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DiluteAcid Hydrolysis of Cellulose Assisted By Microwave: How Chlorine and Irradiation Time Play an Important Role

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Running title: Effect of chlorine on cellulose hydrolysis assisted by microwave

Highlights

The addition of NaClenhancescellulose hydrolysis.
NaCl has the ability to tune cellulose hydrolysis products.
NaCl promotes cellulose decrystallization, helping hydrolysis.
Short irradiation time and low temperature avoid humin-like compounds formation.

ABSTRACT:*Cellulose hydrolysis assisted by microwave is lately receiving more attention. Most of these studies are carried out in aqueous phase, and the parameters which are analyzed are microwave power, irradiation time, catalyst nature, catalyst concentration and cellulose loadings. However, in this study, we show how small concentrations of chlorine enhance cellulose hydrolysis to glucose and levulinic acid, against humin-like compounds,at short reaction times and low temperature. As a result, the addition of an inexpensive salt such NaCl, reduces the processing times leading to a more sustainable process.*

KEYWORDS: *cellulose,microwave, hydrolysis, sodium chloride*

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I. INTRODUCTION

Direct combustion remains as the main exploitation route for lignocellulosic materials. However, the different fractions of biomass have a great potential for the production of a wide range of chemical products[1,2]. Biomass' main component, cellulose, is considered as the most abundant polymeric raw material on Earth.Different approaches have been suggested for cellulose hydrolysis, among them the most widespread is enzymatic treatment [3]. Nevertheless, high enzyme cost, strict control of temperature and pH are the current disadvantages which increase the expenses of the final product [4]. Due to its energy efficiency, low reaction times and scalability, microwave technology is a good candidate for replacing enzymatic hydrolysis.

Recently, cellulose hydrolysis assisted by microwave has gained more attention[5,6]. Most of these studies are carried out in aqueous phase, and the parameters which are optimized were microwave power, irradiation time, catalyst nature, catalyst concentration and cellulose loadings[7–9]. However, not so many studies concerning the influence of electrolytes present in this aqueous media are available. For instance, chlorine has been reported to breakdown the hydrogen bond network of cellulose and speeding up cellulose conversion into monomers [10].Furthermore, Potvin et al.hydrolyzed cellulose to glucose and levulinic acid in the presence of NaCl[11]. However, the reaction time, up to 5 days, toobtain a decent yield of products was undoubtedly too long. In order to improvecellulose hydrolysis Tsubaki et al.[12], facilitated the hydrolysis with the microwave assistance.However, the conversion to glucose was only 4%, probably due to the formation of humins at high temperatures [13].For this reason, in this paper we study cellulose hydrolysis assisted by microwave at low temperature, using sulfuric acid as catalyst and adding NaCl in order to reduce the reaction time and increase the products/humins ratio.

II. METHODS

For cellulose hydrolysis, 1 gram of cellulose was placed in a PFTE reactor, dispersed in 20 mL of milliQwater(or 1g/L NaCl solution) and irradiated with a microwave system (Milestone ethos- touch control) at 393 K. All reactions were donein triplicate and the resultswere expressed as mean and standard deviation.The raw cellulose and the obtained solid phase after the hydrolysis reactions, were characterized by XRD[5]. The crystallinityindex (CI) of cellulose was calculated according to a modified Segal method [14].The transformation of cellulose during the hydrolysis experiment was followed by FTIR [15,16]. The FTIR spectra were recorded with a Jasco FT/IR-600 Plus equipped with ATR Specac Golden Gate, with 64 scans using 2 cm^{-1} resolution.

Obtained products were determined by HPLC (Agilent 1100 series) and conversion was determined as means of total organic carbon present in solution after reaction (Shimadzu, TOC-L CSN).

III. RESULTS AND DISCUSSION

During dilute acid hydrolysis of cellulose, different competitive reactions take place. Initially, cellulose chains are broken down into glucose oligomer units, which eventually lead to glucose formation. Glucose can be dehydrated to form 5-hydroxymethylfurfural (HMF), which itself is already a valuable building-block and a desired end product for many research purposes[17–20]. However HMF is not stable under hydrothermally treated acidic aqueous solutions, and rapidly rehydrates forming levulinic and formic acids[21]. Indeed in both cases, cellulose hydrolysis with and without NaCl (Fig 1 and Fig 2, respectively), yielded mostly these products.

