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Article

Synthesis of 1,2,3-Triazolium-Based Ionic Liquid and Preliminary Pretreatment to Enhance Hydrolysis of Sugarcane Bagasse

Arturene M. L. Carmo,[a,b] Pedro H. F. Stroppa,[a,b] Roberta C. N. R. Corrales,[b] Anna B. N. Barroso,[b] Viridiana S. Ferreira-Leitão[b,c] and Adilson D. Silva[,a]*

[a]*Departamento de Química, Universidade Federal de Juiz de Fora, Campus Universitário, 36036-900 Juiz de Fora-MG, Brazil*

[b]*Laboratório de Biocatálise, Divisão de Catálise, Instituto Nacional de Tecnologia, 20081-312 Rio de Janeiro-RJ, Brazil*

[c]*Programa de Pós-graduação em Bioquímica do Instituto de Química da Universidade Federal do Rio de Janeiro, 21949-900 Rio de Janeiro-RJ, Brazil*

Os líquidos iônicos (ILs) são sais líquidos a baixas temperaturas, tipicamente com pontos de fusão abaixo de 100 °C. Nos últimos anos, as propriedades de vários ILs têm sido extensivamente estudadas e, em casos específicos, podem ser considerados como solventes verdes capazes de substituir solventes orgânicos tradicionais. Neste trabalho, ILs derivados de triazol tem sido sintetizados e a solubilidade em diferentes solventes aumenta com a constante dieléctrica dos solventes considerados. Três novos ILs 1,2,3-triazólicos foram utilizados para o pré-tratamento do bagaço de cana. O efeito deste pré-tratamento da biomassa lignocelulósica foi analisado por microscopia eletrônica de varredura, mostrando um aumento da superfície de exposição das amostras de bagaço como alterações estruturais na fibra.

Ionic liquids (ILs) are salts which are liquid at low temperatures, typically with melting points under 100 °C. In recent years, the properties of many ILs have been extensively studied and have been considered as green solvents capable of replacing traditional organic solvents. Herein, ILs derived from triazole have been synthesized, thus solubility in different solvents increases with the dielectric constant of the considered solvents. Three novel 1,2,3-triazolium-based were used for the pretreatment of sugarcane bagasse. The effect of this pretreatment on lignocellulosic biomass was analyzed by scanning electron microscopy, showing an increase in the exposure surface of the bagasse samples as structural changes in the fiber.

Keywords: sugarcane bagasse, synthesis, ionic liquids, click reaction, pretreatment

Introduction

Recently, the growing awareness of environmental issues has focused attention on the need for greener and more sustainable technologies in the chemical industry.[1,2]

One of the principles of green chemistry concerns the use of auxiliary substances in order to reduce or eliminate solvent waste in the chemical industry.[2-4] Considering that solvents are often necessary in chemical reactions, alternative solvents have been developed. The ideal solvent should have very low volatility, and it should be chemically and physically stable, recyclable, reusable and easy to handle. One such candidate is ionic liquid (IL).[5] Unlike volatile organic compounds, ILs have a low vapor pressure, which results in safer chemical processes, thereby preventing explosions and fires.[4]

ILs are organic salts, which are liquid at temperatures below 100 °C, show very low vapor pressure, high boiling points and their polarity can be varied in a wide range, depending on the nature of both anions and cations.[5-8] In addition, recycling and reuse and their application in the so called "working solutions".[3-8] ILs have gained wide interest and broad application in academia and also in industries[1,2,9-11]

The most important properties of ILs are: thermal stability, low vapor pressure, electric conductivity, tunable

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*e-mail: david.silva@ufjf.edu.br

solubility (possibility for biphasic systems), liquid crystal structures, high electroelasticity, high heat capacity.[9-14]

Among the various classes of ILs, those containing *N*-heterocyclic cations are most widely used.[12] Imidazolium salts (Figure 1) represent the most prominent subclass in this area and a number of them are commercially available.[15] Their solvent properties, such as melting points, solubility, and viscosity can easily be tuned in a wide range by varying the substituent at the nitrogen atoms, as well as by varying the counter-ions. This makes ILs, in general, real tailor-made solvents.[12-16] Even if imidazolium salts have found very wide application in organic synthesis and catalysis,[17,18] they have some limitations.[12]

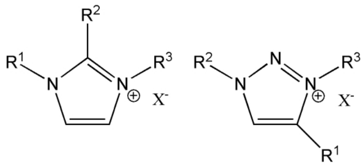
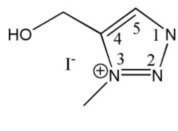


Figure1. General structure of common imidazolium salts and 1,2,3-triazolium salts.

