

Development of Polyoxometalate-Ionic Liquid Compounds for Processing Cellulosic Biomass

Jude A. Abia^a and Ruya Ozer^{b,*}

A unique approach was used in which polyoxometalate-based ionic liquids (POM-IL) were synthesized and employed for the one-pot dissolution and conversion of biomass. A library of four functional POM-IL compounds was synthesized using two cationic organic groups (1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium) and two anionic POMs (phosphotungstate and tungstosilicate). The POM-IL compound serves a dual-purpose. First, it dissolves approximately 30 wt% of cellulosic biomass in 2 h at 200 °C. Second, analysis using HPLC confirmed that the POM-ILs catalyze conversion of biomass into commodity monosaccharides such as glucose and xylose. All of the prepared POM-IL compounds demonstrated dynamic thermal stabilities exceeding 300 °C and were characterized using IR and thermogravimetric analysis.

Keywords: Cellulose; Polyoxometalate; Ionic liquids; Hydrolysis; Biomass; Monosaccharides; Biofuel

Contact information: a: Department of Chemistry, Northeastern State University, 3100 E New Orleans St Broken Arrow, OK 74014 USA; b: Department of Chemistry, University of Tulsa, 800 South Tucker Drive, Tulsa, OK 74104 USA; *Corresponding author: ruya-ozero@utulsa.edu

INTRODUCTION

Biomass materials are dominated by carbohydrates (cellulose and hemicellulose) and exist commonly with substituted aromatics (lignin) such as in lignocellulosic biomass (Kuster 1990; Klemm *et al.* 2005; Roman-Leshkov *et al.* 2007). The high energy cost and difficulty in processing biomass are the main roadblocks to the widespread commercialization of this renewable energy source. The major technological barrier to using cellulosic biomass has been the depolymerization step in which sugars are produced. The very nature of these materials poses a major challenge for their efficient hydrolysis since cellulose forms a highly crystalline structure with extensive intra- and inter-molecular hydrogen bonds and van der Waals interactions. Therefore, the development of an effective and economical conversion process is pivotal for the use of cellulosic biomass for the large-scale production of fuels and chemicals. A successful technology would be one that efficiently deconstructs cellulosic biomass to release cellulose and hemicellulose and hydrolyzes cellulosic components to generate oligosaccharides. These sugars can in turn be converted to fuel products and commodity chemicals; thus alleviating our dependency on fossil fuel-based products and securing the future of our environment and hence our society.

Aqueous phase acid and enzyme-catalyzed hydrolysis are the most commonly used methods for the depolymerization of biomass (Swatloski *et al.* 2002; Marzioletti *et al.* 2008). For both processes, the feedstock needs to be pretreated to increase its digestibility. Enzyme-catalyzed processes yield monosaccharides with high selectivity, but one of the drawbacks of this process is that it typically requires several days to

achieve the desired conversion. Faster conversion of biomass can be achieved *via* acid-catalyzed hydrolysis, but the selectivity of the reaction is difficult to control under typical process conditions (Sun *et al.* 2009). Therefore, a process that eliminates the need for pretreatment and uses mild reaction conditions for the hydrolysis of biomass would be highly desirable. ILs, which are composed of organic cations and inorganic anions, are not a new class of materials, but they do have a set of physical properties such as very low vapor pressures, unusual modes of coordination, and tendencies to form solvent cages which make them highly attractive for the biomass depolymerization reactions. (Inman and Lovering 1981; Copeland 1974; Hsu *et al.* 2011). There have been numerous studies reporting the dissolution of cellulose and wood in ILs, forming a highly viscous solution in which the cellulose chains are left intact and accessible to chemical transformations. For example, Li and associates demonstrated that the IL 1-butyl-3-methylimidazolium chloride (IMC) is capable of dissolving up to 25 wt% of cellulose, forming a highly viscous solution (Li *et al.* 2006). The unusual solubility of cellulose in IMC was attributed to the disruption of hydrogen bonds in cellulose by the chloride anions of the ionic liquid. Cellulose has a highly crystalline structure as a result of regular inter-molecular and intra-molecular hydrogen-bonding interactions. Besides cellulose, biomass also contains lignin, with the latter possessing a three-dimensional network character of π - π interactions among its aromatic groups. ILs exhibit the ability to interact with π -systems in lignin and also disrupt the hydrogen-bonding interactions present in cellulosic materials. The action of the ILs includes dispersion, π - π , n- π , hydrogen bonding, dipolar, and ionic/charge-charge interactions (Hunter and Sanders 1990).

