Effective Dissolution of Biomass in Ionic Liquids by Irradiation of Non-thermal Atmospheric Pressure Plasma

メタデータ	言語: eng
	出版者:
	公開日: 2017-10-03
	キーワード (Ja):
	キーワード (En):
	作成者:
	メールアドレス:
	所属:
URL	https://doi.org/10.24517/00010862

Effective Dissolution of Biomass in Ionic Liquids by Irradiation of Non-thermal Atmospheric Pressure Plasma

Kosuke Kuroda[A,D], Kai Shimomura[A], Tatsuo Ishijima[B], Kenji Takada[A], Kazuaki Ninomiya[C], and Kenji Takahashi[A,D]

[A]*Division of Natural System, Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*

[B]*Research Center for Sustainable Energy & Technology, Institute of Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*

[C]*Institute for Frontier Science Initiative, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*

[D]Corresponding authors: kkuroda@staff.kanazawa-u.ac.jp (K. Kuroda) and ktkenji@staff.kanazawa-u.ac.jp (K. Takahashi)

Abstract

Biomass was dissolved in ionic liquids under non-thermal atmospheric pressure plasma irradiation. On plasma irradiation, the amount of dissolved biomass in the ionic liquids increased from 15 to 29 mg for bagasse and from 26 to 36 mg for Japanese cedar. The high solubility is attributed to the deconstruction of the lignin network by active chemical species generated by the plasma. Selective extraction of cellulose from biomass was observed under the plasma irradiation.

Introduction

Lignocellulosic biomass has attracted attention as a renewable resource for materials and energy. Because lignocellulose cannot be used as food, it is a potential fossil fuel substitute. However extraction of polysaccharides, the main components of biomass, using solvents is very difficult. This difficulty is mainly due to the tight lignin network,[1, 2] and the inter and intra-molecular hydrogen bonding in cellulose.[3, 4] Therefore, an effective method for extracting polysaccharides is required.

Some liquids are known to act as solvents for cellulose, for example NaOH/water mixtures,[5] LiCl/*N,N*-dimethylacetamide mixtures,[6] and *N*-methylmorpholine *N*-oxide monohydrate.[7] These solvents have some disadvantages, which include their toxicity and limited range of suitable conditions. Recently, ionic liquids (ILs) have been identified as promising solvents for lignocellulose.[8-18] However, dissolution of lignocellulose into ILs is still difficult because destruction of the lignin network with ILs is not easy, while ILs easily dissolve crystalline cellulose. We also have confirmed that

native lignin (cellulolytic enzyme lignin) is hardly soluble in

1-ethyl-3-methylimidazolium acetate ([Emim]OAc, the structure is shown in

Fig. S2, Supplementary Material) (unpublished data). Even 1 wt% of the

native lignin did not completely dissolve in [Emim]OAc at 60 °C, but 14 wt%

of cellulose dissolved in [Emim]OAc at the same temperature. Li *et al.*

overcame this problem by applying high temperatures (over 170 °C) because

high temperatures lead to liquefaction of lignin.[19] However, these harsh

conditions led to considerable decomposition of the ILs (40% decomposition

over 2 h).[20] Abe *et al.* have suggested methodology for the efficient

dissolution of lignocellulose under mild conditions.[21, 22] They generated OH

radicals by adding H_2O_2 to an aqueous solution of tetrabutylphosphonium

hydroxide, an analogue of ILs. The radicals decomposed the lignin structure

and the biomass became highly soluble, even at 60 °C. Although this method

suggested by Abe *et al.* is attractive, it is only applicable to limited types of

ILs—only ILs that contain a hydroxide anion—because lignin decomposition

has been confirmed only under strongly basic conditions.[23] Therefore, this

method is not applicable to most types of ILs.

