RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Co- and Ca-phosphate-based catalysts for the depolymerization of organosolv eucalytpus lignin

Thepparat Klamrassamee[1], Navadol Laosiripojana[1], Kajornsak Faungnawakij[2], Lalehvash Moghaddam[3], Zhanying Zhang[3], William O. S. Doherty[3]*

[1]The Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi, Prachauthit Road, Bangmod, Bangkok 10140, Thailand

[2]Nanomaterials for Energy and Catalysis Laboratory, National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Klong Laung, Pathumthani 12120, Thailand

[3]Centre for Tropical Crops and Biocommodities, Queensland University of Technology, Brisbane, Queensland 4001, Australia

*Corresponding author

Postal address: GPO Box 2432, 2 George St, Brisbane, QLD 4001, Australia.

Tel.: +61 7 31381245; fax: +61 7 3138 4132.

*Corresponding author's E-mail: w.doherty@qut.edu.au

RSC Advances Accepted Manuscript

Abstract

Depolymerization of purified organosolv eucalyptus wood lignin by the heterogeneous catalysts, cobalt polyphosphate (CoP_2O_6) and calcium phosphate (β-CaP_2O_6) was investigated. A total syringol yield of 16.7% was achieved with β-CaP_2O_6 in a methanol/water (50/50, wt/wt) solvent system after depolymerization at 300 ºC for 1 h, showing selectivity of the catalyst.

Value-adding of lignin by conversion to phenol and phenol derivatives has attracted great interest because they are valuable products and can be used as feedstocks for the production of industrial mono-aromatic compounds (*e.g.*, benzene, xylene), liquid fuels and polymers. As summarized in a recent review paper, various lignins (*e.g.*, Kraft, organosolv, soda etc.) in different solvent systems (water, alcohol, organic acids, ionic liquids, etc.), catalyst types (acid, alkaline, heterogeneous, etc.) and reaction modes (direct depolymerization, hydrogenolysis, etc.) have been studied for the conversion of lignins to chemicals.[1] However, lignin conversion to useful products remains challenging, and product yields are low due to its highly recalcitrant and complex structure linked together by various types of ether, aryl and carbon-carbon bonds consisting of mainly β-O-4, 5–5 and 4–O–5 bonds. Depolymerization of lignin with heterogeneous catalysts has received increasing research interests because of the significant advantages including high reaction activity, high selectivity and the ability to readily recover the catalyst. In our previous work, [2] depolymerization of organosolv eucalyptus wood lignin with mesostructured silica catalyst, SBA-15 in a methanol/water (50/50, wt/wt) reaction system resulted in a total syringol yield of 23.0% after depolymerization for 1 h at a reaction temperature of 300 °C. This was the first reported study on lignin that gave such a high syringol yield. However, the production cost of mesostructured silica catalysts are high due to the use of expensive starting materials.

RSC Advances Accepted Manuscript

Therefore, low cost and effective heterogeneous catalysts are preferred for syringol production from lignin.

Metal phosphates are relatively low cost heterogeneous catalysts, and are well known for their catalytic performance to convert sugars, sugar alcohols and cyclic alcohols to other value-added chemicals such as 5-hydroxymethyl furfural (HMF) and isosorbide. [3-5] We have previously reported the synthesis of phosphates of alkaline earth metals (Ca and Sr) and their applications in conversion of fructose, glucose, and cellulose to HMF [6], and the effect of calcination temperature on catalytic performance of these catalysts. [7] In the present study, we report the use of the phosphates of Co and Ca as solid catalysts for the depolymerization of treated (*i.e.*, purified) organosolv lignin (TOL) from woody eucalyptus to phenols. To the best of our knowledge, it is the first time that phosphate-based heterogeneous catalysts have been used to produce syringol by depolymerization of lignin.