Recently, there has been growing interest in early transition metal oxygen anion clusters (polyoxometalates, POMs), specifically in the biomass catalytic transformation to value-added chemicals. POMs are an important class of solid acid catalytic materials with Brønsted acidity (Misono 2001; Timofeeva 2003; Okuhara *et al.* 1996). Among the several types, Keggin-type POMs are the most widely used in catalytic applications and have the general formula as $\text{XM}_{12}\text{O}_{40}^{-n}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{X} = \text{P}^{5+}, \text{Si}^{4+}$). POMs are catalytic; they are reduced as a result of the oxidation reaction, and reduced POMs are re-oxidized to its original state by oxygen or any oxidant in the system, completing the catalytic cycle. An excellent review surveying the catalytic applications of POMs to the transformation of cellulose into platform chemicals have been recently published (Deng *et al.* 2012). Due to their high negative charge and large metal-oxide framework, POMs can react with a variety of cationic organic groups to form novel functional ionic liquids (POM-IL) (Dai *et al.* 2004). There have been very few reports on the preparation of POM-IL ionic complexes (Bourlinos *et al.* 2004; Rajkumar and Rao 2009; Rickert *et al.* 2007); however, no applications of POM-IL combinations to biomass dissolution and possible conversion have ever been reported.

Here, we report on the synthesis and characterization of POM-IL compounds composed of an imidazolium cation and a Keggin-type POM anion. This report focuses on our initial findings on the synthesis and process parameters governing the conversion of biomass with the POM-IL system. The molecular structure and thermal stability of the synthesized hybrid compounds were examined by infrared spectroscopy and thermogravimetric analysis. The hydrolytic products from biomass dissolution were examined using high pressure liquid chromatography.

EXPERIMENTAL

Materials

All materials were of reagent grade and were used without further purification. The ILs 1-butyl-3-methyl imidazolium bromide (MW= 219.12g/mol) and 1-ethyl-3-methyl imidazolium chloride (MW= 174.67 g/mol), and the polyoxometalate compounds phosphotungstic acid hydrate (MW = 2880.2g/mol), tungstosilicic acid hydrate (MW= 2878.17 g/mol), glucose, xylose, and crystalline cellulose were purchased from Sigma-Aldrich, St Louis, MO, USA. The switchgrass of the Kanlow variety from the Efav Experimental Station in Stillwater, Oklahoma, US was used as the powdered biomass. Before the hydrolysis experiments, biomass and cellulose feedstocks were dried at 50 °C in an oven overnight.

Characterization

The IR spectra of different samples (as KCl pellets) were recorded using an AVATAR 380 FT spectrometer with a resolution of 2 cm⁻¹ in a spectral range of 400 to 4000 cm⁻¹. Thermogravimetric analysis (TGA) of the synthesized POM-IL compounds were conducted in pure N₂ gas at 20 mL/min with a heating rate of 20 °C/min over a temperature range of 25 to 750 °C using a Mettler Toledo TGA-SDTA851 instrument. Melting points of the samples were determined using a DSC Q20 TA Instruments-Waters LLC differential scanning calorimeter investigated at heating rate of 10 °C/min, in the 25 to 250°C temperature range. The melting temperature was determined as the peak onset temperature. Alternatively, a melting point apparatus (Digimelt MPA160) was used, with a pinch of a sample placed in a borosilicate capillary tube, heated at 5 °C/min and observed through a magnifying glass window for melting.

Synthesis of POM-IL Compounds

Starting materials for the synthesis of the library of POM-based ILs is shown in Table 1. Each cation was reacted with each of the two anions to produce a library totaling four POM-IL compounds.

Table 1. Organic Cations and POMs used in the Synthesis of POM- IL Compounds

Organic Cation	Polyoxometalate Anion
1-butyl-3-methyl imidazolium bromide (IMB)	Phosphotungstate; PW ₁₂ O ₄₀ ⁻³ (PT)
1-ethyl-3-methyl imidazolium chloride (IMC)	Tungstosilicate; SiW ₁₂ O ₄₀ ⁻³ (TS)

An example of an acid compound formed from the combination of an organic cation and polyoxometalate anion is shown in Fig. 1.