Plasma chemistry has been studied intensively in recent years for use in green and clean techniques and reports have indicated that the plasma can generate and chemically active species such as radicals and easily inject the active species to various solutions.[24-30] In ILs, plasma techniques are popular for the synthesis of metal nanoparticles,[31] and there are several reports involving organic chemical reactions.[32] When chemically active species are generated in ILs, it is known that the ILs themselves can be converted to secondary active species such as the imidazolium radical, although this depends on the IL species.[33]

Plasma techniques are expected to be useful for the destruction of the lignin network by generating primary and secondary active species, and thus to assist efficient dissolution of biomass into various kinds of ILs. However, there are no studies that use plasma techniques to efficiently dissolve biomass into ILs. In this study, we attempted to efficiently dissolve lignocellulose into the popular IL, [Emim]OAc, by irradiation with

non-thermal atmospheric pressure plasma.

Results and Discussion

Optical emission spectrum of the plasma

The setup for plasma irradiation is shown in Fig. 1. The optical emission spectrum confirmed the presence of active species, OH (309 nm), Hα (656 nm), and O (777 nm)[34, 35], generated by the plasma (Fig. 2). Among these, the OH radical is known to be a particularly strong oxidant; it is stronger than ozone.[36, 37]
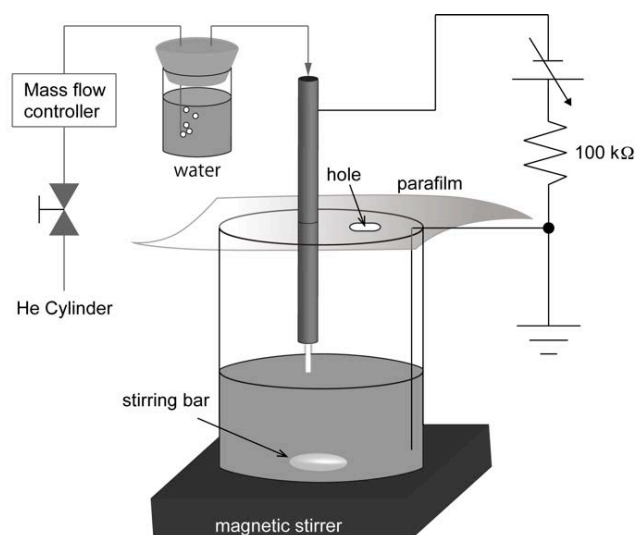
Fig. 1. Experimental apparatus.
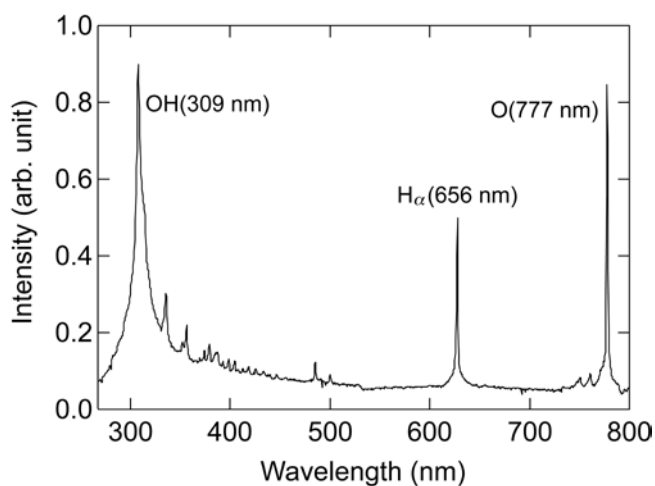
Fig. 2. Optical emission spectrum of the plasma.

Effect of plasma irradiation on biomass dissolution

Table 1 shows the amount of dissolved biomass in [Emim]OAc after 4 h with and without plasma irradiation. On the plasma irradiation, the temperature of the solution increased and became stable at 55–60 °C after 20 min, presumably owing to the electric resistance of [Emim]OAc. As a comparative experiment, biomass was dissolved in [Emim]OAc in an oil bath at 60 °C without plasma irradiation. Bagasse, a herbaceous biomass, was first studied by adding 100 mg to 2.0 g of [Emim]OAc, and the dissolved amount increased from 15 to 29 mg on plasma irradiation. In the case of

Japanese cedar, a woody biomass, the solubilized amount increased from 26 to 36 mg on plasma irradiation. From these results, we concluded that plasma irradiation was effective for the dissolution of biomass.