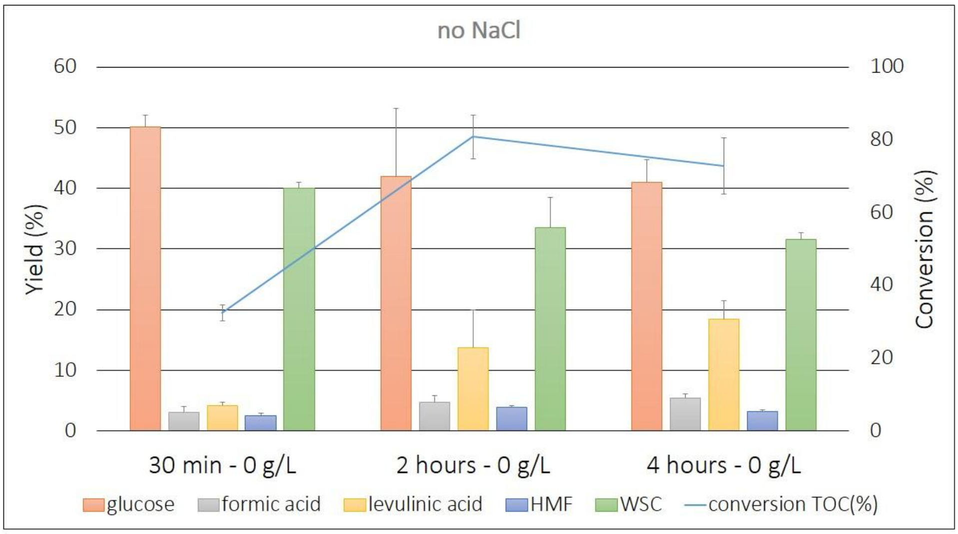

Figure 1. Products and conversion of cellulose hydrolysis at different irradiation times without NaCl

During cellulose hydrolysis without NaCl, besides glucose, which was the main product in all cases, HMF, levulinic and formic acids were detected after hydrolysis plus a percentage of non-identified water soluble compounds (WSC). At 30 minutes, just 32 % of cellulose was converted, and the major detected compound was glucose (around 50 %). When increasing irradiation time, conversion reached 80 % at 2 hours and 73 % at 4 hours, yet glucose was still the major formed product (around 40 %). The slight decrease in conversion after 4 hour of irradiationis attributed to formation of condensation products, potentially humin-like products.

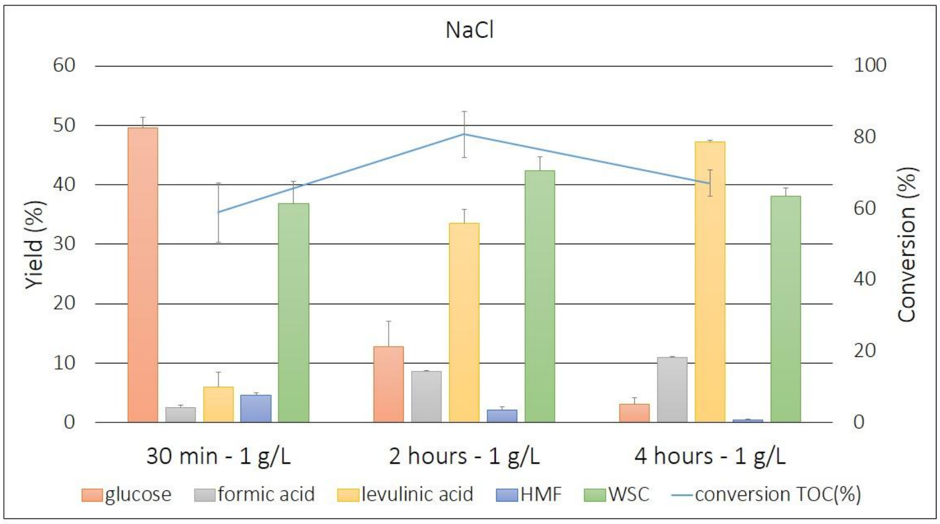

Figure 2. Products and conversion of cellulose hydrolysis at different irradiation times with 1 g/L NaCl.

Interestingly, when 1 g/L of NaClwas added to the reaction media (Fig. 2), cellulose conversion was favored already at 30 min, increasing cellulose conversion from 32 % to 59 %. At 30 min, glucose was still the main product (50%). While at 2 and 4 hours, a strong reduction of glucose formation was observed. In this case, levulinic acid was mainly produced, consequently NaCl does not only increase cellulose conversion; but also influence product formation, producing further glucose degradation products, such as levulinic acid.

FTIR spectra (Fig. 3) showed the different shape for the different recovered solid phases. When cellulose is recovered after 4 hours of treatment, the spectra resembles humin-like structure [13,22] independently whether or not NaCl is present. However, when cellulose is treated during 2 hours, the presence of NaCl changes the FTIR spectrum of cellulose (2 hours 0 g/L) to humin-like spectrum (2 hours 1 g/L). The recovered material after 30 min had a cellulose-like spectrum. Consequently, FTIR also proves that NaCl presence increases degradation rates of cellulose during cellulose dilute acid hydrolysis.

