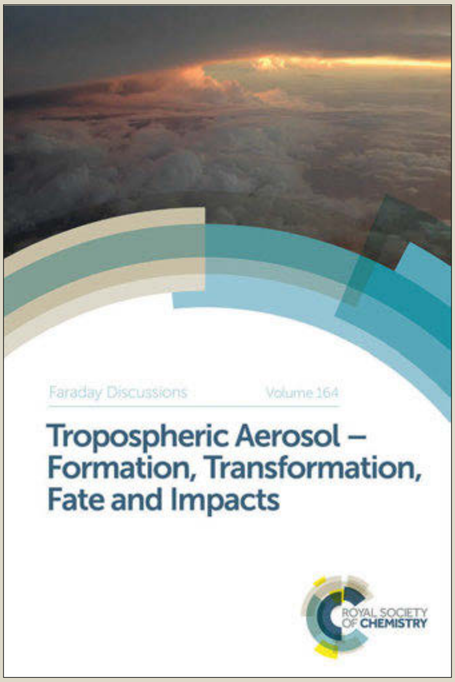
Faraday Discussions

Accepted Manuscript

This manuscript will be presented and discussed at a forthcoming Faraday Discussion meeting. All delegates can contribute to the discussion which will be included in the final volume.

Register now to attend! Full details of all upcoming meetings: http://rsc.li/fd-upcoming-meetings



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/faraday_d

Increasing the Energy Yield of Mechanochemical Transformations: Selected Case Studies

*Anatoly Politov[1,2], Olga Golyazimova[1]

Introduction

Despite the great diversity of mechanochemical reactions, their practical applications still require improvements. In particular, the efficiency of the transformation of mechanical energy into the chemical reaction remains low. A substantial fraction of mechanical energy is consumed for plastic deformation and dissipates in the form of heat to increase the temperature of the substance under treatment and the working volume of the devices. Mechanical initiation of chemical reactions relates to non-thermal methods of increasing reactivity of substances. For the qualitative description of these processes, similarly to the cases of photolysis and radiolysis, it was proposed to describe the efficiency of mechanochemical transformations with the help of the energy-related yield of products [1]

$$G_M \cdot = M/D \quad (1),$$

where M is the amount of product obtained as a result of mechanical treatment, moles;

D is the dose of mechanical energy input, MJ;

G_M is the energy yield (efficiency) of the mechanochemical transformation, mol/MJ.

The energy yield of various processes is $10^{-4} – 10^{2}$ mol/MJ.

Equation (1) can be expressed through the mechanical power input per unit mass of the matter under treatment, and treatment time. The amount of the product will be equal to

$$M = G_M \cdot W \cdot \tau \quad (2)$$

where W is the mechanical powder input, W/g,

τ is treatment time, s.

The energy yield G_M is a characteristic value for a given mechanochemical transformation. According to equation (2), there are two methods to increase the yield of products: to increase either the time of treatment, or the input power. However, both methods cause an increase in energy consumption and result in the contamination of the products. This can be compared with the case of a photochemical reaction: the quantum yield being constant, it is possible to increase the product yield by increasing either the exposure, which in its turn may be increased by increasing the irradiation time or the intensity. For photochemical reactions, in some cases, one may succeed in enhancing the quantum yield by choosing an appropriate sensitizing agent. For

---

* [1]Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk, Russia, [2]Novosibirsk State University, Novosibirsk, Russia. E-mail:anpolitov@yahoo.com, Fax: +7 383 3321550. Tel: +7 903 9981819

many thermal reactions the mechanisms of which have already been studied, catalysts were proposed; they cause an increase in reaction rates and provide the formation of target products at lower temperature and pressure.

The energy yield of a reaction is determined by the physicochemical and mechanical properties of the substances under treatment and seems to be unchangeable. However, in some cases the knowledge of the mechanism of a mechanochemical reaction helps one to find the way to increase the G_M, i.e. to obtain the necessary products with essentially lower power consumption. In the present work we consider selected mechanochemical transformations in inorganic, organic substances, as well as a case study of the enzymatic hydrolysis of biopolymers. We demonstrate how the knowledge of the mechanisms and of the elementary processes allows one to increase the energy yields of these processes. An increase in the efficiency of the mechano-enzymatic hydrolysis of natural polysaccharides is important for such practical applications as obtaining the second-generation biofuel.

The use of mechanical methods to process lignocellulose materials, in order to obtain the second generation biofuel

The biofuel of the second generation is manufactured from fermentable saccharides obtained from natural biopolymers through enzymatic rather than acid hydrolysis. Lignocellulose, and not a food material, serves as the source of biopolymers. Viewed as a solid-state reaction, the formation of saccharides from lignocellulose is a heterogeneous process of depolymerization of natural polysaccharides a resulting from the hydrolysis that takes place at moderate temperature (55 °C) due to the action of a complex of cellulose enzymes. It is important to emphasize, that enzymatic hydrolysis is a solid state reaction, and its course is mainly diffusion controlled. There is a problem related to the delivery of enzymes into the reaction zone. So, first of all, it is necessary to make the substrate surface maximally available for enzymes. Second, the reaction products (saccharides), that inhibit the enzymes and are likely to limit their mobility, are accumulated in the reaction zone. The two problems can be solved using mechanical treatment. It is well-known that grinding of the initial raw material can help to increase the reaction area. However, a wide application of this method is limited by high energy consumption required to obtain fine particles. To solve the second problem, mechanical treatment should be carried out *in situ*, in order to remove the products that get accumulated in the reaction zone. However, as was shown in [2, 3], even mere mixing the solution of reactants in a laminar reactor inactivates the dissolved enzymes. Decreasing energy consumption and increasing the energy yield of the two mechanochemical processes is a challenge.