Table 1. Amount of dissolved biomass and its components (cellulose, hemicellulose, and lignin).

	Solubilized amount (mg)							
	Bagasse				Japanese cedar			
	Cellulose	Hemicellulose	Lignin	Total	Cellulose	Hemicellulose	Lignin	Total
Oil bath (60 ºC)	$-^a$	$-^a$	$-^a$	15	11	3	12	26
Plasma irradiation	$-^a$	$-^a$	$-^a$	29	18	6	13	36^b

^{a}Not measured. ^{b}The mismatch between the sum of the components and the total is due to rounding.

Biomass was dissolved in 2.0g of [Emim]OAc with oil bath heating or plasma irradiation for 4 h. Added amount of biomass was 100 mg.   Components of original Japanese cedar is as follows: 38% of cellulose, 19 % of hemicellulose, and 42 % of lignin.

Next, the solubilized components of Japanese cedar were investigated. As shown in Table 1, the amount of dissolved cellulose was 18 mg with plasma irradiation (38 mg of cellulose is included in 100 mg of

Japanese cedar, as shown in the footnote of Table 1). In contrast, the amount

of dissolved cellulose was 11 mg without plasma irradiation. The difference

in the amount of dissolved cellulose (7 mg: 18−11 mg) made up 70% of the

total increased amount of dissolved Japanese cedar (10 mg: 36−26 mg, as

shown in Table 1). These results therefore show that plasma irradiation

assisted not only the dissolution of biomass, but also the selective dissolution

of cellulose.

To confirm the mechanism for the dissolution, proposed to be the

destruction of the lignin network, the change in the molecular weight

distribution of lignin during plasma irradiation was tracked by gel

permeation chromatography (Fig. 3). We subjected isolated lignin to this

experiment because analysis of the lignin included in biomass is difficult.

Cellulolytic enzyme lignin was selected because this lignin is similar to

natural lignin. This lignin was partly soluble in [Emim]OAc. After plasma

irradiation, the dissolved part was subjected to gel permeation

chromatography.
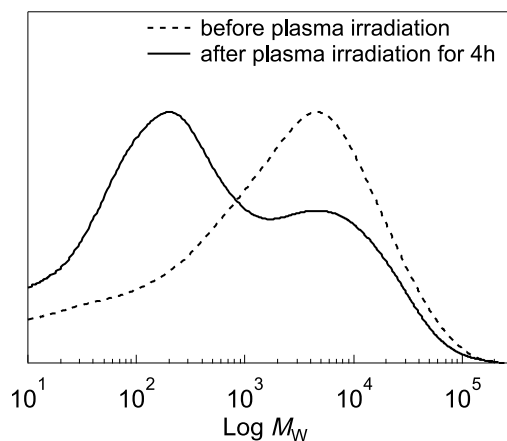
Fig. 3 Molecular weight distribution of lignin before and after plasma

irradiation for 4 h.

The average molecular weight of cellulolytic enzyme lignin without

any treatment was 8,781. After heating at 50 °C for 4h in an oil bath, there is

no significant change of the molecular weight distribution (Fig. S1). On the

other hand, after plasma irradiation for 4 h, the intensity of the peak

corresponding to high molecular weight lignin decreased without shifting

and a new peak in the low molecular weight region was observed. Minor

amounts of phenol, syringaldehyde, and *p*-cresol were found as

decomposition products. These results clearly show that lignin was

decomposed by plasma irradiation, and this is the reason for efficient dissolution. Additionally, the appearance of low molecular weight compounds may indicate that the lignin molecules are easily decomposed from the ends of the network, rather than by random decomposition.

