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Influence of reaction parameters on the depolymerization of H_2SO_4-impregnated cellulose in planetary ball mills

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ABSTRACT

The depolymerization of acid-impregnated cellulose in planetary ball mills was investigated under the perspective of the influence of reaction parameters. Several process, technological and chemical parameters were examined. It was found that with a higher rotation frequency ν_{rot}, smaller milling balls and a milling ball filling degree Φ_{MB} of approximately 0.3, the highest solubility could be reached and the milling time could be reduced. The use of milling vessels with larger diameter was beneficial. Variation of the milling ball material showed huge influence and a linear correlation between solubility and density of the milling ball material was observed. Kinetic investigations indicate that the degradation of the impregnated cellulose follows a first order model.

1. Introduction

The interest in the application of renewable feedstocks is steadily increasing and a particular focus was set on the usage of cellulose. This renewable feedstock offers many benefits, as it represents a non-food, abundant and ubiquitously available material. Cellulose is therefore a material of great interest also with regards to synthesis. Here it can serve as starting material including the synthesis of bioethanol or platform chemicals like furfural and others [1]. Unfortunately, the reactivity of cellulose is low and solubilization is challenging due to its crystalline structure [2]. To overcome these drawbacks, various pretreatment methods can be applied. One of these are chemical methods, among which the treatment with sulfuric acid is common [3,4]. Another approach are physical pretreatments which aim to increase the reactivity by reducing the particle size and crystallinity of cellulose. This can be attained by milling, which is often the first step in cellulose pretreatment or for example by exposing the material to mechanical stress by shear deformation under high pressure [1,3,5,6]. Due to the mechanical energy input, the crystalline content of the cellulose becomes amorphous, the particle size is reduced and as a result, the reactivity and accessibility for reagents is increased [7–9]. Furthermore, ball milling reduces the degree of polymerization (DP) to a certain extent [10–12]. However, a lower DP after milling could not be observed in every case [13]. Although milling led to an increased reactivity of cellulose, the solubility in water is only slightly enhanced, even after milling times of several hundreds of hours. For instance, *Grohn* observed that after 300 h milling in a mixer ball mill a solubility of approximately 30% could be achieved [14]. Such long milling time is indeed unfavorable for industrial application. Higher solubility of 44% was reached if mechanical stress was introduced by shear deformation under high pressure (6 GPa) [6].

Beside chemical and physical pretreatment methods, combination techniques like steam-explosion or liquid hot water can be used [3]. Recently, the combination of acidic treatment and ball milling was proven to be an effective way to convert water insoluble cellulose into water-soluble oligomers with up to 100% total conversion [15–19]. Thereby, the application of solid acids as well as H_2SO_4 or HCl impregnated on cellulose, is possible. The obtained water soluble oligomers have shown to be valuable products that can be further applied for e.g. hydrolysis to sugars, hydrogenation to sugar alcohols or synthesis of platform chemicals, as mentioned above [16–18]. Furthermore, this method is not limited to cellulose, as lignocellulosic substrates like beechwood could be completely solubilized [18]. Milling times of approximately 2 h were necessary for the complete conversion of impregnated cellulose to water soluble oligomers [16]. In the presence of solid acids, the milling time is considerably longer. Especially the chemical aspects of this method of depolymerization, like the type and amount of acid, have been investigated. The influence of milling parameters on the reaction, except for the milling time, has not been reported yet [15,16,19]. However, for an efficient depolymerization of cellulose in planetary ball mills (PBMs) and with regard to a further scale-up, optimization of milling parameters is of major relevance.

Our work is focused on the question how reaction parameters influence the cellulose depolymerization, particularly the rotation frequency

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ν_{rot}, the milling ball diameter d_{MB}, the material of the milling balls, the size of the milling vessel, the milling ball filling degree Φ_{MB} and the cellulose filling degree $\Phi_{Cellulose}$. These parameters appeared to be considerable factors for organic synthesis in ball mills and can significantly affect the outcome of a reaction [20–24].

2. Materials and methods

All chemicals were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification. The reactions were accomplished in a Fritsch Pulverisette P6 classic line (PBM P6) and a Fritsch Pulverisette P7 premium line (PBM P7, Fritsch GmbH, Idar-Oberstein, Germany). As not stated otherwise, milling vessels made from stainless or tempered steel were used with a volume of 250 ml for reactions in PBM P6 and with 45 ml for PBM P7. The milling balls applied were made from magnesia-stabilized zirconia. Particle size distributions were determined by static light scattering using an Analysette 22 MicroTec plus (Fritsch GmbH, Idar-Oberstein, Germany) with wet dispersion unit and water as suspending medium.

In order to identify optimal parameter settings and to predict the cellulose solubility for different parameter combinations, a response surface design, based on a quadratic model, was carried out with Design Expert 9.0.3.

General procedure for the impregnation of α-cellulose with H_2SO_4 [16]: 10 g α-cellulose (powder) were added to a solution of H_2SO_4 (5 mmol, 0.49 g) and 150 ml methyl *tert*-butyl ether (MTBE). After stirring for 30 min, the solvent was removed under reduced pressure at 40 °C.

