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Research paper

Comprehensive study on expeditious conversion of pre-hydrolyzed alginic acid to furfural in Cu(II) biphasic systems using microwaves

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ABSTRACT

Direct expedited conversion of biopolymer alginic acid into the industrially significant compound, furfural, was accomplished using copper (II) salts in various aqueous biphasic systems of defined volume ratios involving successively cyclopentylmethyl ether (CPME), 2-methyltetrahydrofuran (MeTHF) and methylisobutylketone (MIBK); microwave irradiation help perform the reaction at temperatures of ∼200 °C expeditiously in a minute. The deployment of minimum amount of $CuCl_2$ under the optimized conditions afforded furfural in 28, 30 and 31% yields in CPME, MeTHF and MIBK, respectively. However, using the same optimized conditions, both water-soluble and insoluble oligomeric fractions, generated from the pre-hydrolysis of alginic acid, gave furfural in 26 and 35% yields, respectively which were on the basis of oligomers nature found in each fraction.

1. Introduction

Alginic acid is one of the major polysaccharide free of lignin and is easily accessible from biomass [1–3]. This biopolymer is extracted from a variety of microalgae such as brown sea weeds. Structurally, it comprise a copolymer incorporating two kinds of hexuronic acids, mainly β-D-mannuronic acid (MnA) and α-L-guluronic acid (GlA), these elements being all linked *via* β-1,4-glycosidic linkages [4,5]. This class of carbohydrate polymers are initially deployed as starting materials for the production of ethanol or low molecular weight fatty acids *via* biochemical or enzymatic transformations [6,7].

On the other hand, when subjected to a treatment in sub- and supercritical reaction conditions in aqueous medium, alginic acid could be decomposed into organic acids such as formic and malic acid, especially at 150 °C or higher temperatures [8]. Conversely, under basic conditions using NaOH and $Ca(OH)_2$, the hydrothermal decomposition of the biopolymer can produce lactic acid, alpha-hydroxyglutaric acid and glucoisosaccharinaric acid in a temperature range from 95 to 135 °C [9]. Recently, it has been shown that an acid-catalyzed hydrothermal treatment of alginic acid can potentially afford furfural with sufficient yields at 200 °C [10]. This decomposition of alginic acid involved a three-step mechanism which includes sequentially (i) hydrolysis of the glycosidic linkages between each hexuronic acid subunits; (ii) decarboxylation of released sugar species and (iii) dehydration of the ensuing hexoses into furfural.

Furfural or furan-2-carbaldehyde is legitimately recognized as a high value material employed largely for the preparation of a resin precursor, furfuryl alcohol, by the reduction of its carbonyl group. This alcohol is also the starting material for the production of fuel additives such as alkyl levulinate under acidic conditions. Besides, furfural is also useful for the synthesis of organic solvents such as 2-methyltetrahydrofuran (MeTHF) *via* heterogeneously catalyzed reduction and it is often employed precursor in the synthesis of bioactive compounds.

To the best of our knowledge, the hydrothermal conversion of alginic acid to furfural has been exclusively conducted in a monophasic system under conventional heating conditions. These hydrothermal conversions have been promoted by Cu(II) cations at elevated temperatures [11], with heteropoly acids such as 12-tungstophosphoric acids ($H_3PW_{12}O_{40}$) [12], Amberlyst-15 [13] or sulfuric acid [12] under subcritical conditions and in monophasic systems. Consequently, furfural production in a monophasic system is subjected to possible resinification leading to the formation

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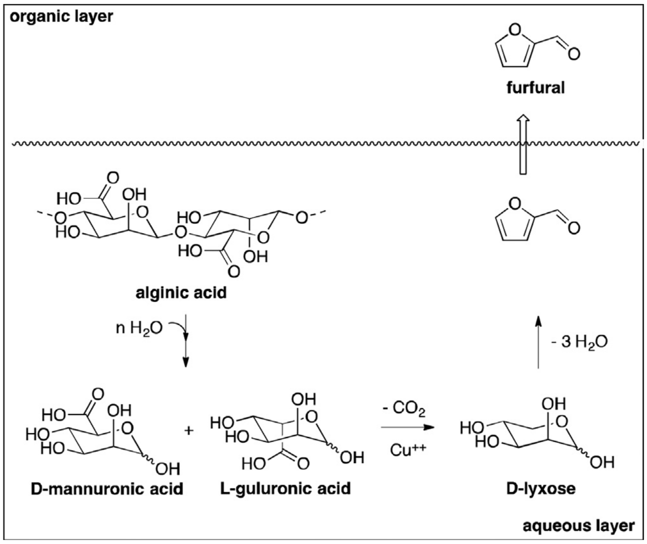

Scheme 1. Copper-catalyzed production of furfural by means of a biphasic system under MW irradiation conditions from native alginic acid.

of a black carbonaceous side-product popularly termed, humin. To prevent humin formation, water immiscible solvent such as methylisobutylketone (MIBK), cyclopentylmethyl ether (CPME) or other aromatic solvent such as toluene could be added to extract and protect the ensuing furfural from the unwanted resinification [14].