A model compound of lignin, 2-phenoxyacetophenone (5 wt%), was subjected to plasma irradiation after dissolution in [Emim]OAc. It was confirmed that 83% of the 2-phenoxyacetophenone was decomposed during 90 min of plasma irradiation. This indicates that the plasma irradiation cleaves the β-O-4 bond.

Lignin is known to be easily decomposed by active species such as radicals,[23] and the active species generated by the plasma must therefore be involved, either directly or indirectly, in the decomposition of lignin. The OH radical is recognized as a strong radical[36, 37] and can thus decompose lignin. Furthermore, the OH radical reacts with the imidazolium cation and generates the imidazolium radical.[33] Here, we speculate that the imidazolium radical involves decomposition of lignin because there is excess

[Emim]OAc, relative to lignin molecules, at the plasma–solution interface. However, further research is necessary to elucidate the mechanism for the decomposition.

The stability of [Emim]OAc during the plasma treatment was investigated by ^{1}H NMR spectroscopy. Fig. S2 shows the ^{1}H NMR spectra of [Emim]OAc before and after plasma irradiation for 4 h. No new peaks appeared and the integral values of the signals did not change after plasma irradiation (Table S1). This indicates that plasma irradiation does not decompose [Emim]OAc, although it does decompose lignin.

Conclusion

Non-thermal atmospheric pressure plasma was suggested as an efficient method for dissolving biomass into [Emim]OAc. On plasma irradiation, the dissolved amount of biomass increased from 15 to 29 mg (bagasse) and from 26 to 36 mg (Japanese cedar). Selective extraction of cellulose was also assisted by the plasma irradiation. The dissolution

mechanism was confirmed to be destruction of the lignin network. ^{1}H NMR spectroscopy confirmed that decomposition of [Emim]OAc did not occur at all.

Experimental

Materials

Bagasse and Japanese cedar powder (approximately 3 mm particle diameter) were purchased from Sanwa ceruciron. The biomass was ground using a mill and then sieved to obtain a powder with 250–500 μm particle diameter. The biomass was used after drying in a oven at 50 °C for 12h. [Emim]OAc was purchased from Kanto Chemical Co., Inc. and used after drying (water content: 0.3 wt%). 2-Phenoxyacetophenone was purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Non-thermal atmospheric pressure plasma with a He jet

As shown in Fig. 1, a cylindrical glass vessel (15 mm in diameter, 45 mm in length) was partly filled with 2.0 g of [Emim]OAc. In a typical discharge, the applied peak voltage was 3 kV, the pulse width was 5 μs, the repetition frequency was 10 kHz, the distance between the nozzle electrode and the surface of [Emim]OAc was 4 mm, and the He gas flow rate was 600 ml/min. He gas was passed through water before using for plasma irradiation.

Measurement of optical emission spectra

A system consisting of a 300-mm monochromator (ACTON, SpectraPro 2358i) and a gated intensified charge-coupled device camera (Princeton Instruments, PI-MAX-II, UNIGENII) was used.

Dissolution of biomass with plasma irradiation

Dried biomass particles (100 mg) were added to [Emim]OAc (2.0 g). Discharge was performed under stirring for 4 h. The glass vessel was covered

with parafilm to maintain the He atmosphere. The film was perforated to allow the successive flow of He gas.