An increase in the energy yield of grinding lignocellulose materials

The surface-active additives (surfactants) are well-known to have a pronounced effect on decreasing the energy consumption on grinding solids. For example, water is a surfactant for sand, so that the comminution of sand and quartz proceed with higher efficiency (that is, with lower power consumption) in the presence of water. Quite on the contrary, in the case of plant materials, water is a plasticizer for natural biopolymers that are present in plants, and prevents grinding by directing the mechanical energy to plastic deformation. Plants can be considered as a composite material in which sequential hierarchic destruction of components can be achieved. At first, the decomposition of a plant into tissues occurs. At this stage of destruction, particle size becomes comparable with the size of a plant cell and equals tens of micrometers. At the second stage, the cells are destroyed. One cannot fully separate the stages of tissue and cell destruction; long-term treatment involves simultaneous destruction of tissue and cells. To simplify primary destruction, it is necessary to remove the substances that hold tissues together. For fine grinding, it is necessary to affect the cell walls of a plant. Treatment in diluted alkalis or acids destroys the bonds between tissues and simplifies the subsequent destruction of the plant material [4, 5]. However, treatment with acids and alkalis also changes the pH of the plant material and does not belong to ecologically safe technologies. Having studied the structure of the plant cells [6], we have chosen a complex of enzymes to treat the plant material. After this treatment, the destruction of the plant material was even more efficient than after the treatment with acids and alkalis. On the other hand, the treatment with enzymes is an ecologically safe procedure and allows one to use the material for subsequent enzymatic hydrolysis of natural polysaccharides incorporated in the material. The results of this approach are presented in Tables 1 - 2 and in Figures 1 – 2.

Preliminary treatment of plant materials with the enzyme was carried out at 30– 50 °C for 24 h. A so-called empty fruit bunch (EFB) was used as the lignocellulose material in this study. This is a large-scale waste product from the production of palm oil in equatorial countries.

Grinding of dry EFB was performed in the laboratory mill Fritsch pulverisette 5 (Fritsch, Germany) in agate cylinders with agate balls. Rice husk is ground with a laboratory disintegrator DESI 11 (AS Desintegrator, Estonia Republic). The granulometric composition of ground lignocellulose material before and after enzymatic treatment is shown in Table 1.

The efficiency of grinding before and after preliminary treatment of the raw material can be estimated, and the energy yield calculated by a quantitative comparison of the granulometric composition of ground material. The enzymatic treatment increases the efficiency of grinding by a factor of 3 – 4 (Table 2). For instance, after grinding EFB after enzymatic treatment for 10 minutes in the laboratory mill Fritsch pulverisette 5, the amount of the fine fraction is 4 times larger, than after grinding the initial material with the same moisture content.

Table 1 Grinding of lignocellulosic material EFB before and after special pretreatment

Size of particles, micron	Mass fraction of particles, %					
	EFB initial feed stock	EFB before treatment	EFB after treatment	EFB before treatment	EFB after treatment	EFB before treatment
Time of grinding, min	0	10	10	70	70	120
Large 500	69	67	29	26	-	-
300-500	13	18	21	10	1	2
200-300	8	6	15	19	2	5
125-200	5	4	16	13	9	12
80-125	2	2	7	8	15	12
Less 80	3	3	12	24	73	69

The amount of saccharides that passed into solution as a result of preliminary enzymatic treatment was determined. The analysis of the solution showed that the extent of carbohydrate hydrolysis during enzymatic treatment was about 1 – 2 %. So, an insignificant change of the composition causes substantial changes of the mechanical properties of the raw material, and this, in turn, causes an increase in grinding efficiency by a factor of 3 – 4.5 (depending on the particle size).

This effect can be explained in the following way. First of all, the bonding between the tissues is destroyed, which causes an increase in the content of the fraction with particle size less than 125 micrometers. On the other hand, the hydrolysis causes a partial destruction of the cellulose fibers. These defect sites become the concentrators of strain, similarly to the case when a small crack or a cut in the material causes a substantial decrease in its strength.

An increase in grinding efficiency is observed for all kinds of plant material and with different types of mills. It is shown in Table 2 that grinding of rice shells in the disintegrator after preliminary enzymatic treatment occurs is more than 2 times more efficient. The same amount of input energy causes different results. On the other hand, the same size is achieved on treatment of preliminarily processed raw material with lower energy consumption. The particle size distributions in the powders shown in the two last columns of Table 1 are approximately the same.

Table 2 Increase of energy yield of grinded lignocellulosic materials

Feed stock	Time of grinding, type of mill	D < 125 μm, Mass % before treatment	D <125 μm Mass % after treatment	G_M^a / G_M^b	D <50 μm Mass % before treatment	D <50 μm Mass % after treatment	G_M^a / G_M^b
EFB	10 min Fritsch	5	20	4	-	-	-
EFB	70 min Fritsch	32	88	2.75	11	48	4.4
Rice husk	Disintegrator DESI 11	42	90	2.1	-	-	-

However, the energy consumption required to grind the material after preliminary enzymatic treatment was 1.7 times lower.

The rate of substrate hydrolysis depends not only on the particle size, but also on the amorphization degree of cellulose. Efficient grinding (let us call it “smart grinding”) not only destroys the material efficiently, but it also promotes cellulose amorphization.

The diffraction patterns 1 and 2 recorded from the particles 71 – 40 micrometers in size, and diffraction patterns 3 and 4, recorded from the particles smaller than 40 micrometers are plotted in Figure 1. Samples 1 and 4 were obtained after EFB grinding for 120 minutes, while samples 2 and 3 were obtained after EFB grinding for 70 minutes. The crystallinity index of cellulose, calculated from the intensities of diffraction reflections at 17 and 22 angular degrees, is equal to 43 for the 71 - 40 μm fraction and 29 for the fraction less than 40 micrometers. The same degree of cellulose amorphization is almost twice faster if achieved after smart grinding.

