KBr)/cm^{-1} 3403 (O-H), 2917 (C-H), 1617 (C=C). ^{1}H NMR (400 MHz, CDCl$_3$): δ_H 7.03 (s, 2H, ArH), 2.28 (s, 6H, CH$_3$), 1.32 (s, 9H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 16.3, 31.7, 34.0, 122.5, 125.7, 143.0, 150.0. MS (+ESI); m/z; 178.14 [M+]

Synthesis of ionic liquid 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS])

[emim][ABS] was prepared using the reported procedure.[32] v_{max} (KBr)/cm^{-1} 3053, 2964, 2924, 2855, 1654, 1465, 1327, 969, 771. ^{1}H NMR (400 MHz, D$_2$O) δ_H 8.55–8.45 (s, [emim] ArH), 8.21–8.19 (s,[ABS] ArH), 7.80–6.90 (m, [ABS] ArH), 4.15–4.00 (q, [emim] -CH$_2$-CH$_3$), 3.73 (s, [emim] -CH$_3$), 3.00–2.75 (m, [ABS] -CH$_3$-CH-CH$_3$), 2.65–2.55 (q, [ABS] -CH$_2$-CH$_3$), 2.53–2.40 (m, [ABS] CH$_3$-Ar), 2.28 (s, [ABS] -CH$_3$-Ar), 2.24–2.12 (m, [ABS] -CH$_3$-Ar), 1.45–1.25 (t, [C$_2$mim] -CH$_2$-CH$_3$), 1.20–1.11 (m, [ABS] -CH$_2$ -CH$_3$, CH$_3$-CH-CH$_3$). ^{13}C NMR (100 MHz, D$_2$O): δ_C 139.40, 137.21, 130.01, 128.24, 122.81, 123.04, 42.01, 27.22, 21.3 m/z(+ESI) 282.1.

Synthesis of (*E*)-*N-sec-butyl*-1-(pyridin-2-yl)methanimine (L4)

N-Alkyl-(2-pyridyl)methanimine ligand was synthesized using the reported procedure.[33] B.p. 74°C at 5.0 Torr. v_{max} (KBr)/cm^{-1} 1630, 1571, 1454. ^{1}H NMR (CDCl$_3$, 400 MHz): δ_H 8.50 (d, 4.56 Hz, 1 H), 8.24 (s, 1 H), 7.86 (d, 7.68 Hz, 1 H), 7.57 (t, 7.36Hz, 1 H), 7.14 (dd, 4.92, 6.32 Hz, 1 H), 3.17 (sext, 6.32 Hz, 1 H), 1.50 (m, 7.72 Hz, 2 H), 1.13 (d, 6.28 Hz, 3 H), 0.72 (t, 7.36 Hz. 3 H). ^{13}C NMR (CDCl3, 100 MHz,): δ_C 161.60, 154.49, 149.16, 136.29, 124.38, 120.96, 69.36, 29.27, 22.50, 10.90. m/z (ESI) 163.1.

Synthesis of (*E*)-*N-tert-butyl*-1-(pyridin-2-yl)methanimine (L5)

This compound was obtained as a yellow liquid (322.2 mg, 85%) following the reported procedure.[34] v_{max} (KBr)/cm^{-1} 1637, 1569, 1451. ^{1}H NMR (400 MHz, CDCl$_3$) δ_H 8.63(d, 4.0Hz,1H), 8.36(s,1H), 8.02(d, 7.9Hz, 1H), 7.73(t, 7.7Hz,1H),7.29(ddd, 7.5,4.9,1.2Hz,1H), 1.31 (s, 9 H). ^{13}C NMR (CDCl$_3$, 100 MHz,): δ_C 161.60, 154.49, 149.16, 136.29, 124.38, 120.96, 69.36, 29.27, 22.50. m/z (ESI) 163.1.

General procedure[33] for synthesis of ligand of (*E*)-*N*-(pyridin-2-ylmethylene)aniline (L6) and (*E*)-4-methoxy-*N*-(pyridin-2-ylmethylene)aniline (L7)

To a solution of pyridine carboxaldehyde (1.2 eq) in dichloromethane DCM was added dry MgSO$_4$ (5 g, 41.5 mmol) followed by *N*-based ligand (1.0 eq).