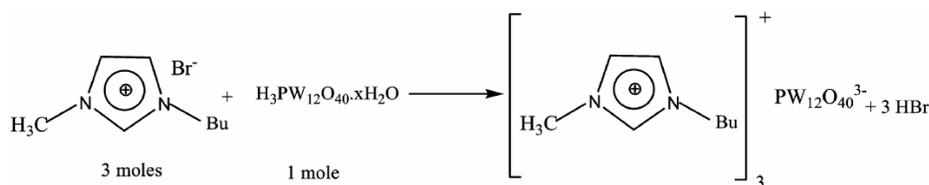


Fig. 1. Reaction involving the imidazolium cation and POM anion to form hybrid material POM-IL compound.

To prepare one mole of the acid compound, the imidazolium compound and aqueous solution of POM were taken in a 3:1 mole ratio. In a typical experiment, 0.5912 g of the imidazolium compound was heated in a capped 20-mL EPA vial at 80 °C until complete melting. The POM anion (2.6033 g) was dissolved in 5 mL of deionized (DI) water, and into this solution, the imidazolium solution was added dropwise using a plastic pipette with constant magnetic stirring at room temperature. A visible white precipitate was immediately formed following the addition of the imidazolium solution. To ensure the product was free from impurities, the precipitate was washed several times with DI water, after which an AgNO_3 test was performed on the wash filtrate. The product was clean enough when no residual Cl^- or Br^- was detected in the filtrate. The product was vacuum-dried overnight at 60 °C before use. The products were determined to be soluble in DMF, but not in water.

Biomass Hydrolysis Reactions with POM-IL Compounds

The hydrolysis reactions of biomass with POM-IL were conducted in open air flasks under heat with a magnetic stirrer. Each reaction batch consisted of 5.0 g of vacuum-dried POM-IL and 1 wt% of oven-dried biomass (particle size of biomass ranges from 0.1 to 2 mm, reported by the supplier). For comparison purposes, Avicel Cellulose was also treated under identical conditions using each POM-IL sample. All of the reactions were carried out in an oil bath. The reactions were repeated three times, and the standard deviations are reported in the graphs. Soluble samples were withdrawn and quenched by adding room temperature water. The aqueous solutions were centrifuged for several minutes, and they were subjected to sugar (glucose and xylose) analysis using HPLC.

Analysis of Hydrolysis Products

Before the HPLC analyses, a 150 μL of 72 wt% H_2SO_4 was added to each 5 mL of hydrolysis product (analyte) to match the acidity of the analyte with the mobile phase. After that, the analyte was filtered using a 0.2 μm PTFE membrane, centrifuged, and the supernatant was separated and analyzed using an Agilent 1260 Infinity Binary LC system equipped with a refractive index detector set at 35 °C. The experiments were performed with sample injection amount of 10 μL at a flow rate of 0.6 mL/min on an Aminex HPX-87H 300 x7.8 mm column with 9 μm stationary phase, under isocratic conditions of 45 °C. The mobile phase was a 5.0 mM of H_2SO_4 solution prepared from concentrated H_2SO_4 by diluting in DI water. Glucose and xylose standards for external calibration with the following concentrations were also prepared in DI water with the concentrations of 1.25×10^{-6} , 2.50×10^{-6} , 3.75×10^{-6} , 5.00×10^{-6} , and 6.25×10^{-6} g/mL. Calibration factors were determined from the peak areas in the chromatogram of standard samples. Any possible contamination of the column by the POM-IL was minimized by utilizing a guard column of the same stationary phase.

RESULTS AND DISCUSSION

Characterization of the Synthesized POM-IL Compounds

Structural properties of the synthesized POM-IL compounds were evaluated using FTIR spectroscopy. Figure 2 depicts the FTIR spectra of the imidazolium bromide (IMB), phosphotungstate (PT), and PT-IMB compounds, respectively.