In this present work, we describe an expeditious microwave (MW)-expedited reaction that enhances both, the production and selectivity of the hydrothermal conversion of alginic acid into furfural (Scheme 1). Copper salts were employed as the main catalysts and subsequent hydrolysis of alginic acid or its related oligomers, decarboxylation of carbohydrate monomer and finally, the dehydration were investigated by varying successively temperature, residence time, volume ratio's of the biphasic systems and substrate to catalyst ratio's in three different extractive solvents: CPME, MeTHF and MIBK. Optimum conditions were then deployed to effectively produce furfural from the biopolymer.

2. Materials and methods

2.1. Materials

Substrates (alginic acid >95% and glucuronic acid 98%) and the catalysts ($CuCl_2$, $2H_2O$, $CuSO_4$, $Cu(NO_3)_2$ and $Cu(acac)_2$ ≥99%) were purchased from Acros Organics. NaCl were obtained from Carlo Erba. Solvents were purchased from Acros (cyclopentylmethylether), Carlo Erba (dimethylsulfoxide) and Fisher Scientific (2-methyltetrahydrofuran, methylisobutylketone, tetrahydrofuran and acetonitrile ≥99%). Standard (furfural 99%) was obtained from Acros. All materials were used without further purification. Distilled H_2O was used for preparation of all aqueous solutions.

2.2. Typical procedure for conversion of alginic acid into furfural

In a typical experiment, a 10-mL glass vessel was charged with water (0.75 mL), MIBK (3.25 mL), alginic acid or an oligomer rich fraction generated by incubation in an HCl solution (25.0 mg, 0.140 mmol in average based on hexuronic acid units), $CuCl_{2.}$ H_2O (25.0 mg, 0.147 mmol). The vessel was sealed with a septum, placed in the MW cavity (AntonPaar Monowave 300) and heated at 220 °C for 1 min *via* a resonant single mode under magnetic stirring (600 rpm). The reaction temperature in the vessel was monitored by means of an IR sensor. At the end of the reaction, the vessel was cooled down to 40 °C using compressed air. Then, the two phases were separated. The aqueous phase was diluted with 200 mL of distilled water and filtered prior to analysis through a filter paper (10–20 μm, VWR, Fontenay-sous-Bois, France). The organic phase was diluted with 200 mL of acetonitrile and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

2.3. Biopolymer hydrolysis in large batch scale

The partial hydrolysis of alginic acid was conducted as follow: a solution of 0.25 wt% of the polyhexuronic acid was treated with an HCl aqueous solution. The pH was adjusted to 1.7 and the resulted solution was incubated at 95 °C for 20 h. Then, an insoluble material was filtrated and the recovered filtrate was freeze-dried to afford a clear yellow solid.

2.4. Analytical method

Each sample of the reaction mixture was analyzed separately by means of Shimadzu Prominence HPLC. After reaction, the possible hexose and hexuronic traces were detected with a low temperature evaporative light scattering detector (ELSD-LTII) and the furfural concentration was quantified with a UV–vis detector (SPD-H20A) at 280 nm; Grace C18 column (250 × 4.6 nm 5 m) was used as the stationnary phase. The mobile phase used was MeOH-H_2O (1:1) solution flowing at a rate of 0,5 mL min^{-1}. The column oven was set at 40 °C. The calibration was regularly checked in order to avoid eventual experimental errors associated with all measurements reported below. Both materials produced by acidic bath incubation of alginic acid were analyzed by ^{1}H NMR or FT-IR. The ^{1}H and ^{13}C NMR spectra of freeze-dried water soluble hydrozylate were recorded in D_2O and DMSO-d_6 on a Bruker Avance 400 spectrometer. The insoluble fraction was only analyzed by FT-IR.

3. Results and discussion

3.1. Effect of the nature of the organic solvent for the production of furfural

The type of extractive solvent used has a remarkable influence on the partition coefficient of furfural between the two layers of a biphasic system, especially exposed to an acid or a homogeneous catalyst for an extended period. It could also influence the selectivity of different reactions leading to the formation of platform chemicals through the biomass conversion. Herein, water-CPME biphasic system was compared to water-MeTHF and water-MIBK. Prior to the experiments, attempts were made to determine the evolution of the partition coefficient. For instance, when 2.0 mL of an aqueous solution of 0.7 g L^{-1} of furfural was heated up in MW oven at 220 °C for 1 min, in presence of 2.0 mL of fresh CPME, 30% of the initial furfural amount was degraded. Substitution of CPME by MeTHF led to the degradation of 50% of the aldehyde. However, for MIBK, the stability of the furfural was much improved (15% of degradation). These differences could be explained by the properties of the studied organic solvent and of each mixture of aqueous biphasic system. The relationship between the dielectric constants at 25 °C (CPME 4.8; MeTHF 7.0 and MIBK 13.1) and the degradation of furfural is not linear. On the other hand, two good correlations have been discerned for the degradation of furfural: (i) the boiling points (CPME 106 °C, MeTHF 80 °C and MIBK 116 °C) and (ii) the azeotropic temperature (H_2O-CPME 83 °C (16.3:83.7, v/v); H_2O-MeTHF 71 °C (10.6:84.9, v/v) and H_2O-MIBK 87.9 °C (24.3:75.7, v/v)). It is clear that the degradation of furfural