The reaction mixture was stirred at room temperature for 24 hours, filtered and the solvent removed in vacuo. Ligands were then purified by distillation at reduced pressure.

Synthesis of (*E*)-*N*-(pyridin-2-ylmethylene)aniline (L6)

2-Pyridinecarboxaldehyde (0.32 g, 3.0 mmol, 1.2 equiv.), aniline (0.23 g, 2.5 mmol, 1.0 equiv.) and dichloromethane (20 ml) was subject to the general procedure[33] for the synthesis of ligands. Purification by vacuum distillation resulted with dark orange oil (0.45 g, 2.5 mmol, 99 %); υ_{max} (neat, cm^{-1}) 3053, 1627, 1591, 1485; ^{1}H NMR (400MHz, CDCl$_3$): δ_H 8.72 (1H, d, 4.8 Hz), 8.61 (1H, s), 8.21 (1H, d, 7.7 Hz), 7.82 (1H, td, 7.7, 1.6 Hz), 7.45 – 7.40 (2H, m), 7.37 (1H, ddd, 7.7, 4.8, 1.0 Hz), 7.32 – 7.24 (3H, m); ^{13}C NMR (100 MHz, CDCl$_3$): δ_C 160.7, 154.6, 151.0, 149.7, 136.7, 129.3, 126.8, 125.2, 121.9, 121.1; m/z (ESI) 183.1.

Synthesis of (*E*)-*4*-methoxy-*N*-(pyridin-2-ylmethylene)aniline (L7)

2-Pyridinecarboxaldehyde (0.32 g, 3.0 mmol, 1.2 equiv.), and p-anisidine (0.31 g, 2.5 mmol, 1.0 equiv.) in dichloromethane (20 ml) were subjected to the general procedure[33] for the synthesis of ligands. Purification by vacuum distillation resulted with dark orange oil (0.45 g, 2.12 mmol, 86 %); υ_{max} (neat, cm^{-1}) 3051, 2834, 1624, 1579, 1503, 1242; ^{1}H NMR (400MHz, CDCl$_3$): δ_H 8.62 (1H, d, 4.7 Hz), 8.55 (1H, s), 8.10 (1H, d, 7.8 Hz), 7.71 (1H, td, 7.8, 1.6 Hz), 7.31 – 7.21 (3H, m), 6.94 – 6.81 (2H, m), 3.76 (3H, s, OCH$_3$); ^{13}C NMR (100MHz, CDCl$_3$): δ_C 158.3, 157.6, 154.3, 149.0, 143.1, 136.0, 124.2, 122.1, 121.0, 113.8, 54.9; m/z (ESI) 213.1.

Screening depolymerisation of lignin in DMF

A typical lignin depolymerisation procedure is summarized as follows: For each reaction, lignin (0.31 g), TBDMP (0.45 g, 2.5 mmol), Cu(I)Cl (0.025 g, 0.25 mmol) and pyridine/ligands (2 mL, 0.25 mmol) were added to DMF (20 mL). The reaction mixture was stirred under oxygen at 120°C and samples of the reaction mixture (5 mL) were withdrawn at the following time intervals: 1h, 3h and 6h. At the end of 6 h, the reaction was stopped by dropwise addition of 1M HCl until pH 2 was reached, causing precipitation of the depolymerised product. The suspension was centrifuged several times with distilled water until the pH of the supernatant reached 7. The precipitate was then dried under vacuum at room temperature. The initial acidified supernatant was then extracted with 3 volumes of dichloromethane and the dichloromethane removed under vacuum to give a residue. The molecular weight of all of the products obtained in this way was analysed by GPC. A control reaction was carried out without TBDMP (monomer) or catalyst (Cu(I)Cl/ligands) under the same conditions in order to compare the results.