Lignin and the phosphate solid catalysts were prepared and characterized according to previous publications. [2,7] Phosphate solid catalysts were prepared using conventional precipitation in acetone-water mixture and calcined at 900 °C, which led to the formation of β-CaP_2O_6 [7] and CoP_2O_6 (Supplementary Figure 1) with confirmation by x-ray powder diffraction analysis (PDF no. 00-027-1120 for CoP_2O_6). The depolymerization of the treated and purified organosolv lignin (TOL) firstly was carried out in a stainless steel tubular reactor (3/8 inch O.D. and 12 cm, length) in which 35 mg of TOL was mixed with 2 mL water with and without catalyst (35 mg) and reacted at 250 °C for 1 h with a solution initial pH of 7. The pressure of the reactor rose from atmosphere to ~4.0 mPa during the depolymerization reaction. Commercial sulfided $NiMo/Al_2O_3$ catalyst was used for comparison. After depolymerization, the products were fractionated (Supplementary Figure 2) and characterized using the methods described in a previous publication. [2] The total mass of the isolated three

RSC Advances Accepted Manuscript

fractions (aqueous, residual lignin, and solid residue) was not dissimilar in the presence or absent of catalyst considering the error ranges (Figure 1). The least proportion of the solid residue fraction and the highest proportion of residual lignin fraction were detected with CoP_2O_6 catalyst, followed by β-CaP_2O_6, $NiMo/Al_2O_3$ and control in that order (Figure 1). Phosphate-based catalysts have significantly lower surface area of 0.5 m^2/g compared to the $NiMo/Al_2O_3$ catalyst which has a value of 108 m^2/g, while the acid strength of the former is in the range of +3.3 to +4.8 and that of $NiMo/Al_2O_3$ +1.7 to +2.0. Low acidity corresponds to greater acid strength. [6] Therefore it is clear that the better performance of the phosphate catalysts relative to the commercial catalyst is not controlled by these properties, but rather by type of the acid type. There are two types of active sites in the phosphate catalysts that are involved with catalytic activities: one belongs to the hydroxyl group or Bronsted site, while the other is the predominant Lewis site. It is therefore likely that it is the Lewis acid sites that play an important role in the improvement of the catalyst selectivity as NiMo/Al2O3 has only the Bronsted acid sites.

The yields of monomeric phenols in the aqueous and residual lignin fractions were analyzed by GC-MS [2] and the results are shown in Table 1 and Supplementary Figure 3. It is known that hardwood (*e.g.*, *Eucalyptus grandis*) lignin contains mainly guaiacyl and syringyl units. [8] The results therefore demonstrated that the presence of the phosphate catalysts selectively produced syringol during the depolymerization process. The highest syringol yields in both aqueous and residual lignin fractions were achieved with the β-CaP_2O_6 catalyst. The total syringol yield with β-CaP_2O_6 was 8.47%, followed by 6.67% with CoP_2O_6 and 5.96% for sulfide $NiMo/Al_2O_3$ catalyst. Without catalyst, the total syringol yield was only 1.85% despite having the highest proportion of 1-(4-hydroxyl-3,5-dimethyoxyphenyl)-ethanone. Benzoic acid was detected in the aqueous fractions derived from CoP_2O_6 and sulfide NiM_O/Al_2O_3, while small quantities of 4-hydroxy-3,5-dimethoxy-benzaldehyde was detected

RSC Advances Accepted Manuscript

from the aqueous fraction derived from sulfide NiM_O/Al_2O_3. Guaiacol was not detected possibly because of the structural features of the purified organosolv lignin. The use of β-CaP_2O_6 and CoP_2O_6 catalysts significantly increased the syringol content from 25.9% (without catalyst) to 74.3% and 53.1% respectively in the aqueous fraction, while the syringol contents in all the lignin residues were no more than 5.7% (Supplementary Figure 3).

FT-IR spectra of residual lignin after depolymerization using the various catalysts are shown in Supplementary Figure 4. Assignments of the major peaks were based on previous publications (and the references therein). [9, 10] The peaks at 2840 cm^{-1} − 2975 cm^{-1} were assigned to C−H stretching in aromatic methoxyl groups and in methyl or methylene groups of side chains. These peaks became very significant after depolymerization due to the formation of lignin subunits with these groups.

