Revisiting the thermal recrystallization of mechanically amorphized lignocellulose

Revisiting the thermal recrystallization of mechanically amorphized lignocellulose

E M Podgorbunskikh[1], A L Bychkov, N V Bulina and O I Lomovsky

Institute of Solid State Chemistry and Mechanochemistry, Russian Academy of Sciences, 630128, Novosibirsk, 18 Kutateladze str., Russia

[1] E-mail: podgorbunskikh@solid.nsc.ru

Abstract. The products of mechanical activation of lignocellulose are subject to the process of recrystallization of amorphized cellulose sections in some cases, this process reduces the efficiency of subsequent chemical and enzymatic treatment of plant raw materials. The process of recrystallization was studied on lignin-containing raw material – wheat straw. The crystal structure, particle and crystallite size of wheat straw ware studied by X-ray diffraction and granulometric analysis. It was found that the degree of crystallinity of cellulose in the composition of wheat straw decreases from 70 to 19 % in the process of mechanical activation in an AGO-2 planetary ball mill, the destruction of cellulose chains is observed predominantly along the [010] direction. The grinding limit was reached after 10 minutes of activation. Thermocycling at the boiling point of liquid nitrogen (-196 °C) and at 180 °C of lignocellulose revealed that under these conditions the degree of recrystallization of amorphous regions of cellulose is negligible, which can be explained by the presence of lignin and a low water content in a material with a material moisture content (about 5.0 wt. %).

1. Introduction

Many researchers note the relationship between the degree of crystallinity decrease in the pretreatment process [1-5] and an increase in the reactivity of lignocellulosic materials in subsequent biotechnological processes. Mechanical activation of lignocellulosic materials is one of the most effective type of pretreatment, designed to enable maximum disordering of crystalline regions of cellulose [6]. Also, thermomechanical treatment of plant materials has been widely used for delignification of lignocellulose, for example, in the production of biofuel [7-8]. However, in some cases, pretreatment can lead to the opposite effect – the recrystallization of cellulose. Amorphized cellulose-containing materials partially undergo ordering of amorphous regions of cellulose [9]. The degree of recrystallization depends on the initial degree of crystallinity of cellulose, the more disordered samples are more susceptible to the action of solvents (for example, water), leading to the recrystallization of amorphous regions [10]. Thus, wetting in water of amorphized microcrystalline cellulose results in a strong reordering of disordered areas of cellulose [11].

However, when comparing the process of recrystallization of pure cellulose and lignin-containing materials, it was found that the presence of lignin tends to restrict the recrystallization cellulose I into cellulose II [12]. In some works, there is no correlation between the degree of crystallinity of cellulose being a constituent of the plant raw material and, for example, the degree of enzymatic hydrolysis [13, 14]. The aim of the present work was to study the process of thermal recrystallization of amorphized lignin-containing plant raw material (wheat straw). We studied the process at a humidity of 5%, but to

gaining a complete understanding of the recrystallization process it is necessary to perform a screening of more water concentrations (for instance 2.0 %, 10.0 %, and 15.0 wt. %) and show that recrystallization increases with increasing water content above 5.0 wt. % loadings.

2. Experimental

We used straw wheat *Triticum durum L* as a lignin-containing material (it was collected in September, 2017 in the Iskitim District of the Novosibirsk Region).

The initial straw wheat was ground in a knife mill to a particle size of less than 500 μm. The mechanical activation of wheat straw was carried out in an AGO-2 laboratory planetary ball mill (Figure 1) with a rotor speed of 630 rpm (the acceleration of the grinding bodies was 200 m/s^2) and a thermostating system. The grinding body mass (steel balls with a diameter of 5 mm) was 200 g, the activated material mass was 10 g; the activation time ranged from 2 min to 20 min. Grinding bodies and wheat straw were loaded into the reactor drums.

