Ultrasound-assisted acid hydrolysis of cellulose to fine chemicals

Daniel dos Santos (PG), Ubiratan F. Silva (PQ), Cezar A. Bizzi (PQ), Paola A. Mello (PQ), Fábio A. Duarte (PQ), Érico M. M. Flores (PQ) *

**ericommf@gmail.com*
Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil.

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Abstract

Optimized conditions for acid hydrolysis of cellulose were obtained using ultrasound with 4 mol L^{-1} HNO_3, at 30 °C and 60 min.

Introduction

Apart from conventional procedure for biofuels production (e.g. bioethanol), the conversion of biomass has also the potential to provide fine chemicals. It offers the opportunity to access furanic compounds, carbohydrates, aromatic chemicals and an assembly of other chemicals.[1] Biomass transformation on industrial scale uses acid hydrolysis processes at temperatures from 100 to 200 °C by 2 to 6 h. This process can be intensified using ultrasound energy, which improves mass transfer by enhanced turbulence, leading to a micro level mixing.[2] In this work, the conversion of cellulose by acid hydrolysis assisted by ultrasound was investigated at relatively milder operational conditions.

Results and Discussion

Experiments were performed in a cup horn system operating at 750 W and 30% amplitude (Sonics, USA). The study was carried out using a 2^3 factorial design with 6 axial points, 3 central points, in replicates. The following parameters were evaluated: HNO_3 concentration (4, 6 and 8 mol L^{-1}), reaction time (30, 45 and 60 min) and temperature (30, 50 and 70°C). Microcrystalline cellulose, used as sample, was mixed with HNO_3 in a mass ratio according to the factorial design. Sample mass was fixed at 500 mg and the volume of solution was limited to 20 mL. Analysis was performed by using a mass spectrometer with electrospray ionization (Xevo G2 Q-Tof, Waters, USA). Comparison with conversion without using ultrasound was performed under conventional heating (200°C). When ultrasound-assisted hydrolysis was carried out it was possible identify the formation of furfural, furfuryl alcohol and hydroxymethylfurfural. The more intense peaks of furfural were observed when 4 mol L^{-1} HNO_3 was used at 30°C and 60 min of reaction (Figure 1). It is important to mention that incomplete depolymerization of cellulose was observed in all conditions.

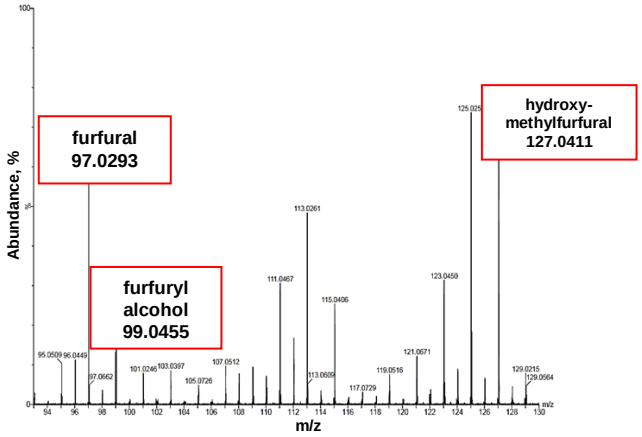

Figure 1 Mass spectrum (4 mol L^{-1} HNO_3, 60 min at 30 ° C).

When the ultrasound-assisted hydrolysis was performed using 6 or 8 mol L^{-1} HNO_3. It was observed a significant reduction in the signal intensity. Biomass conversion for furfuryl alcohol was affected by higher acid concentration. Temperature increase from 30 to 70°C dramatically affected the reaction. Using the conventional process (200°C), furfuryl alcohol and hydroxymethylfurfural were not detected. In addition, higher intensities peaks of cellulose degradation (oligomers and monomers) were observed. Nitric acid did not presented significant effect for biomass conversion by using conventional heating, which suggests that the main effect in the conventional procedure is the high temperature employed.

Conclusions

The proposed ultrasound-assisted acid hydrolysis of cellulose results in fine chemicals at reduced reaction time and temperature, promoting energy gains. The proposed process has the advantage of using lower temperatures and allow the formation of intermediate compounds able to be used in various chemical processes, with high associated value.

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