It was discovered that the fine fraction of lignocellulose material is hydrolyzed to higher transformation degree than the coarse fraction. The results of the enzymatic hydrolysis of the cellulose incorporated in EFB are shown at Fig. 2. The extent of hydrolysis was estimated as the amount of saccharides that passed into the solution. The size of particles in sample 2 was 200 – 300 micrometers. Sample 1 was a fine powder obtained as a result of smart grinding, with the particle size less than 80 micrometers. One can see, that the hydrolysis of the raw material composed of the particles of 200 – 300 micrometers stops at the conversion degree of 15 – 17 %, while the hydrolysis of fine particles proceeds to a higher conversion degree and reaches 35 % after 40 - 45 hours.

An increase in the efficiency of the mechano-enzymatic treatment of the reaction mixture *in situ*

The hydrolysis stops before completion, if the substrate is composed of coarse particles (sample 1, Figure 2). The process stops not only because of a decrease in the substrate availability, but also due to the inactivation or sink of enzymes. If a fresh portion of the enzyme is added to such a sample, the reaction of hydrolysis of natural polysaccharides is resumed and reaches a somewhat higher degree. Our experiments showed that intense mixing of the solution is necessary, to remove the products efficiently from the reaction area. However, it was found, that the activity of the enzyme is very sensitive to mixing. Thus, mixing solution at medium rates causes a noticeable inactivation of the enzymes. The changes of activity on mixing the solution of cellulase enzymes at the frequency of 400 r.p.m. are shown in Figure 3. The activity of the initial solution before mixing was taken as 100 %. After mixing the solution for 2 hours at a temperature of 55 °C the activity of the enzyme accounted for 60 – 70 % of the activity of the initial enzymes. The activity of the enzyme recovered after storage at a temperature of 12 -15 °C. If the activity of the enzyme decreased to 70 %, it recovered almost completely within 6 hours, as it was in the case of experiment 1. A decrease in activity to 60 % occurred either reversibly (as in case 2), or irreversibly (as in case 3). The decrease in activity was observed not only during turbulent mixing (as in our case), but also in the laminar mixing mode [2, 3]. This behavior can be explained considering that the enzyme exhibits its catalytic activity in a certain conformation only. Stretching strain imposed on the enzyme during mixing causes small conformational changes. If deviations from the active conformation are small, this conformation can be recovered. If the conformation changes, however, exceed some critical value, the enzyme partially loses its catalytic activity, and its inactivation is observed. An alternative method of mechanical treatment in situ is using ultrasound. On the one hand, the action of ultrasound accelerates the enzymatic process due to the acceleration of enzyme diffusion and the removal of products. On the other hand, however, the ultrasonic action (similarly to mixing) can cause enzyme inactivation. It this happens, the best treatment mode will be the batch mode, when the ultrasonic treatment is stopped for a certain time interval, in order to allow the enzymes relax and recover to the active conformation.

The correctness of this approach was demonstrated by experiments, the results of which are shown in Figure 4. The treatment with ultrasound was carried out at a temperature below 10 °C, to prevent hydrolysis. The ultrasonic treatment was carried out a) continuously for 45 minutes before the start of hydrolysis (curve 2), and b) discretely, 3 times for 15 minutes (curve 3). In case of the discrete treatment, the sample was first treated before the hydrolysis. After that, the substrate was placed into the reactor, and the enzymatic hydrolysis continued at a temperature of 55 °C for 1 hour. The short treatment with ultrasound was repeated after hydrolysis for 1 hour and after hydrolysis for 2 hours. The discrete (batch mode) treatment of the reaction mixture was shown to be more efficient, than a continuous one; with the same consumption of mechanical energy, the efficiency of hydrolysis after 3 hours is 1.4 times higher; after 6 hours the efficiency is 1.8 times higher. We relate an increase in the energy yield of this process to the higher activity of the enzyme, which is preserved, if mechanical treatment is interrupted and the enzyme conformation can relax. Ultrasonic treatment of the reaction mixture causes an efficient increase in hydrolysis rate (curve 1 in Fig. 4). Hydrolysis without ultrasonic treatment during 3 hours is 1.4 times less efficient, than that in the case of simultaneous mechanical treatment. For hydrolysis during 6 hours, the extrapolation of kinetic curves gives an estimated increase in the efficiency of ultrasonic assistance by a factor of 2.5. We proposed to term the enzymatic hydrolysis proceeding simultaneously with mechanical treatment as mechano-enzymatic hydrolysis.

The case study of the heterogeneous enzymatic hydrolysis of natural oligosaccharides has shown that the effect of mechanical treatment on a process can be not simple. Understanding the mechanisms of the complicated processes involved in the heterogeneous solid-state hydrolysis allowed one to increase the efficiency of the procedure of mechanical action on the reaction.

The efficiency of the mechanical treatment could be improved also for some other reactions which are important for practical applications (Table 3). The improvements became possible after the elementary mechanisms of the reactions, including the nature of the short-lived states arising during mechanical treatment, became clear.