The peaks at 1605 cm^{-1}, 1512 cm^{-1} and 1426 cm^{-1} are assigned as the characteristic vibrations of aromatic skeletal structures in lignin. The peaks at 1512 cm^{-1} and 1426 cm^{-1} are not significant in the residual lignin after depolymerization with $NiMo/Al_2O_3$ compared to others possibly due to the reduced proportion of aromatic skeletal structures. The peak at 1462 cm^{-1} is related to C−H deformation in lignin, which was significant in all the lignin samples. The peak at 1326 cm^{-1} is assigned to C−O stretching of syringyl rings. Despite similar levels of syringol in all the residual lignins, this peak was very weak with NiM_O/Al_2O_3, indicating perhaps of the conversion of the syringl subunits to other compounds and/or the selective removal of other subunits. The peak at 1261 cm^{-1} is assigned to guaiacyl ring breathing with C−O stretching. This peak was very weak in the TOL but increased in residual lignins after depolymerization possibly due to the conversion of the other subunits to the guaiacyl units. The peak at 1218 cm^{-1} is related to ring breathing with C−O stretching of both syringyl and guaiacyl structures. It was not clear why the peak intensity of the NiM_O/Al_2O_3 derived sample

RSC Advances Accepted Manuscript

was much weaker compared to those of other samples. The peak at ~1150 cm^{-1} is associated with the C–O–C antisymmetric bridge stretching vibration in cellulose and hemicelluloses. The low peak intensities in all the residual lignin samples indicated a very low content of carbohydrates. The peaks at ~1118 cm^{-1} and ~1124 cm^{-1} are assigned to aromatic C−H in-plain deformation of syringyl units. These peak intensities of the $NiMo/Al_2O_3$ derived sample are weaker. For each of the spectrum, the ratio of the peak area associated with the *p*-hydroxyphenyl propane units at 1161 cm^{-1} to that of the syringyl units at 1124 cm^{-1}, an indication of the relative proportion of the *p*-hydrxyphenyl propane units, was in the order of CoP_2O_6 > β-CaP_2O_6 > $NiMo/Al_2O_3$ = no catalyst > TOL. In summary, some of the characteristics syringyl peaks were reduced in intensity with the residual lignin obtained with NiM_O/Al_2O_3, possibly due to the conversion of syringyl subunits to 4-hydroxy-3,5-dimethoxy-benzaldehyde and 1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone in the aqueous phase (Table 1).

β--CaP_2O_6 catalyst was used to evaluate the effect of temperature on lignin depolymerization in the water solvent system. The highest syringol yield (9.77%) in the aqueous fraction was achieved at 300 °C, while the highest syringol yield (4.95%) in residual lignin fraction was achieved at 350 °C (Table 2). The total syringol yields at 300 °C and 350 °C were similar, 13.82% and 13.77% respectively. However, the solid residue fraction was negligible at 300 °C whereas it was 6.00% at 350 °C (Figure 2). The syringol content in aqueous phase was the highest at 250 °C and decreased thereafter (Supplementary Figure 5) due to the formation of higher proportions of other monomers (Table 2).

Previous studies have shown that alcohol-water solvent could improve lignin depolymerization [2, 11] possibly due to increased lignin solubility and therefore decreased mass diffusion limitation. In this study, depolymerization of lignin was also investigated in a

RSC Advances Accepted Manuscript

methanol-water (50/50, wt/wt) solvent system. Depolymerization was conducted in the presence of β-CaP_2O_6 at 300 ºC for 1 h. As shown in Figure 2, the proportion of aqueous fraction formed with methanol/water is 11.20%, higher than that (6.29%) with water. The solid residue content was negligible and similar to that with water. However, the syringol content in aqueous fraction with methanol/water is 45.70%, 18.70% lower than that with water (Supplementary Figure 5), indicating the production of other undetected water soluble lignin depolymerization products. The syringol contents in the aqueous phase and the lignin residue obtained at 300 ºC for the methanol water mixture were 5.12% and 11.55%, respectively, leading to a total of 16.67% (Table 2).