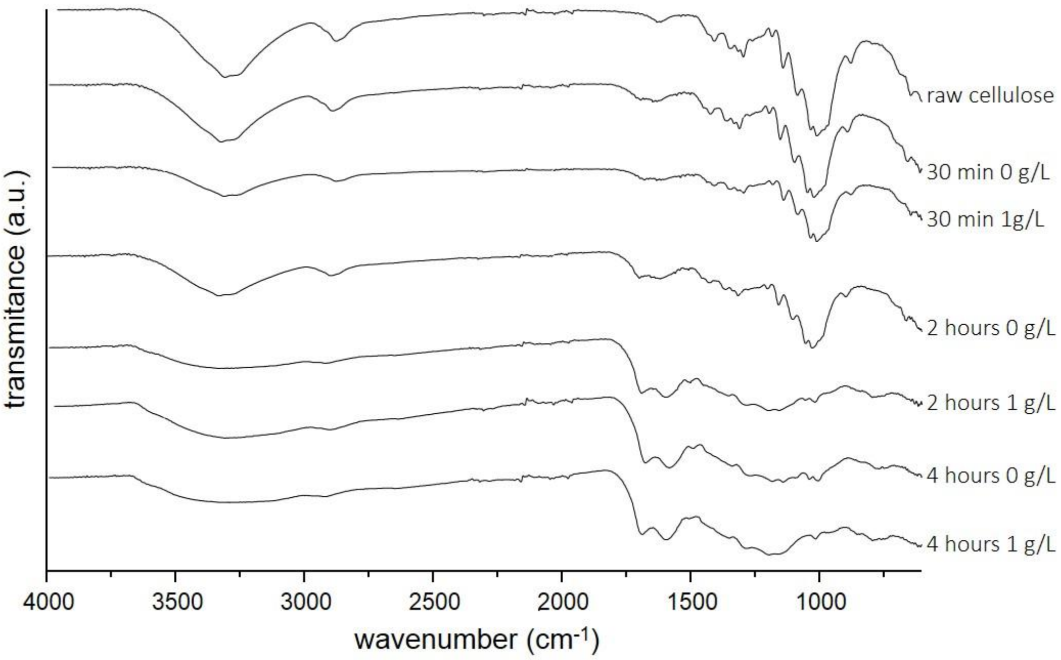

Figure 3.FTIR spectra of all the recovered solid phases after hydrolysis.

Additionally, XRD spectra and CI (Fig. 4), show how CI decreases after treatment. After 4 hours, the recovered material is completely amorphous, for both samples with NaCl and without. However, after 2 hours of irradiation, NaCl has a strong effect on the decrystallization of cellulose as can be seen in Fig.4, having 57 % of CI for the sample without NaCl and 0 % when 1g/L NaCl is present. All together, we suggest that destabilization of the hydrogen bond network of cellulose by chlorine ions or stabilization of intermediate products might facilitate cellulose hydrolysis.

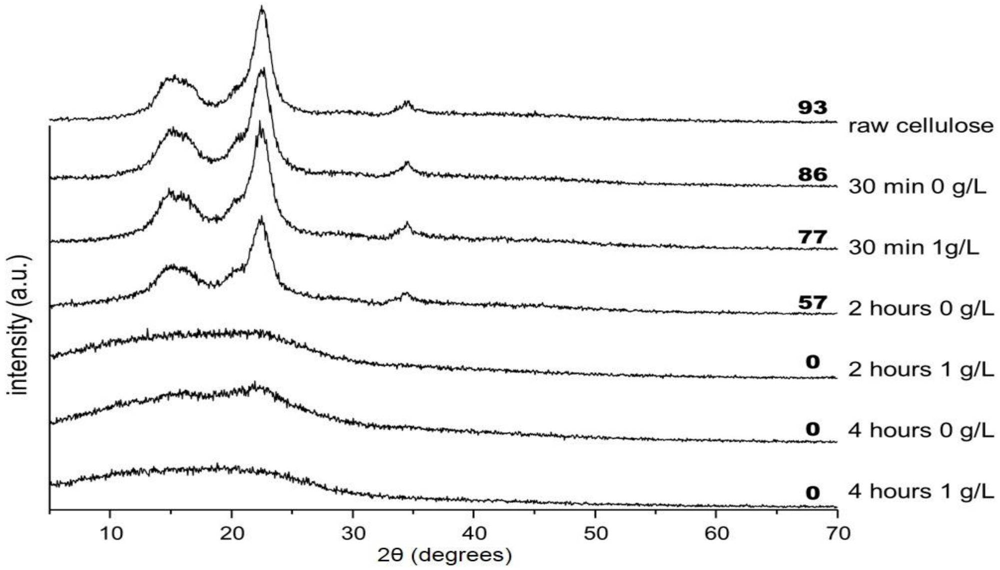

Figure 4.XRD spectra and CI of all the recovered solid phases after hydrolysis.

IV. CONCLUSIONS

In this study, we showed how small concentrations of sodium chloride enhance cellulose hydrolysis, assisted by microwave irradiation, even at short reaction times. As a result, the addition of an inexpensive salt such NaCl, reduces the processing times leading to a more sustainable processes. We also observed that electrolytes have also an influence on the further degradation of glucose, leading to formation of levulinic acid and formic acid. The application of low temperature in the reactor favored the conversion to glucose and levulinic acid againsthumin-like compounds.

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Declaration of interest: none conflict of interest

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