Increasing the efficiency of the formation of stable radicals on mechanical treatment

Another example when the energy yield of a mechanochemical reaction could be efficiently increased is provided by the decomposition of persulfates giving radicals (SO_4^- and SO_5^-) as reaction products. Persulfates, for example, are widely used in advanced oxidation processes (AOPs) for water purification and for the treatment of wastes. This reaction attracts much attention as a pure and efficient method permitting to decrease the amount of organic pollutants. Persulfates dissociate in water to form persulfate anions with a high oxidation potential (E_o = 2.01 V). However, this anion reacts only slowly with many organic compounds. The sulfate radical SO_4^- is a stronger oxidizer (E_o = 2.6 V), than the initial persulfate anion. Similarly to hydroxyl radicals, sulfate radicals act as strong oxidizers with respect to many organic compounds. SO_4^- was shown to be a more efficient oxidant than $OH^\bullet$ is. There are many methods to activate a persulfate anion, for example, with the help of high temperature, UV or using heterogeneous systems, such as photocatalysis with TiO_2 [7]. We demonstrated that SO_4^- and SO_5^- radicals are formed on mechanical treatment of potassium, sodium and ammonium persulfates, and can be preserved in the sample at room temperature for an indefinitely long time. This stability of the radicals allows one to carry out preliminary activation of persulfates at one place and then, even at another place and after a long time, to perform a reaction in which these preliminarily produced radicals would participate. The solid matrix acts as a specific “storage container for the radicals”, since the mobility of the fragments of persulfate molecule at room temperature is low. The amount of radicals that can be obtained during the mechanical treatment of persulfate with the mechanical energy input of 1 W/g is 10^{17} spin/g. So, the energy yield of the formation of mechanical radicals G_M is about 10^{-4} mol/MJ. The value of G_M does not change within the measurement error limit, if different types of mills with different mechanical energy input are used.

The radical mechanism was proposed for the mechanochemical transformations in potassium persulfate [8]. Its limiting stage is the homolytic breaking the S – O bond in the persulfate anion. Mechanical treatment involves the formation of the SO_4 - radical pairs, then – of the isolated SO_4^- – and SO_5^- radicals. Heating causes the transformation of the radicals according to scheme 2 - 4, to give potassium pyrosulfate and molecular oxygen, which are also the products of thermal decomposition of potassium persulfate [8]. The two types of radicals – SO_4^- and SO_5^-

could be detected at a ratio of 1:3 during mechanical treatment, while the expected ratio of primary radicals according to the scheme of the chain radical decomposition of a persulfate ion should be 1:1. To explain this discrepancy, mechanical treatment was supposed to be accompanied, along with the primary reaction of homolytic breakage of O – O and S – O bonds, by the electron transfer from one persulfate ion to another, with the formation of two anion radicals – $S_2O_8^-$ and $S_2O_8^{3-}$. These radicals can be preserved at room temperature in the dark without any noticeable changes for several years. However, under even slight mechanical action, the anion radicals decompose with the formation of SO_4^- and SO_5^- radicals. The $S_2O_8^-$ and $S_2O_8^{3-}$ anion radicals formed during preliminary irradiation are transformed quantitatively into the SO_4^- and SO_5^- radicals under mechanical treatment with the specific power of 1 W/g and the input energy dose of 300 J/g.

Enhancement of the efficiency of silicate amorphization on mechanical treatment

Mechanical treatment of isle silicates and chain silicates in laboratory mills was shown previously to result in the amorphization of their crystal structures [9, 10]. When treated in the planetary mills with the specific mechanical power input up to 10 W/g, they become X-ray amorphous after 25 – 60 minutes, depending on the mineral. So, depending on the mineral, the energy-related yield of the amorphous phase is 0.3 – 0.6 mol/MJ. According to the theory of non-equilibrium short-lived active states, mechanical treatment results in the disordering of the crystal structure and deformation of covalent bonds at the surface of solids. These excited non-equilibrium molecules relax to less deformed and more equilibrated stated within short time intervals $10^{-7} – 10^{-3}$ s. These states can be preserved at low temperatures. The second method to prevent the dissipation of excited states into heat is to use the energy accumulated in the deformed bonds in a chemical reaction, for example with carbon dioxide. During mechanical activation, the gas can react with the solid surface within 10^{-8}-10^{-7} s at atmospheric pressure, when fast relaxation processes are not completed yet. As a result, carbonates will be accumulated, which will promote the amorphization of silicates. Actually, the rate of amorphization during the mechanical treatment of diopside and titanite in the atmosphere of carbon dioxide is about 4 times higher, than that for the activation of these silicates in the air (for equal energy input) [11]. So, treatment in the environment of a chemically active gas causes the formation of carbonates, increases the energy-related yield of the amorphous phase, and finally causes the increase in the reactivity of silicates.

Dimerization of solid anthracene under pressure and shear

"9-10"- Dimerization of anthracene is observed in its ethanol solutions under irradiation with the wavelength of 365 nm (3.4 eV). The absorption of energy quantum with the energy of 3.4 eV causes the formation of an eximer, which can during decomposition convert into a dimer, or relax to restore the initial molecules. To make the dimerization possible, it is important that anthracene molecules should be parallel to each other, and the distance between them should be about 4 Å (Cohen-Schmidt rule) [12].

Table 3 Increasing the Energy Yield of Mechanochemical Transformations G_M

Substance	Products of mechanical Treatment	G_M^b before treatment	Type of pretreatment or *in situ* treatment	G_M^a after treatment	G_M^a / G_M^b
Titanite $CaTiSiO_5$	$CaTiSiO_5$ Amorphous	G_M^b	CO_2 medium	4 G_M^b	4
Anthracene	Dianthracene	G_M^b	hν + shear deformation	500 G_M^b	500
$K_2S_2O_8$	SO_5^- , SO_4^- radicals	$6 \cdot 10^{-4}$	e - irradiation, dose is 0,1 Mrad/g	$6 \cdot 10^{-1}$	1000

These conditions are not fulfilled in the anthracene crystal structure, in which the planes of the nearest molecules are turned with respect to each other nearly at the right angle. Because of this, the photodimerization in this solid should be impossible. Nevertheless, M. Thomas and J. Williams [13] did observe the formation of dimers on irradiation of anthracene crystals in the absorption band at the sites of dislocations. It is necessary to combine irradiation of solid anthracene with shear deformation, in order to carry out anthracene dimerization. These conditions can be created in diamond anvils, which are transparent for the UV radiation. Indeed, almost complete transformation of anthracene into dianthracene was observed under shear and irradiation [14]. The reaction does not proceed at all without shear. However, unexpectedly, shear in the dark (without irradiation) also caused the formation of the dimer [15-17]. No simple explanation of this phenomenon could be suggested, though quantum chemical calculations showed that this reaction should be possible [15]. Dimerization in the dark was followed quantitatively measuring the luminescence and analyzing the products by means of HPLC. The transformation degree was proportional to the shear angle. During dimerization in the dark, a comparable transformation degree was achieved for the shear angle about 500 times larger, than that in the case of light-induced dimerization. The examples of the three reactions considered in this contribution, are very different from each other, some of them shown in Table 3.

