Catalysis Today 223 (2014) 11–17

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Task-specific ionic liquid for the depolymerisation of starch-based industrial waste into high reducing sugars

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ARTICLE INFO

Article history:
Received 10 January 2013
Received in revised form 24 July 2013
Accepted 16 September 2013

Keywords:
Task-specific ionic liquids
Carbohydrates
Reducing sugars
Microwaves
Ultrasounds
Hydrolysis

ABSTRACT

Development of a simple route for the catalytic conversion of starch-based industrial waste (potato peels) and potato starch into reducing sugars was investigated in two ionic liquids for comparison – 1-allyl-3-methylimidazolium chloride [AMIM]Cl and 1-(4-sulfobutyl)-3-methylimidazolium chloride [SBMIM]Cl. Over a two hour period, a 20 wt% solution containing up to 43% and 98% of reducing sugars at low temperature in aqueous [SBMIM]Cl was achieved for the starch-based waste and the potato starch, respectively. In addition, the use of microwave and low frequency ultrasound to perform the depolymerisation of the raw starch-based material was explored and compared with conventional heating processes.

1. Introduction

A growing concern in environmental sustainability in our society has become an important aspect for both ecosystem health and economic development. The intensive consumption of fossil fuels that will eventually run out renders renewable resources as an attractive proposition. Some by-products can be considered as sustainable energy for the synthesis of chemicals [1]. Currently, a Finnish company, which produces pre-cooked vacuum potatoes, generates several tonnes of waste from potato peels daily. In our previous study [2], a weight percentage of sugars were performed on by a total hydrolysis of the by-product, which is mainly composed of glucose (80.2%), mannose (4.9%) and galactose (3.2%). More than 88% can be subsequently considered as the total sugar potential. This by-product is mainly composed of starch, the principal constituent of potatoes. Starch is basely composed of two macromolecules, amylose and amylopectin, trapped into granules. Its depolymerisation into reducing sugars is mainly performed under concentrated strong acidic conditions and/or high temperature, for long reaction time [3,4]. However, starch molecules are not prone to accept water dissolution, notably due to the strong intra and intermolecular hydrogen bonds. These latters can be generally broken down under high temperature, shear and acidic conditions, yielding both free macromolecules [5]. The depolymerisation process in a water medium is therefore of a heterogeneous nature and suffers some inevitable limitations (existence of diffusion layers, limitation of the mass transfer, lack of efficient mixing, etc.), whereas homogeneous media will certainly bring a higher reactivity [6,7]. One possibility for the dissolution of starch is to use ionic liquids [8]. Known as salt with a melting point below 100 °C, ionic liquids possess attracted properties as new generation of solvents, negligible vapour pressure, wide liquid ranges (up to 400 °C) and the ability to dissolve carbohydrate [9]. Dissolution of carbohydrates up to 20-wt% in ionic liquids has been reported previously [10]. In 2006, Remsing et al. investigated the solvation of cellulose in an imidazolium-based ionic liquid bearing a chloride counter-anion [11]. Due to their high nucleophilic capacity, chloride ions are enabled to interact with the hydroxyl protons of carbohydrates and to break down the hydrogen-bonding network to promote dissolution. In our experiments, the first selected ionic liquid was 1-allyl-3-methylimidazolium chloride [AMIM]Cl, which has an excellent ability to dissolve carbohydrates [12] and depolymerise them in the presence of solid catalysts [13] or acid

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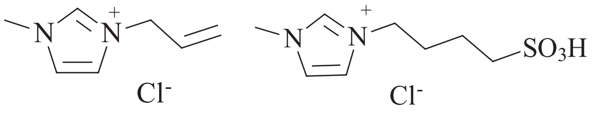
http://dx.doi.org/10.1016/j.cattod.2013.09.027



(A) (B)

Fig. 1. (A) 1-Allyl-3-methylimidazolium chloride [AMIM]Cl and (B) 1-(4-sulfobutyl)-3-methylimidazolium chloride (Brønsted-acidic ionic liquid) [SBMIM]Cl.

[14]. Brønsted acidic ionic liquids (BAILs) possess simultaneously a proton acidity with the Brønsted function and properties of ionic liquids – non-volatile, recyclable [7,15,16]. A wide range of moieties can be classified in the Brønsted framework: mineral acids, sulfonates, phosphonates, and carboxylic acids. Johnson et al. [17] published a detailed review about fundamentals of BAILs and their use in various organic reactions with different location of the Brønsted acid function (anion or/and cation). The strength of the acidity depends on the position of the acidic function; —COOH or —SO_3H function on cation possess strong intrinsic acidity [17]. SO_3H-functionalised ionic liquids are strong Brønsted acids [6,15,18] and possess great potential as dual catalyst/solvent system and non-volatile acidic materials [19]. 1-(4-Sulfobutyl)-3-methylimidazolium chloride [SBMIM]Cl possesses Brønsted-acidic sulfonic group on the cation to play the role of both solvent and catalyst. The chloride anion was preserved to enable the primary target, i.e. the solubilisation of the solute [20].

Both ionic liquids (see Fig. 1 for structures and abbreviations) are already well known in literature as they have been previously employed mainly for the dissolution and hydrolysis of cellulose into reducing sugars [7,21,22,23], and to the best of our knowledge, no studies have been performed on native potato starch and particularly on a real industrial waste material.