1,2,3-triazolium-based ILs are prepared in a two-step procedure in good yield. In the first step, azide and alkynes are transformed using Cu(I)-catalyzed click reaction and after alkylation affords the ILs. This reaction is an ideal synthesis platform to systematically probe ILs properties due to its excellent molecular control, ease of synthesis, benign reaction conditions, and fidelity.[6,18,19] In short, the Cu(I)-catalyzed click reaction allows easy access to regioisomers and simple variation of functional groups, which enables us to study the effect of structural changes on properties.[6,7,19]

The development of a chemically inert 1,2,3-triazolium-based IL is reported in this work. The stereotype of our novel 1,2,3-triazolium IL is shown in Figure 2.



10 R= $CH_2CH_2CH_3$
11 R= CH_2COOH
12 R= $CH_2CH_2CH_2OH$

Figure 2. Novel 1,2,3-triazolium ILs.

In Brazil, ethanol is largely produced from sugar cane juice, known as first generation ethanol (1G). The residual lignocellulosic biomass from the 1G ethanol industry is currently, for several reasons, the most promising resource for the production of lignocellulosic ethanol, also called second generation (2G).[20] Biofuels produced from lignocellulosic biomass minimize competition with the food chain and increase overall yields in comparison to biofuels from the first generation.[21] Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. The predominant component of lignocellulosic biomass is cellulose, a linear β (1,4)-linked chain of glucose molecules. The main steps for ethanol production from lignocellulosic biomass are pretreatment, hydrolysis, fermentation and distillation/purification. The pretreatment should enhance the fiber accessibility and consequently facilitate the subsequent steps of enzymatic hydrolysis and fermentation.[22]

ILs have been reported to be capable of dissolving cellulose and lignocellulosic materials such as rice straw, wheat straw, sugarcane bagasse and woody biomass.[14,23,24] Pretreatment with ILs can reduce cellulose crystallinity and partially remove hemicelluloses and lignin, not generating degradation products which are inhibitory to enzymes or fermenting microorganisms.[19] Pretreatment with ILs are less energy demanding, easier to handle and more environmentally friendly than other pretreatment methods such as mechanical milling, steam explosion, acid, base, or organic solvent processes.[25-29]

Lee *et al.*[25] have reported a set of ILs which can be used to selectively extract lignin from wood flour and have provided a new route for fractioning lignocellulosic biomass.[4] Cellulose dissolved in ILs can be precipitated by the addition of anti-solvents, like water. A solute-displacement takes place. The ions of the ILs are extracted into the aqueous phase through hydrogen bonding, dipolar and Coulombic forces.[30,31] Water molecules form hydrodynamic shells around the ILs ions. Therefore, the direct interactions of ILs ions with cellulose are shielded. Thus, intra- and inter-molecular hydrogen bonds are rebuilt and cellulose precipitates. However, the structure changes significantly, which can be observed by scanning electron microscopy (SEM).[32]

The cellulose-rich fraction can be precipitated with water, and lignin and other extractives can be removed through multiple washing and solvent evaporation. It is important to mention that the saccharification time can be drastically reduced and the yields of nearly 100% can be achieved after biomass pretreatment using ILs. Li *et al.*[23] have reported that a 12 h saccharification time was sufficient for switchgrass and more than 90% of hydrolysis yield was achieved, whereas the use of dilute sulfuric acid for pretreatment required 72 h for saccharification and resulted in 80% of hydrolysis yield. Although the feasibility of ILs for a large-scale application is still hindered by ILs costs, the use of ILs improved the enzymatic digestibility of biomass significantly in comparison to other known pretreatment methods. Moreover, the use of ILs can provide a better understanding of the interaction mechanisms of ILs with biomass and can be an interesting research topic.[20]

This study reports the synthesis of three non-commercial ILs readily obtained from low-cost reactants. These compounds were assessed as solvents for the pretreatment of sugarcane bagasse. Moreover, their effects on the surface morphology of the pretreated biomass were evaluated by scanning electron microscopy (SEM).