A number of heterogeneous catalysts (*e.g.*, supported metal catalysts such as Pd, Pt, Ru, Ni, Co-Mo, and Ni-Mo supported on C, Al_2O_3, and SiO_2-Al_2O_3) have been used for the depolymerization of lignins as summarized in a review paper. [1] In one of these studies, a maximum guaiacol yield of 10% was achieved from lignosulfonate with Ni/C at 200 °C via hydrogenolysis, followed by a guaiacol yield of 4.7% from Kraft spruce lignin with Pd-Nafion SAC in aqueous formic acid solution at 300 °C.[12] Guaiacol and syringol derivatives were also obtained in previous studies, which included 4-propylguaiacol (7.8%) and 4-methylguaiacol (5.0%) from organosolv switchgrass lignin with Pt/C in the mixture of formic acid and ethanol solution via hydrodeoxygenation at 350 °C [13] and higher yields of propenylguaiacol (12%) and propenylsyringol (36%) from with Ni/C in alcohol via a hydrogenolysis process. [14] Other phenols such as pyrocatechol and resorcinol were also obtained in these studies but the yields of these products were generally low, less than 5.0%. [1] These studies indicated that these types of catalysts are able to selectively produce momolignol derivatives from lignin. Although in the present study, the total syringol yield of 16.7% was lower than that reported in our previous study with SBA-15 catalyst, [2] it is worth noting that the β-CaP_2O_6 catalyst, is of lower cost than the SBA-15 catalyst. The results

RSC Advances Accepted Manuscript

indicated that the β-CaP_2O_6 catalyst is more selective towards syringol formation as only smaller proportions of other phenolic compounds are produced relative to the SBA-15 catalyst. The β-CaP_2O_6 catalyst can be readily recovered by calcination of the solid residue in air. However, it should be noted that while the recyclability and the structure of the catalysts after depolymerization were not studied in the present study, the post-reaction pH of the aqueous phase dropped to pH 5.5, an indication of catalyst deactivation. From our previous study on glucose conversion to HMF, [6] Ca leaching was 8.4%, though under more severe conditions than the present study.

In summary, the study demonstrated that β-CaP_2O_6 did produce reasonable yields of syringol from lignin. Preliminary results showed that reaction temperature and the type of solvent system had impacts on the yield of syringol produced from eucalyptus wood lignin. It is recommended future studies should be focused on the catalyst recyclability, optimization of reaction conditions, and understanding the reaction mechanism.

Acknowledgements

The authors would like to express sincere appreciation of the Royal Golden Jubilee Scholarship (RGJ), Thailand Research Fund, and the Queensland University of Technology (QUT), Queensland, Australia for financing this project.

References

1. H. Wang, M. Tucker and Y. Ji, *Journal of Applied Chemistry*, 2013, 2013, 1-9.
2. T. Klamrassamee, N. Laosiripojana, D. Cronin, L. Moghaddam, Z. Zhang and W. O. S. Doherty, *Bioresource technology*, 2015, 180, 222-229.
3. F. S. Asghari and H. Yoshida, *Carbohydrate research*, 2006, 341, 2379-2387.
4. M. Gu, D. Yu, H. Zhang, P. Sun and H. Huang, *Catal Lett*, 2009, 133, 214-220.

RSC Advances Accepted Manuscript

5. F. M. Bautista, J. M. Campelo, A. García, D. Luna, J. M. Marinas, R. A. Quirós and A. A. Romero, *Applied Catalysis A: General*, 2003, 243, 93-107.