In all the cases, in order to suggest an optimum procedure of mechanical treatment and to increase the energy-related reaction yield, it was necessary to study first the mechanisms of the processes. For mechano-enzymatic hydrolysis, it was important to interrupt mechanical treatment and let the system relax. For the formation of radicals, the generation of precursors by means of preliminary irradiation with electrons or UV light was efficient. We think that this procedure will also be applicable to similar reactions that follow the radical mechanism. These compounds include, first of all, peroxides and ionic compounds with covalent bonds, such as dithionates, dithionites, oxalates, etc. As amorphization on mechanical treatment is concerned, it should proceed in the atmosphere of gaseous carbon dioxide not only for silicates, but also for aluminosilicates and zeolites. The proposed procedures are not universal. On the contrary, each reaction requires an individual approach. This holds for mechanochemistry, as it does for reactivity of solids in general [18]. We expect that the investigation of the mechanisms of mechanochemical reactions will allow one to increase the efficiency of mechanical treatment, and to achieve numerous practical applications of mechanochemistry [19].

References

1. P. Yu. Butyagin, I. K. Pavlichev, Reactivity of Solids, 1986, **1**, 361–372.
2. S. E. Charm, B. L. Wong, Biotechnology and Bioengineering, 1970, **12**, 1103 – 1109.
3. Daisuke Taneda, Yoshiki Ueno, Makoto Ikeo, Shohei Okino, Bioresource Technology, 2012, **12**, 154 – 160.
4. O. V. Golyazimova, A. A. Politov, O. I. Lomovsky, Chemistry of Plant Raw Materials, 2009,. **2**, 53 – 57 (Khimiya Rastitelnogo Syrya, in Russian).
5. O. V. Golyazimova, A. A. Politov, Chemistry for Sustainable Development, 2008, **16**, 589 – 592, (Chimiya v Interesach Ustoichivogo Razvitiya, in Russian).
6. T. A. Gorshkova, Plant Cell Wall as a Dynamic System, Nauka, Moskow, 2007 (Rastitelnaya Kletochnaya Stenka kak Dinamicheskaya Sistema, in Russian).
7. B. Roshani, N. Vel Leitner, Journal of Hazardous Materials, 2011, **190**, Issues 1–3, 403–408.
8. V. F. Radtsig, A.A. Politov, Kinetics and Catalysis, 1985, **26**, issue 1, 33 – 40.

9. A. M. Kalinkin, A. A. Politov, V. V. Boldyrev, E. V. Kalinkina, V. N. Makarov and V. T. Kalinnikov , Journal of Materials Synthesis and Processing, 2002, **10**, No. 1, 61-67.

10. A. M. Kalinkin, E. V. Kalinkina, A. A. Politov, V. N. Makarov, V. V. Boldyrev, Journal of Materials Science, 2004, **39**, 5393 – 5398.

11. A. A. Politov, A. M. Kalinkin, E. V. Kalinkina, V. N. Makarov, V. V. Boldyrev, Proceedings of the Fourth International Conference on Mechanochemistry and Mechanical Alloying, Braunschweig, Germany, 2003.

12. A. R. West, Solid State Chemistry and its Applications, John Wiley & Sons, 1985, 742 p.

13. M. Thomas, J.O. Williams. Progress in Solid State Chemistry, 1971, **6,** 119 – 154.

14. A. A. Politov, B. A. Fursenko, V. V. Boldyrev, Doklady Physical Chemistry, 2000, **371**, issue 1-3, 28 - 30.

15. V. M. Tapilin, N. N. Bulgakov, A. P. Chupakhin, A.A. Politov, J. Struct. Chem., 2008, **49**, issue 4, 581 - 586.

16. V. M. Tapilin, N. N. Bulgakov, A. P. Chupakhin, A. A. Politov, A. G. Druganov, J. Struct. Chem., 2010, **51**, issue 4, 635-641.

17. A. A. Politov, A. P. Chupakhin, V. M. Tapilin, N. N. Bulgakov, A. G. Druganov, J. Struct. Chem., 2010, **51**, issue 6, 1064-1069.

18. V.V. Boldyrev, M. Bulens, B. Delmon, Control of the Reactivity of Solids, Elsevier, 1979.

19. E.V. Boldyreva, ChemSocRev, 2013, **42**, issue 18, 7719-7738.

"Increasing the Energy Yield of Mechanochemical Transformations: Selected Case Studies"

Politov A.A., Golyazimova O.V.