Experimental

Materials and methods

Sodium azide (Vetec), 1-bromopropane (Aldrich, 99%), bromoacetic acid (Aldrich, 97%), 3-bromo-1-propanol (Aldrich, 97%), propargyl alcohol (Aldrich, 97%), (+)-sodium L-ascorbate crystal (Aldrich), copper(II) sulfate pentahydrate (Aldrich, 98%), iodomethane (Aldrich, 99%). Solvents: ethanol (EtOH), acetonitrile, dimethylformamide (DMF), distilled water.

Instrumentation

^{1}H NMR spectra were recorded on Bruker AC-300 and 500 spectrometers at 300.13 and 500.13 MHz and ^{13}C NMR spectra were recorded on a Bruker AC-300 at 75 MHz. The chemical shifts are given in parts per million relative to tetramethylsilane. Mass spectra were recorded on LC-MS/MS-TOF API QSTAR PULSAR spectrometer, and samples were introduced by infusion method using electro spray ionization technique.

Synthesis of the triazoles

Synthesis of (1-propyl-1*H*-1,2,3-triazole-4-yl)methanol (**7**)

In a dry 250 mL round-bottomed flask, sodium azide (15.8 g, 0.243 mol) in 40 mL of EtOH and 40 mL of H_2O distilled was added. Bromopropane **1** (30.0 g, 0.243 mol) was added to sodium azide at room temperature with stirring. Later, the reaction temperature was raised to 60 °C and stirred for 12 h. The mixture was cooled to room temperature, and propargyl alcohol (14.2 mL, 0.244 mol), $CuSO_4.5H_2O$ (0.05 equiv, 0.012 mol) and sodium ascorbate (0.40 equiv, 0.062 mol) were added. The reaction was allowed to proceed at room temperature and monitored by ^{1}H NMR analysis of aliquots. The solvent was evaporated under reduced pressure, and the crude product was washed with EtOH. The precipitate was filtered off and the EtOH evaporated. After that step, were obtained 31.0 g (90%) of the triazole form of brown oil. ^{1}H NMR (300 MHz, D_2O) δ 0.79 (t, 3H, *J* 7.25 Hz, CH_3), 1.83 (sex, 2H, *J* 7.25 Hz, CH_2), 4.32 (t, 2H, *J* 6.97 Hz, CH_2), 4.65 (s, 2H, $C\underline{H}_2OH$), 7.92 (s, 1H, H-triazole); ^{13}C NMR (75 MHz, D_2O + dioxane) δ 16.8, 29.5, 58.3, 61.6, 136.0, 146.7.

2-(4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl)acetic acid (**8**)

Azidoacetic acid **5** (266 mg, 2.00 mmol), propargyl alcohol (196 mg, 2.00 mmol), $CuSO_4$ (16 mg, 0.10 mmol), and sodium ascorbate (40 mg, 0.20 mmol) were suspended in mixed solution of EtOH/water (4 mL, 1/1) at room temperature. After the mixture was stirred for 48 h, a brown oil from the reaction was obtained. Filtration and washing with EtOH afforded **7** (460 mg, 100%) as a brown oil. ^{1}H NMR (300 MHz, D_2O) δ 4.64 (s, 2H, $C\underline{H}_2OH$), 5.18 (s, 2H, $C\underline{H}_2COOH$), 7.91 (s, 1H, H-triazole); ^{13}C NMR (75MHz, D_2O + dioxane) δ 59.9, 63.0, 133.9, 155.6, 179.8.

3-[4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl]propan-1-ol (**9**)

3-azidopropan-1-ol **6** (6.0 g, 0.06 mol), propargyl alcohol (2.6 g, 0.05 mol), $CuSO_4$ (0.58 g, 0.002 mol), and sodium ascorbate (3.68 g, 0.018 mol) were suspended in mixed solution of EtOH/water (40 mL, 1/1) at room temperature. After the mixture was stirred for 48 h, a brown oil from the reaction was obtained. Filtration and washing with EtOH afforded **9** (5.8 g, 80%) as a brown oil. ^{1}H NMR (300 MHz, D_2O) δ 2.09 (q, 2H, *J* 6.5 Hz, CH_2), 3.52 (t, 2H, *J* 6.2 Hz, $C\underline{H}_2OH$), 4.47 (t, 2H, *J* 6.9 Hz, CH_2), 4.66 (s, 2H, $C\underline{H}_2OH$), 7.96 (s, 1H, H-triazole); ^{13}C NMR (75 MHz, D_2O + dioxane) δ 38.0, 53.4, 60.8, 64.3, 130.3.