6. P. Daorattanachai, P. Khemthong, N. Viriya-Empikul, N. Laosiripojana and K. Faungnawakij, *Carbohydrate research*, 2012, 363, 58-61.

7. P. Daorattanachiai, P. Khemthong, N. Viriya-empikul, N. Laosiripojana and K. Faungnawakij, *Chemical Engineering Journal*, 2015, in press.

8. Y. Pu, S. Cao and A. J. Ragauskas, *Energy & Envrionmental Science*, 2011, 4, 36154-33166.

9. L. Moghaddam, Z. Zhang, R. M. Wellard, J. P. Bartley, I. M. O'Hara and W. O. S. Doherty, *Biomass and Bioenergy*, 2014, 70, 498-512.

10. A. Casas, M. Oliet, M. V. Alonso and F. Rodríguez, *Separation and Purification Technology*, 2012, 97, 115-122.

11. A. K. Deepa and P. L. Dhepe, *RSC Advances*, 2014, 4, 12625-12629.

12. L. Liguori and T. Barth, *Journal of Analytical and Applied Pyrolysis*, 2011, 92, 477-484.

13. W. Xu, S. J. Miller, P. K. Agrawal and C. W. Jones, *ChemSusChem*, 2012, 5, 667-675.

14. Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yu and J. Xu, *Energy & Environmental Science*, 2013, 6, 994-1007.

RSC Advances Accepted Manuscript

Legends of Tables and Figures

Tables

Table 1 Effect of catalysts on the yields of phenolic monomers at 250 ℃ for 1 h.

Table 2 Effect of reaction temperature and solvent on the yields of phenolic monomers with β-CaP_2O_6 catalyst.

Figures

Figure 1 Effect of catalysts on major fractions after lignin depolymerization at 250 °C for 1 h.

Figure 2 Effect of reaction temperature and solvent on major fractions after lignin depolymerization with β-CaP_2O_6 catalyst.

RSC Advances Accepted Manuscript

Table 1

Catalysts	Monomers in aqueous phase (%)				Syringol in residual lignin (%)	Total syringol (%)
	Syringol	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	4-Hydroxy-3,5-dimethoxy-benzaldehyde	Benzoic acid		
No catalyst	1.32	2.55	-	-	0.53	1.85
CoP_2O_6	3.79	0.05	-	2.09	2.88	6.67
β-CaP_2O_6	4.88	0.55	-	-	3.59	8.47
Sulfided NiM_O/Al_2O_3	2.45	0.47	0.09	2.11	3.51	5.96

RSC Advances Accepted Manuscript

Table 2

T (°C)	Monomers in aqueous phase (%)						Syringol in residual lignin (%)	Total syringol (%)
	Syringol	1-(4-Hydroxy-3,5-dimethoxyphenyl)-ethanone	Butylated hydroxytoluene	4-Hydroxy-3,5-dimethoxy-benzaldehyde	1-(2,4,6-Trihydroxy-3-methylphenyl)-1-butanone	Benzoic acid		
200	0.11	-	-	-	-	-	0.09	0.20
250	4.88	0.55	-	-	-	-	3.59	8.47
300	4.05	-	-	-	-	1.30	9.77	13.82
350	4.95	025	0.5	-	0.44	0.22	8.62	13.57
300 (Methanol/water)	5.12	-	-	-	-	0.55	11.55	16.67