Experimental procedure for reactions in PBMs: The milling vessels were equipped with the milling balls. Afterwards, the impregnated cellulose was added. Milling was accomplished at the respective frequency ν_{rot} and milling time t. In order to reduce the thermal stress of the sample, milling was intermitted by milling pauses. Thereby, pauses of 10 min after $t = 20$ min in PBM P7 and of 7 min after $t = 3$ min in PBM P6 were chosen. The stated milling times refer solely to the milling time, without pauses. The overall reaction times $t_{Reaction}$ can be calculated with Eq. (1) (for PBM P 7) and Eq. (2) (for PBM P6).

$$t_{Reaction} = t + \frac{1}{2}t - 10 \ \text{min} \quad (1)$$

$$t_{Reaction} = t + \frac{7}{3}t - 7 \ \text{min}. \quad (2)$$

Determination of solubility [16,19]: A sample of 1 g was stirred for 5 min in 35 ml water. The solid residue was separated after centrifugation (20 min, 4000 min^{-1}). Afterwards the residue was washed two times with water (35 ml), centrifuged, dried (90 °C, 12 h) and weighed. The solubility was calculated as the difference of the amount of added cellulose and of the solid residue and listed in percentage.

Determination of intrinsic viscosity of the solid residue: The solid residue was treated according to DIN54270 with copper ethylenediamine (CUEN). The viscosity η was determined with an Ubbelohde viscometer. The degree of polymerization DP was calculated based on the following equation (Eq. (3)) [25]:

$$\eta = 2.45 \cdot DP^{0.7}. \quad (3)$$

3. Results and discussion

The outcome of a chemical reaction in a ball mill mainly depends on the amount of energy that is supplied. Several reaction parameters directly influence this energy input. The parameters can be arranged in three categories: process, technological and chemical parameters [26,27].

3.1. Influence of process parameters

Process parameters influence the energy input directly and can be changed or controlled during ball milling. To such significant parameters can be counted variables like the rotation frequency ν_{rot}, milling time t and the temperature T. It could be proven that these three factors are the main ones impacting organic reactions in ball mills [22,28].

3.1.1. Rotation frequency ν_{rot} and milling time t

The effect of the rotation frequency was investigated in a range from 450–650 min^{-1}. The results are presented in Fig. 1 and confirm that a higher frequency leads to increased solubility of the cellulose. For instance, low solubility of approximately 30% was observed at 450 min^{-1} after 20 min milling. An increase to 650 min^{-1} led to considerably higher yields of 80% soluble material. Regarding t, Fig. 1 illustrates that at constant ν_{rot} the solubility increases with longer milling time t. Thus, the solubility increases at 600 min^{-1} from 20% after 10 min to almost quantitative solubility after 50 min. Conversely, the milling time to achieve high solubility could be reduced when ν_{rot} was enhanced.

The results can be explained by the influence of the supplied energy. The energy that is provided to the milled substrate depends on the kinetic energy of the milling balls. A change of the rotation frequency ν_{rot} directly influences the speed of the milling balls and thus their kinetic energy. Furthermore, the number of stress events increases with ν_{rot} and milling time t and in sum more energy is delivered [21,29]. This higher energy input can lead to a higher solubility.

The effect of ν_{rot} and t was shown for several examples, covering a wide field of organic chemistry. For most of the reactions, conversion or yield is increased by increasing the two quantities ν_{rot} and t [23,24,28,30,31]. Only in some cases a plateau like state was observed, indicating that an increase of ν does not lead to an enhancement of conversion [32,33].

3.2. Influence of technological parameters

Technological parameters describe the engineering part of variables that can influence the outcome of a reaction. These include the type of ball mill, the milling vessel size, the filling degree of the milling balls Φ_{MB} and all variables connected with the milling balls e.g. material or diameter d_{MB}. These parameters can be significant, as for example by variation of the ball diameter or material, the kinetic energy of the single balls is changed and thus the energy entry and the outcome of a reaction [20,22].

3.2.1. Vessel size

A parameter that gained less attention when regarding the influence of reaction parameters is the size of the milling vessels [20,34]. Thus, we considered it as worthwhile to investigate the depolymerization of cellulose in several milling vessels that differ in terms of volume and geometry (Table 1). The reactions were performed at constant Φ_{MB}

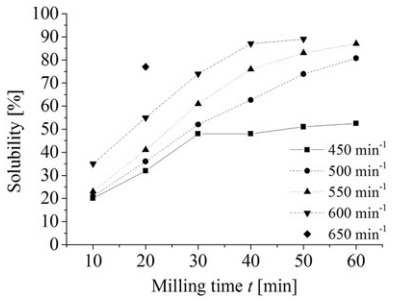

Fig. 1. Influence of the rotation frequency ν_{rot} and milling time t on the solubilization of acid-impregnated cellulose. Conditions: PBM P6, 250 ml steel vessel, ZrO_2-balls, d_{MB} = 10 mm, $\Phi_{MB} = 0.3$, $\Phi_{Cellulose} = 0.5$.