General procedure for synthesis of ILs

In a flask, a mixture of 1,4-dissubstituted-1,2,3-triazole (**7**, **8** or **9**) (5 mmol) and methyl iodide (20 mmol) was stirred at 80 °C for 24 h (procedure used by Y. Jeong and J. S. Ryu).[15] Upon completion of the reaction, the residues formed were removed by filtration, then the reaction mixture was concentrated *in vacuo* to afford 4-(hydroxymethyl)-3-methyl-1-propyl-1*H*-1,2,3-triazole-3-ium iodide **10**, 4-(hydroxymethyl)-1-(carboxymethyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **11** and 4-(hydroxymethyl)-1-(3-hydroxypropyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **12** in 75, 78 and 83% yield, respectively, as a brown liquid.

4-(hydroxymethyl)-3-methyl-1-propyl-1*H*-1,2,3-triazole-3-ium iodide (**10**)

^{1}H NMR (300 MHz, D_2O) δ 0.91 (t, 3H, *J* 7.25 Hz, CH_3), 1.98 (sextet, 2H, *J* 7.25 Hz, CH_2), 4.23 (s, 3H, CH_3), 4.53 (t, 2H, *J* 7.0 Hz, CH_2), 4.85 (s, 2H, $C\underline{H}_2OH$), 8.50 (s, 1H, H-triazole); ^{13}C NMR (75 MHz, D_2O + dioxane) δ 16.1, 28.5, 45.0, 58.3, 61.6, 135.0, 148.9; HRMS (MS-TOF) *m/z*, calcd. for $C_7H_{14}N_3$ [M$^+$]: 156.1137, found: 156.1135.

4-(hydroxymethyl)-1-(carboxymethyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide (**11**)

^{1}H NMR (300 MHz, D_2O) δ 4.26 (s, 3H, CH_3); 4.87 (s, 2H, $C\underline{H_2}COOH$); 5.20 (s, 2H, $C\underline{H_2}OH$); 8.48 (s, 1H, H-triazole); ^{13}C NMR (75MHz, D_2O + dioxane) δ 43.9, 52.9, 135.8; HRMS (MS-TOF) *m/z*, calcd. for $C_6H_{10}N_3O_3$ [M$^+$]: 172.0722, found: 172.0727.

4-(hydroxymethyl)-1-(3-hydroxypropyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide (**12**)

^{1}H NMR (300 MHz, D_2O) δ 2.21 (p, 2H, *J* 6.5 Hz, CH_2), 3.64 (t, 2H, *J* 6.0 Hz, CH_2), 4.24 (s, 3H, CH_3), 4.68 (t, 2H, *J* 6.9 Hz, CH_2), 4.86 (s, 2H, $C\underline{H_2}OH$); 8.53 (s, 1H, H-triazole); ^{13}C NMR (75 MHz, D_2O + dioxane) δ 37.1, 44.2, 57.1, 58.4, 64.1, 135.0, 148.3; HRMS (MS-TOF ES+) *m/z*, calcd. for $C_7H_{14}N_3O_2$ [M$^+$]: 172.1086, found: 172.1084.

Pretreatment

The synthesized ILs (3,0 g) (**10**, **11** and **12**) were mixed with biomass at a 20:1 (ILs:biomass) ratio and heated to 120 °C for 2 h. After pretreatment, 10 mL of distilled water was added into the pretreatment vessel, under ice bath, to recover the biomass. The ILs/water mixture and biomass were separated by vacuum filtration. The solids were repeatedly washed with distilled water to remove any remaining ILs from the samples until the washing solution appeared colorless. Experiments were run in triplicate with three separate batches.

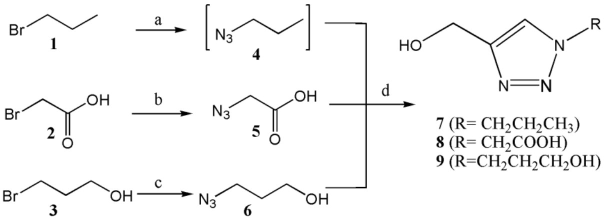
Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM - FEI/FEG-450 model) was used to investigate the morphology of the untreated and treated materials. Samples were adhered to carbon tape, sputter coated with 28 nm gold using an Emitech/K550 model and observed in the SEM through the use of an acceleration voltage of 20 KV and a working distance of approximately 14.5 mm. Several images were obtained on different areas of the samples (at least 20 images *per* sample) to guarantee the reproducibility of the results.