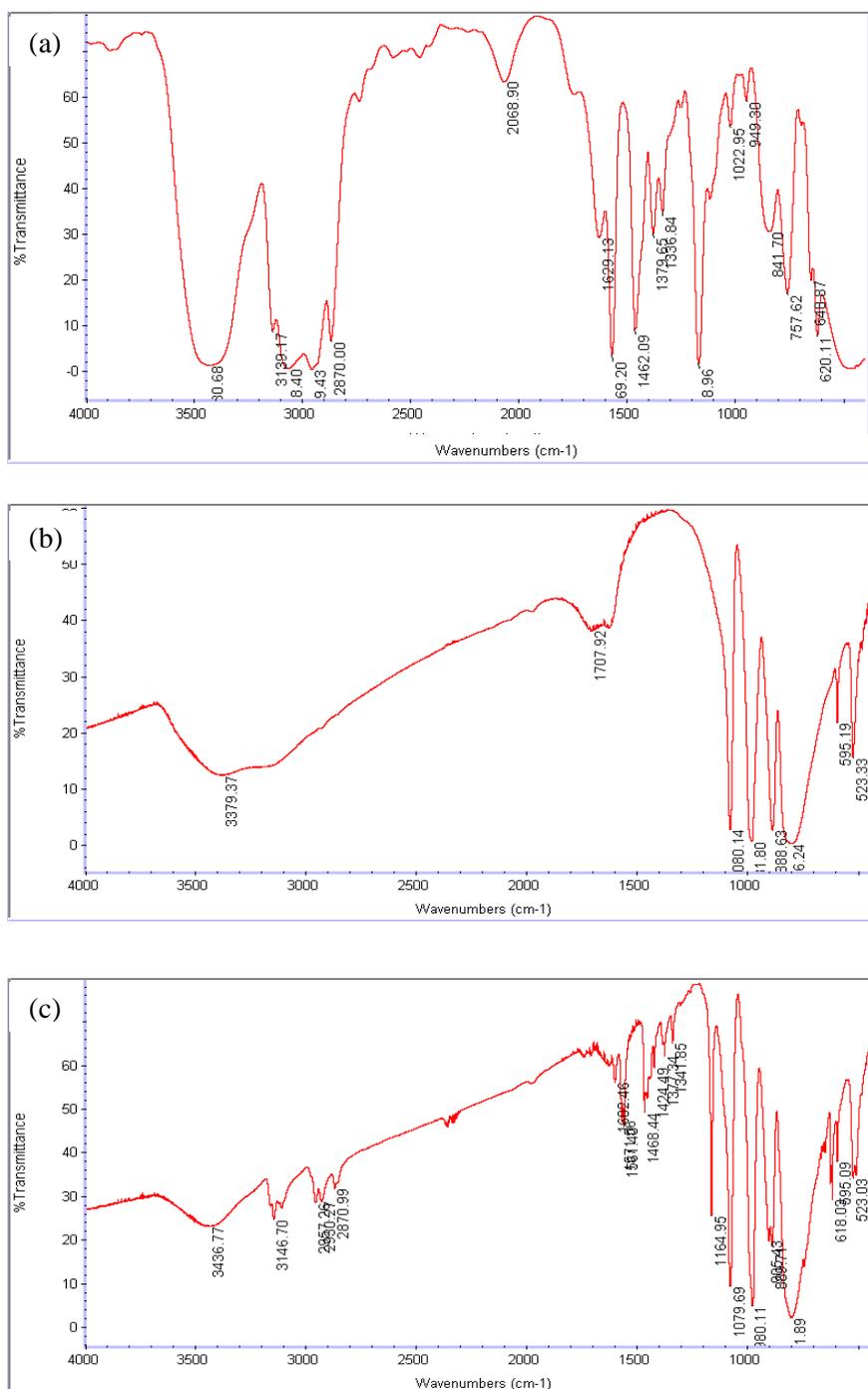


Fig. 2. IR spectra of (a) 1-butyl-3-methyl imidazolium bromide (IMB), (b) phosphotungstate (PT), and (c) phosphotungstic-butyl imidazolium bromide (PT-IMB) compounds.