Abstract

The products of mechanical treatment are surface atoms or molecules, the substance with the crystal structure different from the initial one (another polymorph, amorphous), point or linear defects, radicals, new chemical substances. It is often assumed, that to increase the yield of the products of a mechanical treatment, it is necessary to increase the treatment time and the mechanical power input. In view of the low energy yield of many mechanochemical transformations, this leads to high power consumption and contamination of the matter under treatment with the wear products of the material of a mill or reactor, in which the mechanical treatment is carried out. As a result, the technological attractiveness of mechanochemical processes comes down, so that many mechanochemical transformations that have been discovered recently do not reach the stage of commercialization. In the present paper we describe different examples of a successful increasing the energy yeild of mechanochemical processes, by a factor from several times to several orders of magnitude, for inorganic and organic substances. An increase in the energy yield of mechanochemical transformations opens new possibilities for their practical usage. In particular, the methods of preliminary treatment and the modes of conducting enzymatic processes that may find application in the production of secondgeneration biofuel are discussed using lignocellulose materials as examples.

Ffigure captions

Fig.1. X-Ray patterns of EFB ground before and after enzymatic treatment. Patterns 1 and 4 correspond to samples that were ground for 120 minutes, patterns 2 and 3 - to those ground for 70 minutes.

Fig.2. Influence of mechanical pre-treatment on the hydrolysis of EFB mechanically treated in two different ways, with the mechanical energy being the same: 1 –EFB ground after enzymatic pretreatment, 2 - EFB ground before enzymatic treatment.

Fig.3. Falls of enzyme activities resulting in stirring during 2 hours and renewals of its activity with storage at 15 ^{0}C. 1, 2 and 3 are independent experiments with equal time of stirring and different time of relaxation

Fig.4. Ultrasonic assistance of enzymatic hydrolysis of cellulose: 1 – without treatment, 2 – continuous treatment during 45 min, 3 – batch treatments (15+15+15) min.

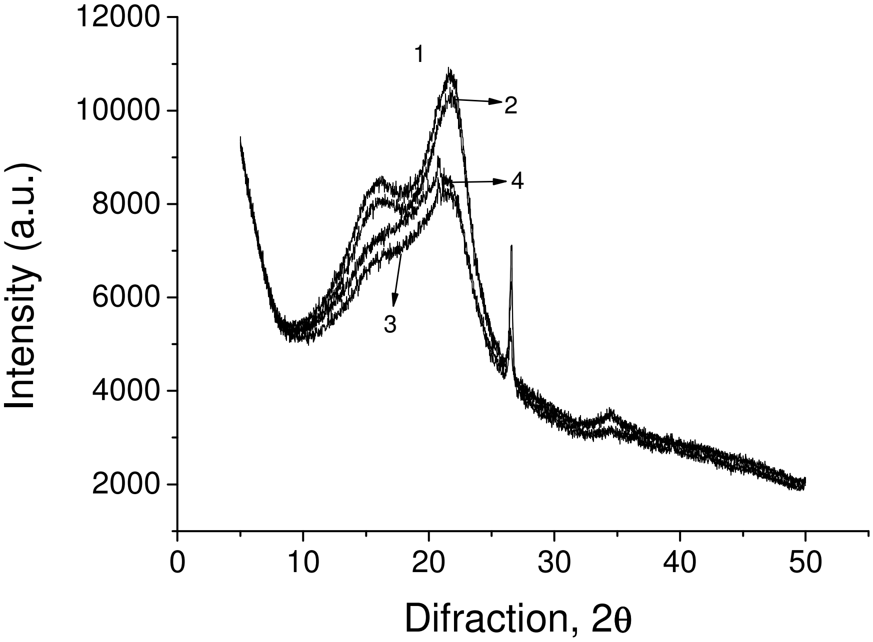


Fig. 1 X-Ray patterns of EFB grinded before and after pretreatment. Patterns 1 and 4 were grinded 120 minutes. Patterns 2 and 3 were grinded 70 minutes.

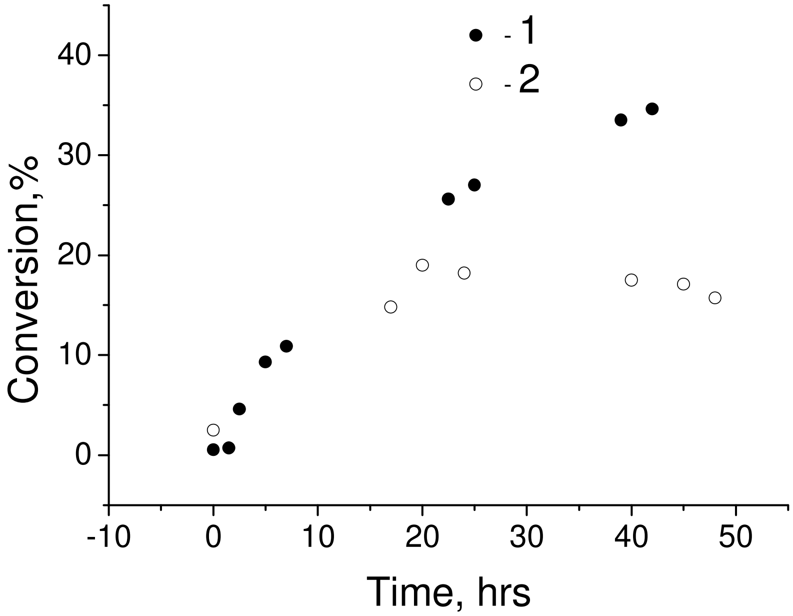


Fig.2 Influence of mechanical pretreatment on hydrolysis of EFB without mechanical with the same mechanic energy but different ways: 1 – grinded EFB after pretreatment, 2 - grinded EFB before pretreatment