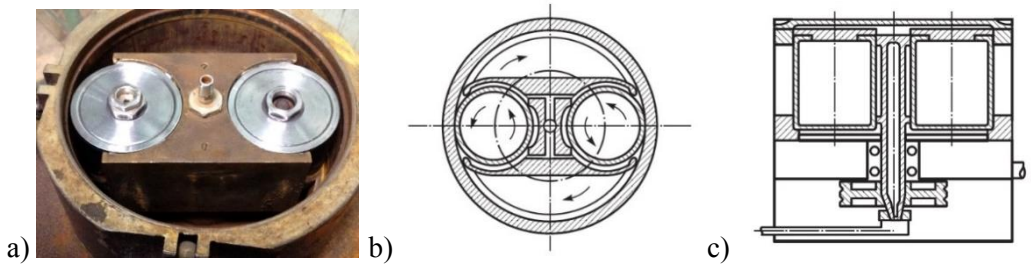

Figure 1. Photo of the planetary ball mill AGO-2 (a); scheme: top view (b), side view (c) [15].

Granulometric analysis of powders was performed on an Analysette-3 Pro vibratory sieve shaker equipped with a set of sieves of 20–2000 μm (FRITSCH, Germany), and using a laser particle size analyzer Microsizer 201 equipped with an ultrasonic disperser (Russia).

After mechanical activation for 20 minutes on the planetary ball mill AGO-2, the samples were subjected to 10 cycles of thermal cycling at boiling point of liquid nitrogen (-196 °C) in an exsiccator and at 180 °C in a laboratory oven with a relaxation time of 60 minutes to room temperature (Figure 2). The samples were held at a thermal cycling temperature for 10 minutes.

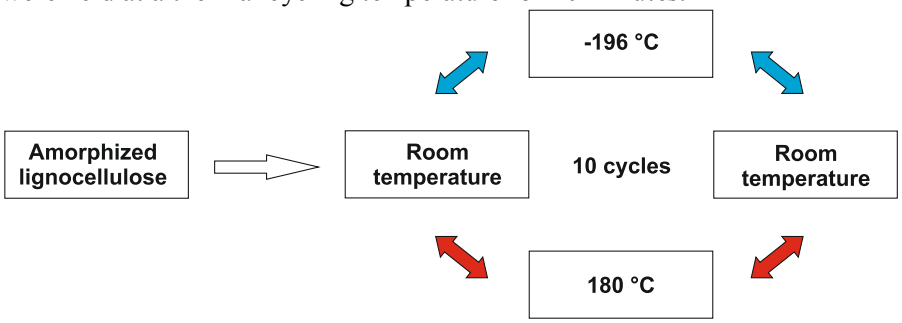

Figure 2. Scheme of thermocycling of lignocellulose.

X-ray phase analysis was carried out on a D8 Advance powder diffractometer (Bruker, Germany) with CuKα radiation in the Bragg-Brentano geometry for reflection. The cellulose crystallite sizes were determined by the Scherrer method using the software package Topas 4.2 (Bruker, Germany). The instrumental contribution was calculated by the fundamental parameter method [16]. The degree of crystallinity of cellulose was determined by the empirical equation proposed by Segal et al [17].

3. Results and discussion

Wheat straw is widely used for the production of second generation biofuels and components of feed additives as a source of cellulose [18]. The used wheat straw is characterized by a high content of

cellulose (50 wt. %), hemicellulose (23 wt. %) with a sufficiently high content of polyphenols (22 wt. % of lignin) [19]. The moisture content of the samples in the experiments was 5.0 wt. %.

The average particle size of the initial lignocellulosic material, previously ground in a knife mill, was 240 μm. The distribution of the particle size of the activation product over 5 minutes of treatment in ball mill is shown in Figure 3. Mechanical activation under these conditions ensures achievement of the grinding limit (Figure 3 (a)). The D50 increased from 240 μm to 14.4 μm (Figure 3 (b)).

