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# CATALYTIC PROCESSING OF PLANT WASTE RESULTS IN PULP AND LIQUID PRODUCTS CAPABLE OF REGULATING THE GROWTH OF PLANTS

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## ABSTRACT

We previously developed a simple biomimetic model of the enzyme complex for the catalytic decomposition of organic plant waste. The catalyst is based on iron (III) oxides, obtained by hydrolysis of Fe (III) salts in water in the presence of a surfactant. It decomposes H2O2 actively and catalyzes the oxidative destruction of lignobiomass under atmospheric pressure in water media at mild temperature (60-70° C). The oxidative destruction of biomass results in dissolved in liquid phase low molecular oxidation products derived from lignin, hemicellulose, lipoproteins and sugars and the solid residue which represent mainly cellulose. The influence of liquid phase products (LPP) on the growth and development of plants was studied on the following crops: sorghum (Sorghum caffrorum Beauv., Jakuschev), oat (Avéna sativa L), wheat Inna (Tríticum aestivum L), pea (Pisum sativum L) and potatoes (Solánum tuberósum L). The treatment of agriculture plants by the liquid fraction of the products of catalytic oxidation of lignobiomass was found to have a positive effect on the development of plants and can be used as a growth-stimulating factor in crop production.

**Keywords:** catalytic oxidation, lignobiomass, iron(III) oxides, plant growth stimulation

## 1. INTRODUCTION

Recycling of organic wastes and biomasses is a significant scientific and technical problem (Kuznetsov and Gradova, 2006; Michel, 2012). Currently, direct combustion is used, but, at the same time, technologies of thermochemical processing of biomasses, such as gasification and pyrolysis are being developed. In recent decades considerable attention has been paid to the chemical processing of biomasses to biofuels. This trend is developing, despite the reasonable objection that the production of biofuels from biomasses is fundamentally uneconomic. It requires a lot of energy and increases, in the end, the production of CO2; therefore, it is preferable to recycle the biomass by direct combustion or processing in the chemical and pharmaceutical production of commercial products, (Michel, 2012).

In nature, lignin-containing biomass is processed by microorganisms, for their development, reproduction and functioning water, containing metal ions is necessary (Kirk, 1984; Boerjan and Ralph, 2003).

We have developed a simple biomimetic model of the enzyme complex for the catalytic oxidative decomposition of organic plant waste with the use of $H_2O_2$ and/or oxygen as the oxidant. The catalyst is a fine dispersion of iron (III) oxide and hydroxide with inclusions of silicon and carbon (Kasaikina et al., 2012; Kasaikina et al., 2013; .Kasaikina et al., 2014; Lesin et al., 2011; Pisarenko et, al., 2014). The catalyst, adsorbed on the waste surface, actively decomposes $H_2O_2$ into free radicals and destroys the solid waste via catalytic oxidation.

## 2. MATERIALS AND METHODS

The catalyst was prepared by hydrolysis of iron (III) chloride in water (Kasaikina et al., 2014). The processing of wood shavings and other plant materials was carried out in a stainless steel reaction vessel filled with 3 liters of a water solution containing ~1M $H_2O_2$. During the reaction, samples were taken, in which the concentrations of $H_2O_2$ and acids were determined by the iodometric method and titration with alcoholic KOH solution accordingly. The escape of ions Fe(III) and Fe(II) to the volume of aqueous phase was controlled by specific qualitative reactions with potassium thiocyanates, red and yellow blood salts respectively. The IR spectra of the reaction products were recorded on a Perkin-Elmer FTIR-1725 spectrometer, equipped with a special attachment for the recording of spectra of diffuse reflection.

## 3. RESULTS AND DISCUSSION

### 3.1. Catalytic process and products description

Using $H_2O_2$ as the oxidizing agent, catalyst, located on the surface of the biomass, sharply increases the rate of generation of radicals which react with macromolecules of biomass and initiate their degradation. The ability of hydrogen peroxide to form oxo- and peroxo-complexes with iron and copper, and to hydroxylate organic compounds is well known (Carvalho and Horn, 2006; Elizarova et al., 2000; Kozlov et al., 2003). Catalytic oxidation of biomacromolecules facilitates their biodegradation.

  

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As a result of the oxidative degradation of wooden biomass, first of all, lignin and hemicellulose are oxidized and washed away from the surface. During this process cellulose also partially oxidizes, supplying the solution with polyols, hydroxy acids, oligosaccharides, and esters (Harmsen et al., 2010; Pisarenko et al., 2014; Zhao et al., 2012).

After all $H_2O_2$ had been consumed, the solid residue was separated from the aqueous solution by filtration and then centrifugation, followed by drying in flowing air. For qualitied (by FTIR) and quantitative analysis of content, water-soluble non-volatile products of oxidative degradation were isolated from the aliquot of liquid phase by evaporation in a current of warm air.

The catalytic process of thermo-oxidative treatment of biomasses leads to the formation of low molecular oxidation products of hemicellulose, lignin, and lipoproteins. The solid residue contains mainly cellulose and its derivatives. The yield of solid residue depends on the nature of the biomasses (see Table 1), the ratio biomass: $H_2O_2$: catalyst and the processing time. In the presence of adequate concentrations of hydrogen peroxide, pure cellulose with a qualification E-460 is produced via the processing of fir and pine wood shavings that is suitable for the food and pharmaceutical industries. Water phase contains low molecular oxidation products.