Results and Discussion

Synthesis of 1,4-dissubstituted-1,2,3-triazoles

The triazole derivatives (1-propyl-1*H*-1,2,3-triazole-4-yl)methanol **7**, 2-(4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl)acetic acid **8** and 3-[4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl]propan-1-ol **9** were easily prepared by Cu-catalyzed Huisgen 1,3-dipolar cycloaddition using the corresponding azides (*n*-propyl azide **4** *in situ,* azidoacetic acid **5** or 3-azidopropan-1-ol **6**) and propargyl alcohol (Scheme 1).



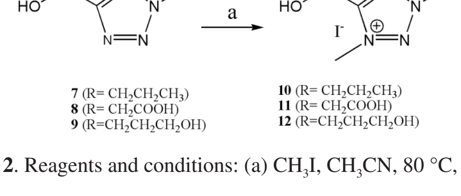
Scheme 1. Reagents and conditions:(a) sodium azide, EtOH/H_2O 1:1, 60 °C, 12 h; (b) sodium azide, H_2O, room temperature, 8 h; (c) sodium azide, DMF, 80 °C, 24 h; (d) $HOCH_2CCH$, $CuSO_4.5H_2O$, sodium ascorbato, EtOH/H_2O 1:1, room temperature, 48 h.

The *n*-propyl azide **4** was generated *in situ* from n-propyl bromide **1** and NaN_3, where it was captured by propargyl alcohol via a Cu^I-catalised azide-alkyne 1,3-dipolar cycloaddition (CuAAC) "click" reaction. The desired triazole product **7** was obtained as a sole product in 80% yield.[33,34] Azidoacetic acid **5**, synthesized by reaction between sodium azide and bromoacetic acid **2** in water,[35] was treated with propargyl alcohol in the presence of copper sulfate and sodium ascorbate in EtOH/H_2O to give 2-(4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl)acetic acid **8** as a sole product in 85% yield.

The 3-[4-(hydroxymethyl)-1*H*-1,2,3-triazole-1-yl] propan-1-ol **9** was obtained through the "click" reaction between propargyl alcohol and azido propanol **6**,[36] previously synthesized by the reaction between bromo propanol **3** and NaN_3 in DMF.

Synthesis of 1,2,3-triazolium ILs[12,21]

4-(hydroxymethyl)-3-methyl-1-propyl-1*H*-1,2,3-triazole-3-ium iodide **10**, 4-(hydroxymethyl)-1-(carboxymethyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **11** and 4-(hydroxymethyl)-1-(3-hydroxypropyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **12** were prepared in one step (Scheme 2). The respective 1,2,3-triazoles **7**, **8** and **9** were treated with an excess of methyl iodide in acetonitrile. The desired dialkylated products **10**, **11** and **12** were isolated as a brown liquid in 75, 78 and 83%



Scheme 2. Reagents and conditions: (a) CH_3I, CH_3CN, 80 °C, 24 h.

yield, respectively. These iodide salts have a boiling point between 191-235 °C.

The three types of 1,2,3-triazolium salts **10**, **11** and **12** are liquids at room temperature. Therefore, all 1,2,3-triazolium salts may be classified as ILs. The thermal stabilities of the 1,2,3-triazoliun compounds might be a concern because they contain three nitrogens. Thermal decomposition temperatures of 1,2,3-triazolium salts were determined by thermogravimetric analysis and are described in Table 1. The solubility of ILs in organic solvents is an important factor for recycling. Thus, we tested the solubilities of 1,2,3- triazolium ILs in several common organic solvents (Table 2). The solubilities increase with the dielectric constant of the solvents. The ionic salts do not dissolve in hexane, AcOEt, Et_2O or CH_2Cl_2 but their solubilities increase in EtOH or H_2O.

Table 1. Thermal decomposition temperatures of 1,2,3-triazolium salts

Ionic liquid	T_d^a / °C
10	191
11	167
12	235

[a]Thermal decomposition temperature.

Table 2. Miscibility of various ILs in organic solvents with dielectric constant ε

Ionic liquid	H_2O	EtOH	CH_2Cl_2	Et_2O	EtOAc	Hexane
10	m	m	nm	nm	nm	nm
11	m	m	nm	nm	nm	nm
12	m	m	nm	nm	nm	nm

m = miscible, nm = nonmiscible. Dielectric constant ε at 20 °C; hexane = 1.89; Et_2O = 4.34; EtOAc = 6 (25 °C); CH_2Cl_2 = 9.08; EtOH = 30.0 H_2O = 78.54.