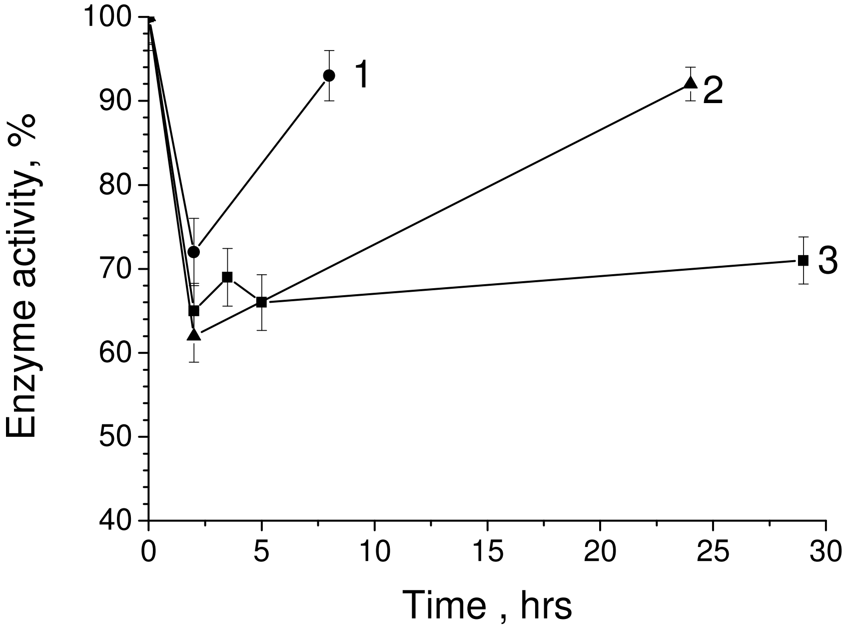


Fig.3 Falls of enzyme activities resulting in stirring during 2 hours and renewals of its activity with storage at 15 ^{0}C. 1, 2 and 3 are independent experiments with equal time of stirring and different time of relaxation

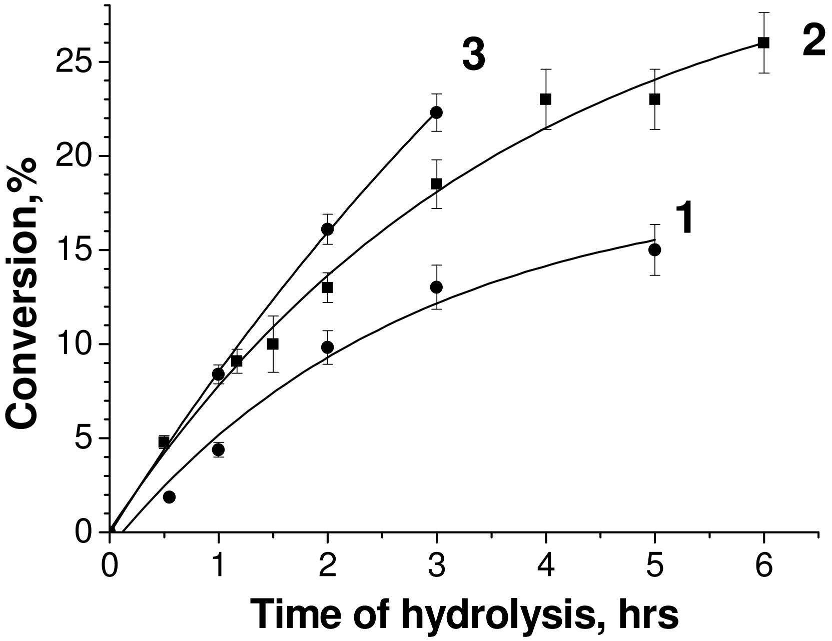


Fig.4 Ultrasonic assistance of enzymatic hydrolysis of cellulose:

1 – without treatment, 2 – continues treatment 45 min, 3 – batch treatments (15+15+15) min

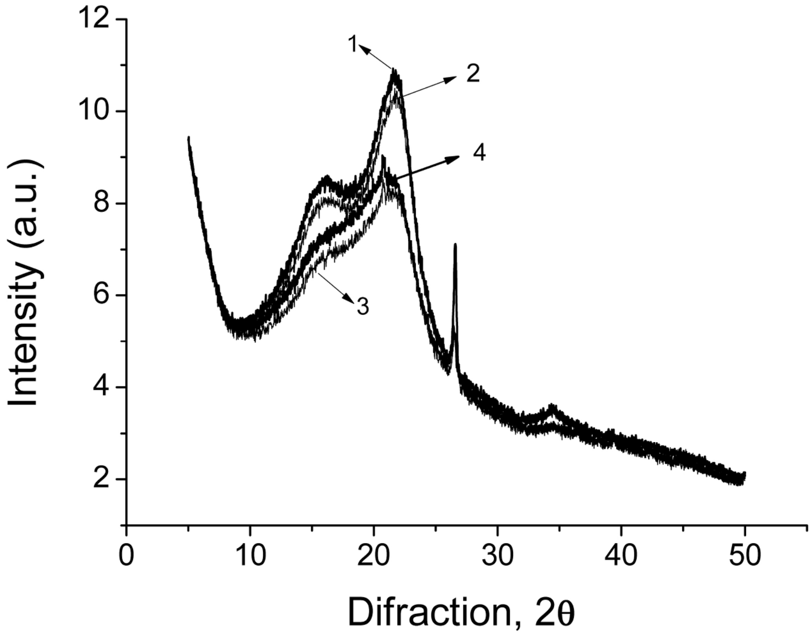
Figure captions

Fig.1. X-Ray patterns of EFB ground before and after enzymatic treatment. Patterns 1 and 4 correspond to samples that were ground for 120 minutes, patterns 2 and 3 - to those ground for 70 minutes.