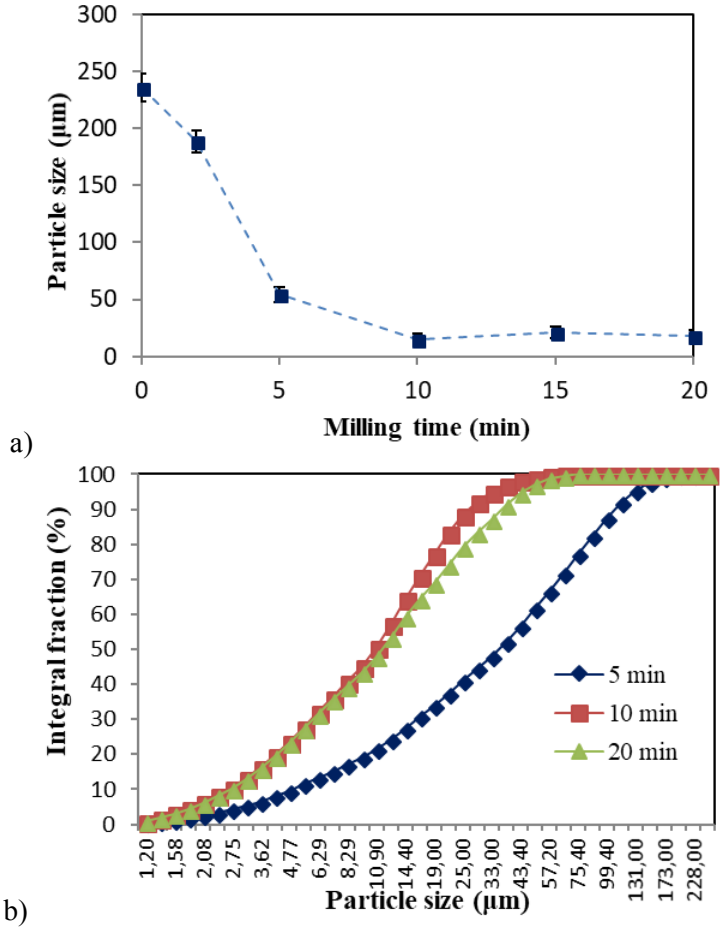

Figure 3. The average particle size of wheat straw after mechanical activation (a), the particle size distribution (b).

The reduction in particle size is one of the indicators of the disordering of the structure of lignocellulosic materials, which is responsible for increasing the available surface area of cellulose for subsequent conversion to low molecular weight sugars.

The crystallite sizes in comparison with the degree of crystallinity calculated by the Segal method for cellulose being a constituent of the plant raw material activated in the AGO-2 laboratory planetary ball mill presented in Table 1. Earlier in our work, a comparison between methods for determining the degree of crystallinity of cellulose in powder X-ray diffraction patterns was made, and the Segal method was shown to be highly applicable [19]. After 10 minutes mechanical activation, a diffuse amorphous halo is observed in the diffraction patterns of the samples, indicating a decrease of cellulose crystallite sizes (Figure 4).

Mechanical activation in the planetary ball mill AGO-2 provides significant disordering of cellulose crystallites. Already after 10 minutes of treatment (Table 1), the degree of crystallinity and cellulose crystallite sizes change slightly. The degree of amorphization directly depends on the mechanical action time on the material.

Table 1. Parameters of the crystalline structure of cellulose in the composition of plant raw materials depending on of the time of mechanical activation.

Activation time (min)	Degree of crystallinity (%)	Crystallite size in the crystallographic directions (nm)		
		[100]	[010]	[110]
Wheat straw initial	70±1	1.1±0.1	2.1±0.2	2.9±0.1
2	66±3	0.9±0.1	1.9±0.1	2.9±0.1
5	57±5	0.8±0.1	1.5±0.2	2.6±0.1
10	24±5	0.8±0.1	0.6±0.1	2.0±0.1
15	27±5	-	-	-
20	19±3	-	-	-

Cellulose is an oriented polymer (orientation of the chain along the *c* axis) [20], which provides an anisotropy of the structure and, as a result, anisotropy of XRD scattering. The cellulose chains of the samples are destroyed under mechanical activation mainly along the [010] direction corresponding to the *b* axis (Table 1). The deep mechanical pretreatment of plant raw materials can lead to an increase in the hygroscopicity of the activation products and the reordering of amorphous regions of cellulose.