The structures of the new ILs are in agreement with their ^{1}H NMR data.

Pretreatment and scanning electron microscopy

The effect of pretreatment of sugarcane bagasse with the synthesized ILs was analyzed by SEM. Figure 3 shows the morphological characteristics of the pretreated bagasse with ILs **12** (C and D), **11** (E and F) and **10** (G and H), as well as of the untreated material (A and B), obtained by SEM. Untreated bagasse sample (Figure 3) presents a compact morphology, while the ones submitted to pretreatment with ILs exhibited a more disorganized morphology, with greater exposure of the fibers. The purpose of the pretreatment step is to improve fiber exposure and increase the accessibility to hydrolytic enzymes. Further studies to evaluate sugarcane bagasse pretreatment with novel ILs should include enzymatic hydrolysis.[14,37]

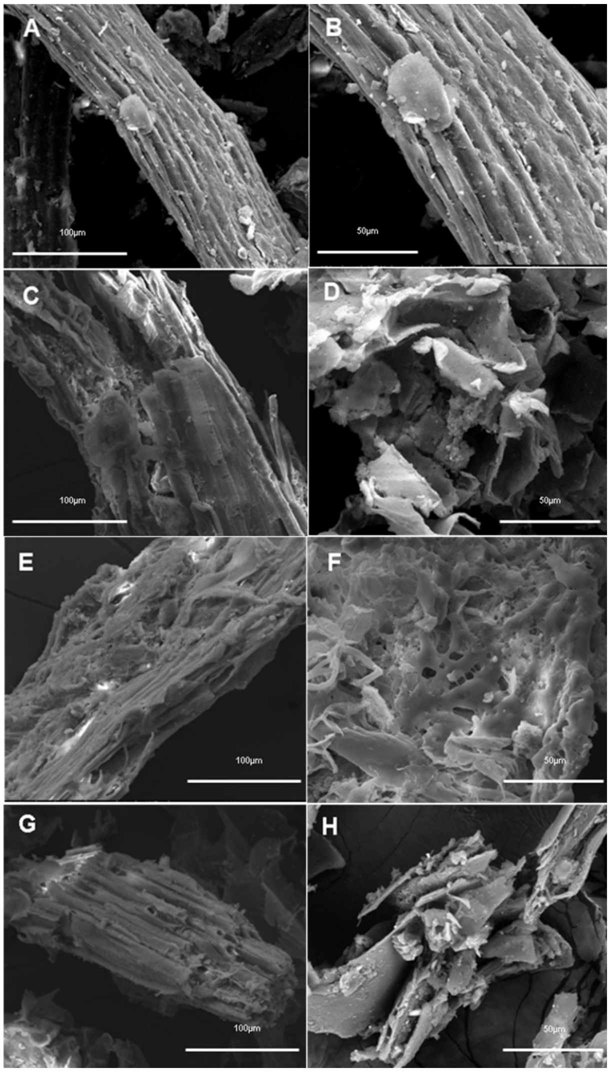


Figure 3. SEM images of the sample of sugarcane bagasse untreated (*in natura*) (A and B), pretreated with ILs **12** (C and D), **11** (E and F) and **10** (G and H). In the left column are the images with magnification of 1000× and in the right column magnification of 2000×.

Conclusions

Three novel ILs chemically inert 1,2,3-triazolium-based 4-(hydroxymethyl)-3-methyl-1-propyl-1*H*-1,2,3-triazole-3-ium iodide **10**, 4-(hydroxymethyl)-1-(carboxymethyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **11** and 4-(hydroxymethyl)-1-(3-hydroxypropyl)-3-methyl-1*H*-1,2,3-triazole-3-ium iodide **12** were prepared in good yields and followed an important principle of green chemistry, which refers to the use of auxiliary substances, in order to reduce or eliminate solvent residues in the chemical industry. Subsequently, the sugarcane bagasse was pretreated with ILs. The effect of pretreatment on lignocellulosic biomass was preliminarily assessed by SEM, showing that the pretreatment promoted structural changes in the fiber, increasing the surface exposure of the bagasse samples, condition required to promote enzyme access for the subsequent step of hydrolysis.

Supplementary Information:

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgements

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