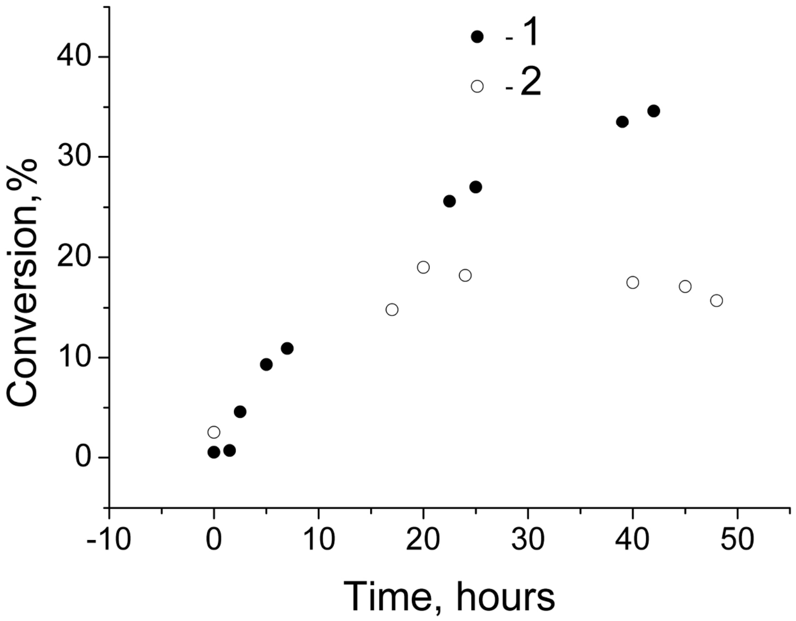
Fig.2. Influence of mechanical pre-treatment on the hydrolysis of EFB mechanically treated in two different ways, with the mechanical energy being the same: 1 –EFB ground after enzymatic pretreatment, 2 - EFB ground before enzymatic treatment.

Fig.3. Falls of enzyme activities resulting in stirring during 2 hours at and renewals of its activity with storage. 1, 2 and 3 are independent experiments with equal time of stirring and different time of relaxation

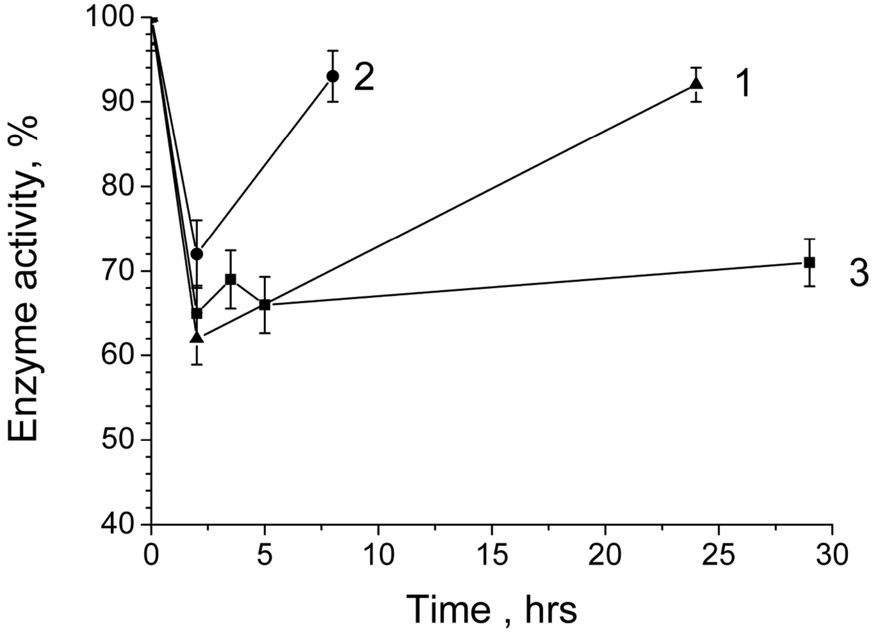
Fig.4. Ultrasonic assistance of enzymatic hydrolysis of cellulose: 1 – without treatment, 2 – continuous treatment during 45 min, 3 – batch treatments (15+15+15) min.



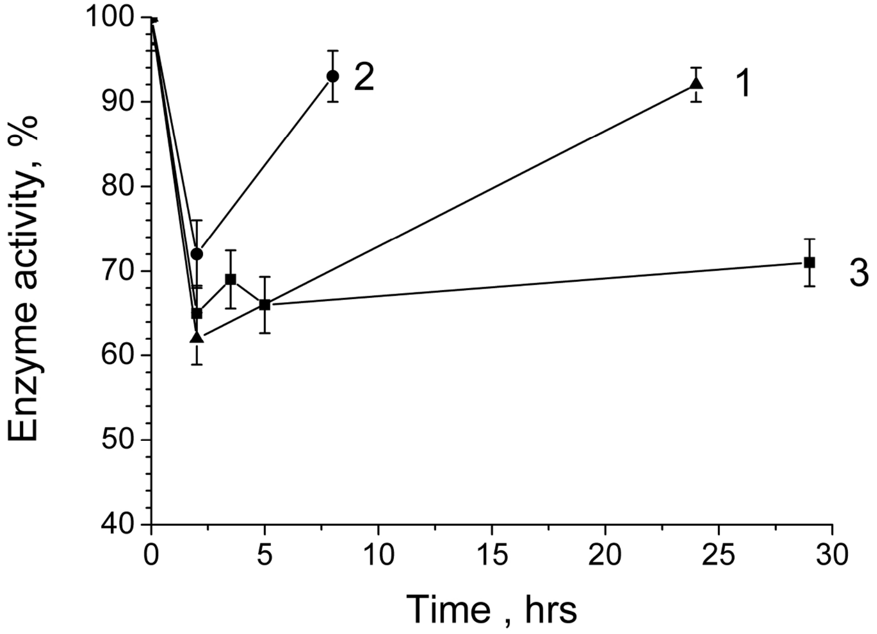
210x148mm (300 x 300 DPI)



207x144mm (300 x 300 DPI)



210x148mm (300 x 300 DPI)



210x148mm (300 x 300 DPI)