The Keggin structure ($PW_{12}O_{40}^{3-}$) has the following IR characteristics: P–O stretching ($\sim 1080\text{ cm}^{-1}$); W–O terminal stretching ($\sim 980\text{ cm}^{-1}$); stretching of W–O–W inter-bridges between corner sharing WO_6 octahedra ($\sim 885\text{ cm}^{-1}$); stretching of W–O–W intra bridges between edge-sharing WO_6 octahedra ($\sim 781\text{ cm}^{-1}$); and P–O bending (595 cm^{-1}). These five key IR features due to $PW_{12}O_{40}^{3-}$ ion cluster in the hybrid material indicated that the primary Keggin structure stays intact in the PT-IMB compound

(Misono 2001). For comparison, the IR spectra of the starting organic cation 1-butyl-3-methyl imidazolium bromide (IMB) and phosphotungstate $\text{PW}_{12}\text{O}_{40}^{-3}$ (PT) are also shown in Fig. 2a and 2b.

Spectral features in the regions of $550\text{--}700\text{ cm}^{-1}$, $1130\text{--}1800\text{ cm}^{-1}$, $2800\text{--}3200\text{ cm}^{-1}$, and $3200\text{--}3800\text{ cm}^{-1}$ were attributable to the IMB cation (Fig. 2a) (Wu *et al.* 2005). A closer examination of the IR spectra within the imidazolium ring C–H stretching ($3000\text{--}3250\text{ cm}^{-1}$) and imidazolium ring stretching ($1500\text{--}1620\text{ cm}^{-1}$) regions in Fig. 2 revealed that there was a strong electrostatic interaction between IMB cation and large Keggin POM anion. Due to this interaction, the five vibration peaks of C–H stretching of the imidazolium ring in IMB were more intense in the PT-IMB compound. This greater intensity was attributed to the specific interaction of the IMB cation with the bulky Keggin POM anion, and is common with other ILs (Yokozeki *et al.* 2007; Jerman *et al.* 2008). Besides the exemplary case of the PT-IMB couple, the IR spectra (results not shown) for the other three POM-based ILs prepared showed the same evidence of bonding changes.

Thermogravimetric analyses of the synthesized POM-IL compounds are depicted in Fig. 3. The TGA curve indicated weight loss regions between $250\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$, and above $430\text{ }^{\circ}\text{C}$. No initial low temperature weight loss was recorded, indicating that the sample was free of water. The weight loss observed between $250\text{ }^{\circ}\text{C}$ to $350\text{ }^{\circ}\text{C}$ was primarily due to the decomposition onset of the imidazolium organic moiety. The pure POM is known to decompose at $550\text{ }^{\circ}\text{C}$, but when the POM ions were attached to imidazolium rings, the weight loss in TGA curve occurred at a temperature lower than $500\text{ }^{\circ}\text{C}$. This observation was another indication of the effective interaction of the POM with the imidazolium in the POM-IL compound (Rao and Rajkumar 2008). Further weight loss was observed above $500\text{ }^{\circ}\text{C}$ and was attributed to the decomposition of the POM units. All of the prepared POM-IL compounds showed dynamic thermal stabilities exceeding $300\text{ }^{\circ}\text{C}$. The effect of water (performed by simply adding DI water to the POM-IL compound) on the thermal stability of two of the POM-IL compound is highlighted in Table 2.

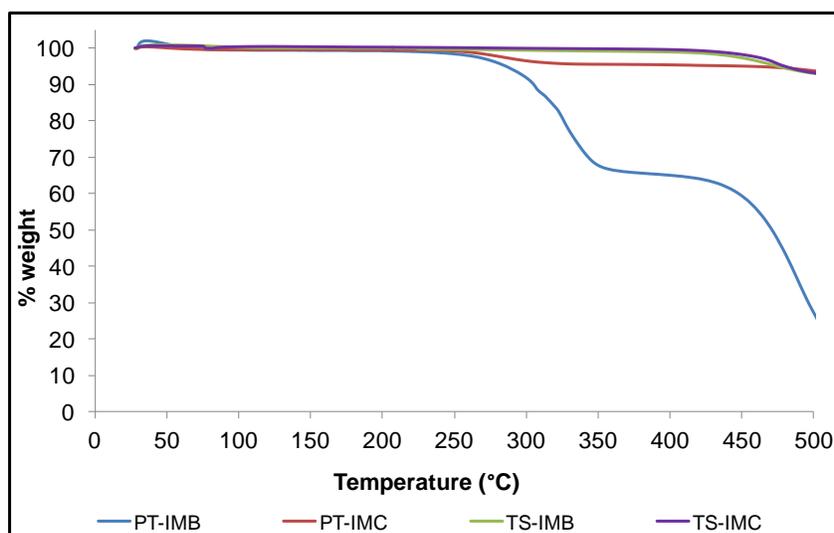


Fig. 3. Thermograms of the synthesized POM-ILs using temperature ramp TGA ($20\text{ }^{\circ}\text{C}/\text{min}$, N_2 flow, alumina pans)