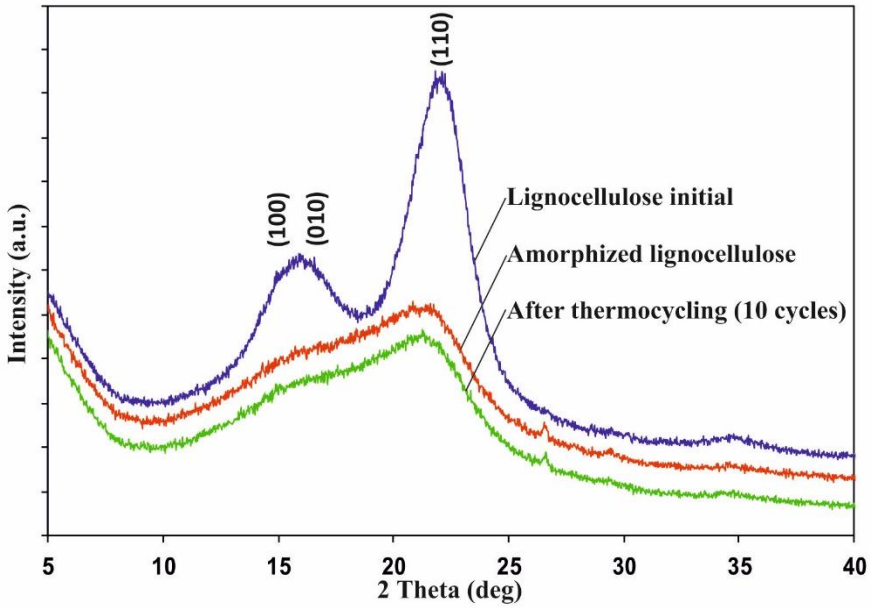

Figure 4. XRD patterns of the initial, after mechanical activation in the AGO-2 planetary ball mill for 20 min and after thermal cycling wheat straw.

The moisture content of plant raw materials affects many technological processes, including the recrystallization of cellulose. Experiments on thermocycling of lignocellulose were carried out according to the data obtained earlier on year-round storage of plant raw materials and products of mechanical activation [21]. It is shown that the use of rooms with reduced humidity provides a moisture content of the material in the range of 4-8%, under these conditions, the physico-chemical characteristics of the lignocellulosic material remain.

The data presented in Table 2 shows a slight change in the degree of recrystallization of amorphized wheat straw in the absence of mechanical action at a moisture content of 5.0%. In the literature [12], there are data on the recrystallization of cellulose I into cellulose II after milling lignocellulosic material.

Table 2. The degree of crystallinity of cellulose before and after thermal cycling.

Pretreatment temperature (°C)	Degree of crystallinity (%)
Lignocellulose initial	70±1
Amorphized lignocellulose (20 min)	19±3
After thermocycling (10 cycles)	20±2

Such a low recrystallization effect can be explained by the fact that supramolecular organization of cell wall polymers of lignocellulose and a low water content (5 wt.%) make it difficult to recrystallize cellulose I into cellulose II. The data mentioned in the literature [9] on the recrystallization of mechanically activated cellulose refers to samples with a high-water content. Thus, in order to exclude the effect of recrystallization during the mechanical treatment of lignocellulose and the associated decrease in reactivity with subsequent chemical and biotechnological processes, the moisture content of the raw materials should be less than 5.0 wt. %.

4. Conclusions

Mechanical activation of wheat straw in the planetary ball mill AGO-2 provides a reduction of the degree of crystallinity from 70 to 19 % and the achievement of the grinding limit to 14.4 μm. A significant decrease in the crystallite sizes from 2.1 to 0.6 nm along the [010] direction is observed. When considering the process of thermocycling of lignocellulosic raw materials, it has been established that the degree of recrystallization of amorphous regions of cellulose with a material moisture content (5.0 wt.%) is negligible. Therefore, when using mechanical treatment to increase the reactivity of lignocellulose, the moisture content of the processed materials should not exceed 5.0 wt.%.

Acknowledgments

This study was supported by the Russian Science Foundation (grant no. 16-13-10200).