To determine the dissolved amount of biomass, the solution was filtered through a glass filter after 4 h irradiation and washed with dimethyl sulfoxide. The solid was recovered and dried under reduced pressure. The amount of dissolved biomass was calculated from the mass of the dried solid. The dissolved components of the biomass (cellulose, hemicellulose, and lignin) were also calculated from the components of the solid residue. The components of the solid residue were analyzed using the NERL method.[38]

Preparation of cellulolytic enzyme lignin

We prepared cellulolytic enzyme lignin with referring the literature.[39] Bagasse (100 g) was added to a mixture of choline acetate (100 g) and dimethyl sulfoxide (100 g), and then stirred. The resulting mixture was heated at 110 °C for 16h without stirring. The treated bagasse was washed with excess of water three times. Ultrapure water (900 mL) and cellulase (10

mL, Cellic® CTec2, Novozymes Japan, Ltd.) was then added to the bagasse

and stirred at 50 °C for 72h. After washing the water-soluble fraction with

excess amount of water, residue was dried and used.

Decomposition of lignin by plasma irradiation and characterization by gel

permeation chromatography

Dried lignin (100 mg) was added to dried [Emim]OAc (2.0 g) and the

lignin partly dissolved. The [Emim]OAc/lignin mixed solution was irradiated

with the plasma for 4 h. The sample was then diluted to 5% of the original

concentration with *N,N*-dimethylformamide/LiCl (10 mM) and filtered before

analysis of the molecular weight distribution.

The molecular weight distribution of lignin was determined by gel

permeation chromatography. The system was composed of an SPD-20A UV

detector (Shimadzu Co., 280 nm) and a TSK-gel α-M column (Tosoh

Bioscience). The injected volume of the sample was 20 µL, and the column

was heated at 40 °C. *N,N*-dimethylformamide/LiCl (10 mM) was used as the

mobile phase, and a flow rate of 1.0 mL/min was applied. A calibration curve was created using standard samples of polystyrene (Tosoh Bioscience).

Supplementary Material

Components of Japanese cedar and their fractions, ^{1}H NMR spectra of [Emim]OAc before and after plasma irradiation for 4 h, and integral values of the peaks of the protons in the ^{1}H NMR spectra of [Emim]OAc before and after plasma irradiation for 4 h are available on the journal's website.

Acknowledgments

References

[1]   E. Adler, *Wood Sci. Technol.* **1977**, *11*, 169.

[2]   P. Oinonen, L. Zhang, M. Lawoko, G. Henriksson, *Phytochemistry*

       2015, *111*, 177.

[3]   T. Kondo, *J. Polym. Sci. Polym. Phys.* **1997**, *35*, 717.

[4]   Y. Nishiyama, P. Langan, H. Chanzy, *J. Am. Chem. Soc.* **2002**, *124*,

       9074.

[5]   A. Isogai, R. H. Atalla, *Cellulose* **1998**, *5*, 309.

[6]   C. L. McCormick, P. A. Callais, B. H. Hutchinson, *Macromolecules*

1985, *18*, 2394.

[7]   H. Chanzy, A. Peguy, S. Chaunis, P. Monzie, *J. Polym. Sci. Polym. Phys. Ed.* **1980**, *18*, 1137.

[8]   R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974.

[9]   H. Wang, G. Gurau, R. D. Rogers, *Chem. Soc. Rev.* **2012**, *41*, 1519.

[10]   Y. Fukaya, A. Sugimoto, H. Ohno, *Biomacromolecules* **2006**, *7*, 3295.

[11]   M. Abe, Y. Fukaya, H. Ohno, *Green Chem.* **2010**, *12*, 1274.

[12]   K. Kuroda, Y. Fukaya, T. Yamada, H. Ohno, *Anal. Methods* **2015**, *7*, 1719.

[13]   M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nature Mater.* **2009**, *8*, 621.

[14]   I. Kilpeläinen, H. Xie, A. King, M. Granstrom, S. Heikkinen, D. S. Argyropoulos, *J. Agric. Food Chem.* **2007**, *55*, 9142.

[15]   K. Ohira, Y. Abe, M. Kawatsura, K. Suzuki, M. Mizuno, Y. Amano, T. Itoh, *ChemSusChem* **2012**, *5*, 388.

[16]   H. Liu, K. L. Sale, B. M. Holmes, B. A. Simmons, S. Singh, *J. Phys. Chem. B* **2010**, *114*, 4293.