Table 2. Thermal Stability of POM-ILs with Water Contamination

Ionic Liquid	Water contamination (wt.%) \pm std dev (n=3)	TGA onset of thermal degradation ($^{\circ}$ C)	
		Dry	Wet
PT-IMB	10.99 \pm 0.44	440	441
	30.01 \pm 0.16	440	438
TS-IMB	20.34 \pm 0.08%	483	486

The newly synthesized POM-IL compounds were found to be unaffected by the presence of water, as evident in the non-significant change in the onset of their thermal degradation with or without water contamination. This was pertinent since the recyclability of these compounds involves the use of aqueous solvents.

Hydrolysis of Biomass with POM-IL Compounds

The melting points of the synthesized POM-IL compounds and dissolution behavior of the biomass in the four different POM-ILs were obtained and are summarized in Table 3. The most promising of the four, in terms of biomass hydrolysis efficiency, was found to be the PT-IMB system.

Table 3. Melting Points and Dissolution Behavior of Biomass in Ionic Liquids

Ionic Liquid	Melting point ($^{\circ}$ C)	Solubilization Conditions	Solubility wt%
Tris(1-butyl-3-methyl imidazolium) phosphotungstate (PT-IMB)	197 ^a	200 $^{\circ}$ C, 2 h	33
Tris(1-butyl-3-methyl imidazolium) tungstosilicate (TS-IMB)	>220 ^b	N/A ^c	N/A ^c
Tris(1-ethyl-3-methyl imidazolium) phosphotungstate (PT-IMC)	>220 ^b	>220 $^{\circ}$ C, >6 h	Partially soluble
Tris(1-ethyl-3-methyl imidazolium) tungstosilicate (TS-IMC)	>220 ^b	N/A ^c	N/A ^c

^aAs determined by DSC. ^bAs determined by DigiMelt melting point apparatus. ^cNot applicable. No noticeable soluble products at 250 $^{\circ}$ C after 8 hours.

Initially, the screening hydrolysis experiments were performed using the model Avicel cellulose with each of the POM-IL using the experimental protocol described above. Our goal was to determine the most efficient POM-IL compound to pursue the hydrolysis of the biomass in hand. Only the PT-IMB system showed considerable amount of sugars being produced from the hydrolysis. This compound was then utilized for the hydrolysis of biomass. Figure 4 shows that within 120 min, approximately 31 wt% of the biomass and 13 wt% of Avicel were converted into water-soluble products (such as the sugars obtained from the deconstructed cellulose); this was a very desirable outcome considering that more than 30 wt% yield achieved within less than 2 h is the current technological benchmark (Pinkert *et al.* 2009). It also compared quite favorably to a series of other experiments of biomass dissolution in ILs in the absence of POM, typically in the range of 3 to 25 wt% solubilization within >2 h of heating (Pinkert *et al.* 2009).

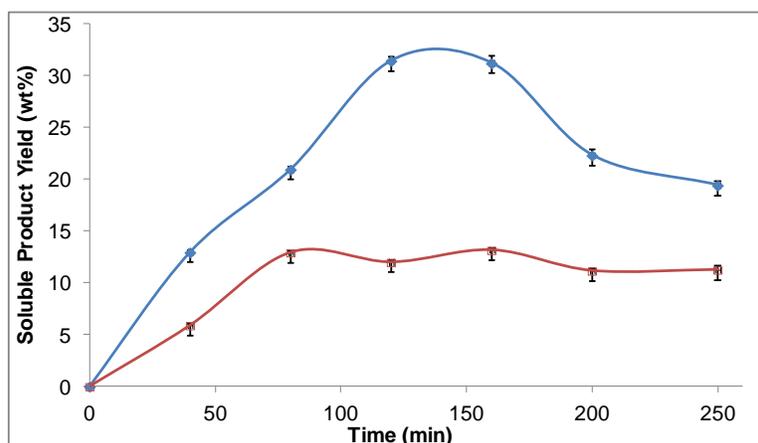


Fig. 4. Soluble product yield for hydrolysis of Avicel cellulose (■) and biomass (◆) with the PT-IMB solution at 200 °C

The total monosaccharide yield as a function of time is shown in Fig. 5. In this reaction occurring at 200 °C, the monosaccharide yield reached a maximum after approximately 150 min; after this point, the rate of consumption of monosaccharides by reactions such as dehydration was faster than the rate of formation of these species.