RSC Advances Accepted Manuscript

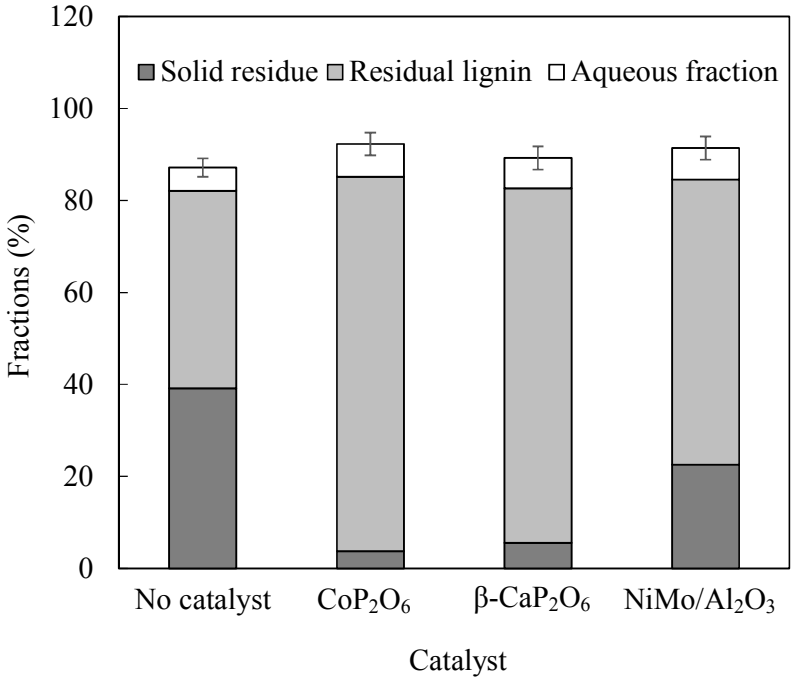

Figure 1

RSC Advances Accepted Manuscript

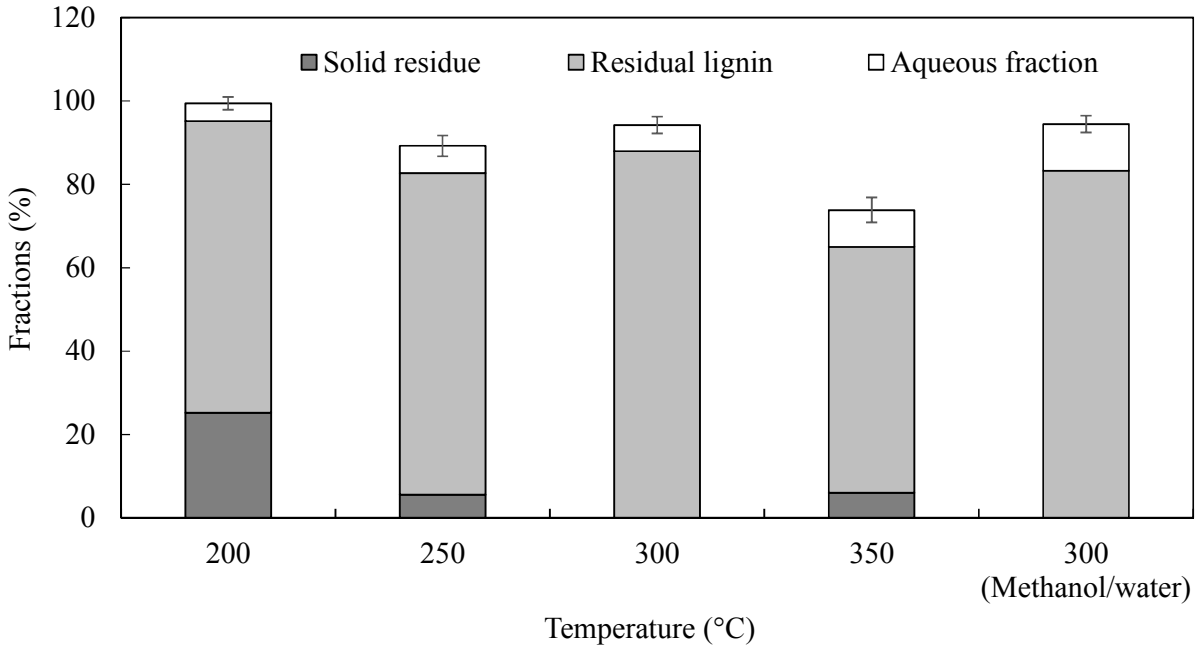

Figure 2

RSC Advances Accepted Manuscript