[17]   K. Yoshioka, T. Yamada, H. Ohno, H. Miyafuji, *RSC Adv.* **2015**, *5*, 72405.

[18]   A. Brandt, J. Gräsvik, J. P. Hallett, T. Welton, *Green Chem.* **2013**, *15*, 550.

[19]   W. Y. Li, N. Sun, B. Stoner, X. Y. Jiang, X. M. Lu, R. D. Rogers, *Green Chem.* **2011**, *13*, 2038.

[20]   M. T. Clough, K. Geyer, P. A. Hunt, J. Mertes, T. Welton, *Phys. Chem. Chem. Phys.* **2013**, *15*, 20480.

[21]   M. Abe, S. Yamanaka, H. Yamada, T. Yamada, H. Ohno, *Green Chem.* **2015**, *17*, 4432.

[22]   M. Abe, Y. Fukaya, H. Ohno, *Chem. Commun.* **2012**, *48*, 1808.

[23]   A. Wu, J. M. Lauzon, I. Andriani, B. R. James, *RSC Adv.* **2014**, *4*, 17931.

[24]   F. Tochikubo, Y. Furuta, S. Uchida, T. Watanabe, *Jpn. J. Appl. Phys.*

2006, *45*, 2743.

[25]   S. Kongmany, H. Matsuura, M. Furuta, S. Okuda, K. Imamura, Y. Maeda, *J. Phys. Conf. Ser.* **2013**, *441*, 012006.

[26]   Y. Himeno, Y. Ogura, T. Shirafuji, *J. Phys. Conf. Ser.* **2014**, *518*, 012021.

[27]   T. Ishijima, H. Hotta, H. Sugai, M. Sato, *Appl. Phys. Lett.* **2007**, *91*, 121501.

[28]   K. Kuroda, T. Ishijima, T. Kaga, K. Shiomomura, K. Ninomiya, K. Takahashi, *Chem. Lett.* **2015**, *44*, 1473.

[29]   T. Ishijima, R. Saito, H. Sugihara, H. Toyoda, *Trans. Mater. Res. Soc. Jpn.* **2011**, *36*, 475.

[30]   T. Ishijima, K. Nosaka, Y. Tanaka, Y. Uesugi, Y. Goto, H. Horibe, *Appl. Phys. Lett.* **2013**, *103*, 142101.

[31]   O. Höfft, F. Endres, *Phys. Chem. Chem. Phys.* **2011**, *13*, 13472.

[32]   M. Yu, L. Y. Zhai, Q. Zhou, C. P. Li, X. L. Zhang, *Appl. Catal. A* **2012**, *419*, 53.

[33]   D. Behar, C. Gonzalez, P. Neta, *J. Phys. Chem. A* **2001**, *105*, 7607.

[34]   S. Mukasa, S. Nomura, H. Toyota, T. Maehara, F. Abe, A. Kawashima, *J. Appl. Phys.* **2009**, *106*, 113302.

[35]   Y. Mizukoshi, R. Katagiri, H. Horibe, S. Hatanaka, M. Asano, Y. Nishimura, *Chem. Lett.* **2015**, *44*, 495.

[36]   G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513.

[37]   P. Neta, R. E. Huie, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 1027.

[38]   A. Suliter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of Structural Carbohydrates and Lignin in Biomass, National Renewable Energy Laboratory, Golden, CO., 2008.

[39]   K. Ninomiya, S. Omote, C. Ogino, K. Kuroda, M. Noguchi, T. Endo, R. Kakuchi, N. Shimizu, K. Takahashi, *Bioresour. Technol.* **2015**, *189*, 203.

Figure captions

Fig. 1. Experimental apparatus.

Fig. 2. Optical emission spectrum of the plasma.

Fig. 3 Molecular weight distribution of lignin before and after plasma

irradiation for 4 h.