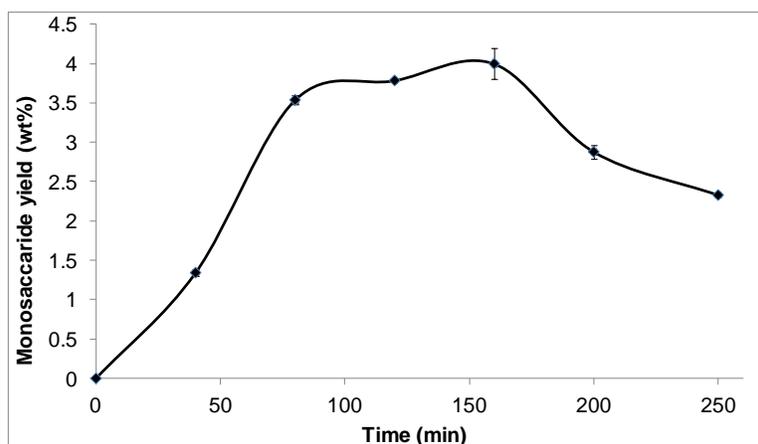


Fig. 5. Total monosaccharide (glucose and xylose) yield (wt%) for hydrolysis of biomass with PT-IMB compound at 200 °C

CONCLUSIONS

A library of four polyoxometalate-based ionic liquid compounds from the combination of two imidazolium ILs and two polyoxometalates was synthesized, and their ability to dissolve powdered switchgrass of the Kanlow variety was investigated. IR spectra revealed that there is effective bonding between the organic cation imidazolium and the POM Keggin anion. The most promising of these synthesized POM-IL compounds was found to be the combination of the phosphotungstic acid hydrate and the 1-butyl-3-methyl imidazolium bromide (IMB). This (PT-IMB) system displayed a biomass solubility of approximately 30 wt%, and the conversion of biomass to

monosaccharides was achieved at 200 °C. After 150 min at this temperature, a maximum monosaccharide (glucose and xylose) yield of approximately 4% (w/w) was recorded, after which a sharp drop in the yield was observed. The observed decrease in the yield might be due to the formation of further products such as furfurals (Ilgen *et al.* 2009). However, this speculation is the subject of further investigations.

ACKNOWLEDGEMENTS

This work was supported primarily by the National Science Foundation under Grant No. EPS-081436. An additional contribution came from the Faculty Research Council grant from Northeastern State University (NSU) and University of Tulsa Department of Chemistry & Biochemistry. The authors would like to thank NSU students Nicholas Hall and Rashad Imayilov for technical assistance.