Isolation of the high molecular weight fraction of lignin using a solubility method

Dried organosolv lignin 5.98 g was added to methanol (600 mL) and the suspension was stirred (500 rpm) with a magnetic stirrer for 2 h at room temperature (23°C), then filtered through a pre-dried (105°C overnight) weighed cellulose filter paper. The solid lignin residue together with the filter paper was then oven-dried overnight at 105°C. After cooling in a desiccator, the dried solid methanol-insoluble residue (M-lignin) was weighed and collected. Evaporation of solvent from the filtrate under vacuum afforded a soluble fraction. The percentage of insoluble material was calculated based on the dry weight. The molecular weight distribution of the methanol-insoluble fraction of M-lignin was determined by GPC.

Screening depolymerisation of lignin in 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS])

M-Lignin (0.005 g), TBDMP (7 mg, 4×10^{-2} mmol), CuCl$_2$·2H$_2$O (0.7 mg, 4×10^{-3} mmol) and ligands (4×10^{-3} mmol) were added to [emim][ABS] (0.5 g). The reaction mixture was stirred under oxygen at 180°C for 6 h. At the end of 6 h, the pH of the mixture was adjusted to 2 by dropwise addition of 1M HCl. The resulting precipitate was collected and washed by centrifugation with distilled water until the pH of the supernatant reached 7. The washed precipitate was dried under vacuum at room temperature. The molecular weight distributions of the depolymerised products were characterized by GPC. A control reaction was carried out in the absence of TBDMP and catalyst (Cu(II)Cl/ligands) as described above in order to compare the results.

Lignin depolymerisation in 1-ethyl-3-methylimidazolium xylenesulfonate ([emim][ABS])

M-Lignin (0.04 g, TBDMP (0.056 g, 0.33 mmol), CuCl$_2$·2H$_2$O (0.0033 g, 0.033 mmol) and ligands (0.66 mmol) were added to [emim][ABS] (4 g). The reaction mixture was stirred under oxygen at 180°C for 48 h. And samples were taken from the mixture at the following reaction time: 3 h, 6 h, 9 h, 12 h, 18 h, 24 h, 36 h and 48 h. After every sample had been taken from the mixture, we followed the previous screening procedure for purification and characterisation.

Electrochemical Measurement

Electrochemical experiments were carried out at the temperature of ^{1} at 23 ± 2°C in a standard three-electrode cell configuration with a Bioanalytical Systems (BAS West Lafayette, Indiana) Model 100B potentiostat at a scan rate of 100 mV•s$^-$. A glassy carbon disc electrode (1 mm diameter, eDAQ) was used as the working electrode. A platinum wire was employed as the reference electrode and another platinum wire as the counter electrode. The reference potential was calibrated against that of the Fc/Fc$^+$ (Fc = ferrocene) redox couple as an internal reference from measurements made on the oxidation of 1 mM Fc present in the same solution.[35] The voltammetric investigation was carried out in 0.5 ml of [emim][ABS] in the presence of 0.0165 mmol Cu(I)Cl, and 0.33 mmol ligands. Prior to voltammetric experiments, the glassy carbon electrode was polished with 0.3 µm alumina slurry on a clean polishing cloth (Buehler, USA), rinsed with deionized water, washed with acetone and finally dried with nitrogen gas.

Conclusions

Seven *N*-based ligands were found to coordinate with copper to form copper complexes and were firstly used to catalyse lignin depolymerisation in DMF and the ionic liquid, [emim][ABS] as solvents. Among all these seven ligands, both **L6** and **L7** were the most efficient ligands to catalyse lignin depolymerisation in [emim][ABS]. Lignin can be depolymerised into oligomers with TBDMP under oxidative conditions involving the redistribution mechanism with the average molecular weight M_n = 2,000 in [emim][ABS] using copper-**L6** and copper-**L7** complex within 12 h and 9 h, respectively. Cyclic voltammetric results showed that copper-**L6** and copper-**L7** have more positive reversible potentials than those of other copper complexes and this could be the reason of the high depolymerisation efficiency of these two ligands compared to the other five ligands.

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Acknowledgements

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Several *N*-based ligands and their copper complexes were investigated as catalysts to depolymerise organosolv lignin in an ionic liquid.

TBDMP   **Cu(II)+*N*-based ligands**

Lignin
(proposed lignin structure)

Ionic
Liquid

Oligomeric lignin