The main goal of this research was therefore to dissolve and to depolymerise natural starch-based raw materials into reducing sugars in ionic liquids. To overcome the viscosity of these ionic liquids, we decided to explore the effect of low frequency ultrasound and microwave irradiation. Whereas the rapid heating of microwave irradiation can decrease the viscosity and thus enhance mass transfer, low frequency ultrasound, through their strong mechanical effects (harsh mixing, local heating, mass transfer, etc.) may help to stir in an efficient way the ionic liquids phase [24,25].

2. Materials and methods

2.1. Materials and preparation of ionic liquids

Three different raw materials were utilised for comparison: potato starch, wet potato sludge and dry potato sludge. Potato starch was purchased at a local supermarket, composed solely of starch extracted from potatoes and utilised as the reference. Wet potato sludge is an industrial by-product composed of waste potato peels. Half centimetre of potato containing peels was roughly removed with a potato rotating peeler machine. The third raw material used is dry potato sludge, which is wet potato sludge dried under a vacuum line and ground with a mortar and pestle prior to use. Loss on drying analyses [2] were performed on potato starch, wet potato sludge and dry potato sludge revealing 10%, 67% and 10%, respectively. These results were confirmed by a thermogravimetric analysis performed in a previous study [26].

1-Methylimidazole, allylchloride, 1,4-butane sultone and solvents were purchased from VWR Finland and Sigma–Aldrich France whilst hydrochloric acid 37% (Baker analysed ACS Reagent®, VWR Finland) was commercially available. The ionic liquid [AMIM]Cl was synthesised according to the procedure published by Zhang et al. [27] with minor modifications. A typical procedure is as follows: in an adapted round-bottom flask flushed with argon (10 min), allylchloride (50 mL, 610 mmol) was added dropwise over 1-methylimidazole placed into a water/ice bath (due to exothermic reaction) to achieve 1:1.25 proportions. Afterwards, the solution was stirred for 18 h at 55 °C. The ionic liquid was washed several times with ethyl acetate (3 × 40 mL) and cyclohexane (3 × 40 mL). In order to obtain a clean ionic liquid, activated charcoal and methanol (gradient grade – 50 mL) were stirred with the ionic liquid for 90 min and then filtered on Celite® [28]. The ionic liquid was then dried under a vacuum line and a water-content of 0.1 wt% was measured by Karl Fisher coulometric titration (Metrohm 831KF coulometer) using Hydranal 34843 Coulomat AG-H (Fluka) as titrant. The synthesis of the [SBMIM]Cl was also based on the literature [29] with minor modifications; the detailed protocol was as follows: 1,4-butane sultone (200 mmol) was added dropwise to 1-methylimidazole whilst being stirred in a 250 mL round-bottom flask, flushed with argon for 10 min beforehand. The solution was then heated to 70 °C for 1 h and the resulting solid was then cooled down, crushed and washed several times with toluene and cyclohexane. The zwitterion obtained was dried in a vacuum oven for 12 h (yield > 98%) followed by adding droplets of hydrochloric acid 37% to the zwitterion in stoichiometric proportions. The solution was stirred and heated at 70 °C for 2 h. The resulting mixture was washed with toluene (3 × 20 mL) and cyclohexane (3 × 20 mL) before being cleaned with activated charcoal in methanol (gradient grade – 30 mL) to obtain a clear solution. Ionic liquids are clear compounds, and a more or less yellowish result from traces of compounds originating from the reagents [30]. The solvents were then evaporated with a rotary evaporator and a yellowish ionic liquid was formed in the inner layer of the pear-bottom flask. The ionic liquid was dried again in a vacuum oven for 12 h at 70 °C. NMR and FTIR were performed on both ionic liquids (see Section 2.3) whilst a low frequency (24 kHz) ultrasound bath (Kerry Pulsatron) and a Prolabo Synthewave S402 (electric power 600 W) microwave were employed for depolymerisation.

2.2. Dissolution and depolymerisation methods

A 10 or 20 wt% solution of starch in an ionic liquid medium was stirred or irradiated for 120 min at several temperatures (60–90 °C). The three previously stated materials were then added to the heated solution to ease dissolution. A conical vial of 5 mL with a dedicated triangle magnet was employed for the mechanical stirring reactions. A 10 mL round-bottom flask and a 20 mL tube flask were used for the ultrasound and microwave irradiations, respectively. For the former, the indirect mode of irradiation, i.e. use of an ultrasonic bath, is justified by the acidity of the selected TSIL, whereas the direct mode of irradiation would suggest the use of an ultrasonic probe directly immersed in the solution. This would exposure the probe to corrosion and other damages. To prevent this, an ultrasonic bath filled with water was selected in which the reactor is immersed. A minimum of 10% (w/w) of distilled water was added to the reaction with [SBMIM]Cl in order to dissociate the sulfonic acid function. Afterwards, the sample was dissolved into 10 mL of distilled water and neutralised with crushed pellets of sodium hydroxide. The opaque solutions were then centrifuged at 3000 tr min^{-1} for 10 min or filtered on a filtering funnel with 5–13 μm porosity. The solid phase was recovered, dried under vacuum and weighted to determine the mass balance, while the percentage of total reducing sugars contained in the liquid phase was determined by adapted analytical procedures (see Section 2.3).