References

[1] Zhu L, O'Dwyer J P, Chang V S, Granda C B, Holtzapple M T 2008 Structural features affecting biomass enzymatic digestibility *Bioresour. Technol.* **99** 3817
[2] Yoshida M, Liu Y, Uchida S, Kawarada K, Ukagami Y, Ichinose H, Kaneko S, Fukuda K 2008 Effects of cellulose crystallinity, hemicellulose, and lignin on the enzymatic hydrolysis of Miscanthus sinensis to monosaccharides *Biosci., Biotechnol., Biochem.* **72** 805
[3] Sahare P, Singh R, Laxman R S, Rao M 2012 Effect of alkali pretreatment on the properties and enzymatic hydrolysis of corn cob *Appl. Biochem. Biotechnol*. **168** 1806
[4] Barakat A, Mayer-Laigle C, Solhy A, Arancon R A D, Vries H, Luque R 2014 Mechanical pretreatments of lignocellulosic biomass: towards facile and environmentally sound technologies for biofuels production *RSC Adv.* **4** 48109
[5] Silva A S, Inoue H, Endo T, Yano S, Bon E P S 2010 Milling pretreatment of sugarcane bagasse and straw for enzymatic hydrolysis and ethanol fermentation *Bioresour. Technol.* **101** 7402
[6] Herawan T, Panjaitan F R, Yamanaka S 2018 Morphological and structural changes in microcrystalline cellulose from OPEFB by mechanical grinding *IOP Conf. Series: Earth and Environmental Science* **166** 012001
[7] Bychkov A L, Podgorbunskikh E M, Ryabchikova E I, Lomovsky O I 2018 The role of mechanical action in the process of the thermomechanical isolation of lignin *Cellulose* **25** 1
[8] Zheng J, Rehmann L 2014 Extrusion pretreatment of lignocellulosic biomass: a review *Int. J. Mol. Sci.* **15** 18967
[9] Hermans P H , Weidinger A 1946 On the recrystallization of amorphous cellulose *J. Am. Chem.*

Soc. **68** 2547
[10] Ago M, Endo T, Okajima K 2007 Effect of solvent on morphological and structural change of cellulose under ball-milling *Polym. J.* **39** 435
[11] Wormald P, Wickholm K, Larsson P T, Iversen T 1996 Conversion between ordered and disordered cellulose. Effects of mechanical treatment followed by cyclic wetting and drying *Cellulose* **3** 141
[12] Liang X H, Gu L Z, Ding E Y 1993 Recrystallization behavior of cellulose and lignocellulose from Pinus massoniana *Wood Sci. Technol.* **27** 461
[13] Grethlein H E 1985 The effect of pore size distribution on the rate of enzymatic hydrolysis of cellulosic substrates *Nat. Biotechnol.* **3** 155
[14] Puri V P 1984 Effect of crystallinity and degree of polymerization of cellulose on enzymatic saccharification *Biotechnol. Bioeng.* **26** 1219
[15] Lomovsky O, Bychkov A, Lomovsky I 2016 Mechanical pretreatment *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery* ed S I Mussatto (Amsterdam: Elsevier) chapter **2** 23-55
[16] Cheary R W, Coelho A A 1992 A fundamental parameters approach of X-ray line-profile fitting *J. Appl. Crystallogr.* **25** 109
[17] Segal L, Creely J J, Martin A E Jr, Conrad C M 1959 An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer *Tex Res J.* **29** 786
[18] Borrion A L. McManus M C, Hammond G P 2012 Environmental life cycle assessment of bioethanol production from wheat straw *Biomass bioenergy.* **47** 9
[19] Podgorbunskikh E M, Bychkov A L, Bulina N V, Lomovskii O I 2018 Disordering of the crystal structure of cellulose under mechanical activation *J. Struct. Chem.* **59** 201
[20] O'Sullivan A C 1997 Cellulose: the structure slowly unravels *Cellulose* **4** 173
[21] Bychkov A l, Bukhtoyarov V A, Podgorbunskikh E M, Abramov S Y, Lomovsky O I, Bychkova E S 2016 Changing of humidity on products mechanochemical treatment of plant raw materials during storage *Storage and processing of farm products* **8** 5