REFERENCES CITED

- Bourlinos, A.B., Raman, K., Herrera, R., Zhang, Q., Archer, L.A., Giannelis, E.P. (2004). "A liquid derivative of 12-tungstophosphoric acid with unusually high conductivity," *J. Amer. Chem. Soc.* 126(47), 15358-15359.
- Copeland, J. (1974). *Transport Properties in Ionic Liquids*, Gordon and Breach Science Publishers, New York.
- Dai, L., Yu, S., Shan, Y., and He, M. (2004). "Novel room temperature inorganic ionic liquids," *Eur. J. Inorg. Chem.* 2004(2), 237-241.
- Deng, W., Zhang, Q., and Wang, Y. (2012). "Polyoxometalates as efficient catalysts for transformations of cellulose into platform chemicals," *Dalton Trans.* 41, 9817-9831.
- Hsu, W., Lee, Y., Peng, W., and Wu, K. (2011). "Cellulosic conversion in ionic liquids (ILs): Effects of H₂O/cellulose molar ratios, temperatures, times, and different ILs on the production of monosaccharides and 5-hydroxymethylfurfural (HMF)," *Catal. Today* 174, 65-69.
- Hunter, C., and Sanders, J. (1990). "The nature of π - π interactions," *J. Am. Chem. Soc.* 112(14), 5525-5534.
- Ilgen, F., Ott, D., Kralisch, D., Reil, C., Palmberger, A., and König, B. (2009). "Conversion of carbohydrates into 5-hydroxymethylfurfural in highly concentrated low melting mixtures," *Green Chem.* 11(12), 1948-1954.
- Inman, D., and Lovering, D. (1981). *Ionic Liquids*, Plenum Press, New York.
- Jerman, I., Jovanovski, V., Vuk, A., Hočevár, S., Gaberšček, M., Jesih, A., and Orel, B. (2008). "Ionic conductivity, infrared and Raman spectroscopic studies of 1-methyl-3-propylimidazolium iodide ionic liquid with added iodine," *Electrochim. Acta* 53(5), 2281-2288.
- Klemm, D., Heublein, B., Fink, H., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chem.* 44(22), 3358-3393.
- Kuster, B. (1990). "5-hydroxymethylfurfural (HMF). A review focusing on its manufacture," *Starch* 42(8), 314-321.
- Li, Z., Zhang, Q., Liu, H., He, P., Xu, X., and Li, J. (2006). "Organic-inorganic composites based on room temperature ionic liquid and 12-phosphotungstic acid

- compound with high assistant catalysis and proton conductivity,” *J. Power Sources* 158(1), 103-109.
- Marzioletti, T., Valenzuela-Olarte, M. B., Sievers, C., Hoskins, T. J. C., Agrawal, P. K. and Jones, C. W. (2008). “Dilute acid hydrolysis of loblolly pine: A comprehensive approach,” *Ind. Eng. Chem. Res.* 47(19), 7131-7140.
- Misono, M. (2001). “Unique acid catalysis of heteropoly compounds (heteropolyoxometalates) in the solid state,” *Chem. Comm.* 2001(11), 1141-1152.
- Pinkert, A., Marsh, K., Pang, S., and Staiger, M. (2009). “Ionic liquids and their interaction with cellulose,” *Chem. Rev.* 109(12), 6712-6728.
- Okuhara, T., Mizuno, N., and Misono, M. (1996). “Catalytic chemistry of heteropoly compounds,” *Adv Catal.* 41, 113-251.
- Rajkumar, T., and Rao, R. G. (2009). “Investigation of hybrid molecular material prepared by ionic liquid and polyoxometalate anion” *J Chem. Sci.* 120(6), 587-594.
- Rao, G. R., and Rajkumar, T. (2008). “Investigation of 12-tungstophosphoric acid supported on $Ce_{0.5}Zr_{0.5}O_2$ solid solution,” *Catal. Lett.* 120(3-4), 261-273.
- Rickert, P.G., Antonio, M.R., Firestone, M. A., Kubatko, K. A., Szreder, T., Wishart, J. F., and Dietz, M. (2007), “Tetraalkylphosphonium polyoxometalate ionic liquids: novel, organic-norganic hybrid materials,” *J Phys. Chem. B.* 111(18), 4685-4692.
- Román-Leshkov, Y., Barrett, J., Liu, Y., and Dumesic, J. (2007). “Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates,” *Nature* 447, 982-985.
- Sun, N., Rahman, M., and Qin, Y. (2009). “Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate,” *Green Chem.* 11(5), 646-655.
- Swatloski, P., Spear, K., Holbrey, D., and Rogers, D. (2002). “Dissolution of cellulose with ionic liquids,” *J. Am. Chem. Soc.* 124(18), 4974-4975.
- Timofeeva, N. (2003). “Acid catalysis by heteropoly acids,” *Appl. Catal A: General* 256(1-2), 19-35.
- Wu, W., Li, W., Han, B., Zhang, Z., Jiang, T., and Liu, Z. (2005). “A green and effective method to synthesize ionic liquids: Supercritical CO_2 route,” *Green Chem.* 7(10), 701-704.
- Yokozeki, A., Kasprzak, J., and Shiflett, B. (2007). “Thermal effect on C–H stretching vibrations of the imidazolium ring in ionic liquids,” *Phys. Chem.* 9(36), 5018-5026.

Article submitted: November 27, 2012; Peer review completed: February 23, 2013;
Revised version received: March 28, 2013; Accepted: March 29, 2013; Published: April 29, 2013.