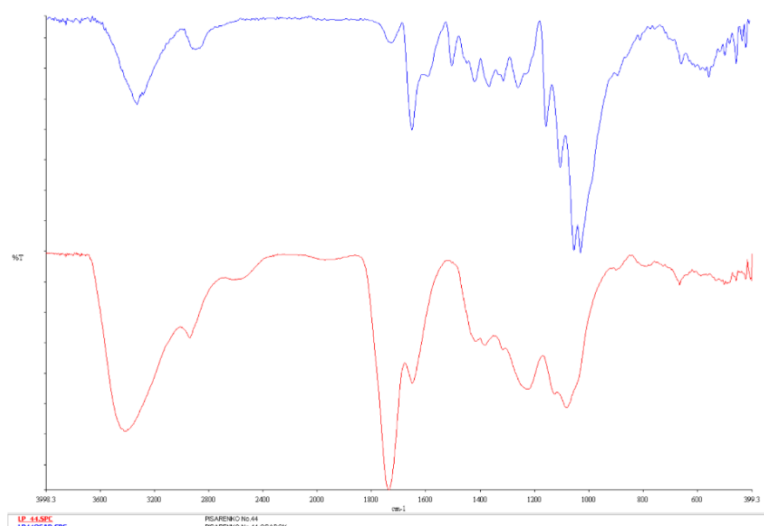

**Fig.1. IR spectra of products of processing of pine shavings: upper blue graph - the solid product: red lower graph - water-soluble product obtained after evaporation of the water.**

The results of catalytic processing of vegetable raw materials of a different nature are given in Table 1.

  

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**Table 1. The influence of biomass nature on the yield of main products**

| Biomass | Cellulose(%)* | Water-soluble products (%)* | Acid, mmol/g** |
|---|---|---|---|
| Pine sawdust | 42 | 32 | 18 |
| Eucalyptus chips | 24 | 22 | 19 |
| Oat straw | 20 | 17 | 3 |
| Rice straw | 29 | 31 | 46 |
| Waste of flax treatment | 20 | 21 | 21 |

*In the ratio to amount of the initial biomass; ** the ratio of total acid content in water phase (mmol) to the amount of biomass (g)

At the end of processing, water phase contains various acids pH~2-2.5. We have found that after neutralization to a pH 5-6, products of wooden biomass (solid and water-soluble products) can be applied as a useful nutritional additive to soils and stimulant for plant growth. In experiments on plants, liquid phase products (LPP) were used, neutralized to a pH 6 by treatment with sodium or potassium bicarbonate.

### 3.2 The effect of catalytic processing products on the growth and development of plants

The effect of catalytic processing products on the growth and development of plants was studied on the following crops: sorghum Pischevoe-614 (*Sorghum caffrorum* Beauv., Jakuschev), oat Kormovoy (*Avéna sativa* L), wheat Inna(*Tríticum aestivum* L), pea Sakharny (*Pisum sativum* L) and potatoes Udacha *(Solánum tuberósum* L*)*.

### 3.2.1 Oats and sorghum

Table 2 shows the results of the influence of the liquid fraction of processed products of wooden biomass on the growth of green masses in cultures of oats and sorghum. Seeds of sorghum and oats were soaked in water (control) and in an aqueous solution of the liquid fraction at a dilution of (1:10) before seedlings emerged. Sprouted seeds were sown in an environment of “Agronom”, a peat soil used for the cultivation of seedlings, with pH 5,0 – 6,5. In the control, there was peat soil moistened with water, but in the experiment, the soil was moistened with a solution of the liquid fraction diluted with water at a ratio of (1:10). On the 22-nd day of cultivation all green mass was weighed, and after was dried in a current of warm air until there was a constant weight.

  

**Table 2. The influence of the liquid fraction of catalytic oxidation products of wooden biomass on the growth of green masses of cereals.**

| Cereals | Green weight control, g | Green mass of experience, g | Gain (relative to control), % | Dry mass, control, g | Dry mass, experiment, g | Gain (relative to control), % |
|---|---|---|---|---|---|---|
| Oats | 9,83 | 14,8 | 151 | 0,92 | 1,45 | 157 |
| Sorghum | 6,22 | 7,96 | 128 | 0,74 | 0,98 | 132 |

The Table 2. shows, that the growth of both green and dried mass of plant stems treated with 10% LPP water solution is 157% for oat and 132% for sorghum.

### 3.2.2 Potatoes tubers and etiolated tuberous cuttings

For the experiment, potato tubers *Udacha* of a specific size were selected: 3 to 4 cm in max. dimension, which were then planted in the cultivation medium. The control tubers were planted in sand moistened with water, while the experiment tubers were planted in sand moistened with LPP water solution. The tubers were then placed in a dark chamber with the temperature of 10 – 12° C. In 45 days the sprouted tubers were counted.

Each experiment involved the planting of 20 tubers. The tubers were counted if their sprouts were at least 1 mm. long. The results are shown in Table 3.

**Table 3. The effect of LPP on the sprouting of potato tubers**

| Variant of the experiment | Number of sprouted tubers, (%) |
|---|---|
| Control tubers (moistened with water) | 15 |
| Experiment tubers (moistened with LPP 1:0) | None |
| Experiment tubers (moistened with 1:1 LPP: water solution) | 10 |
| Experiment tubers (moistened with 1:10 LPP water solution) | 90 |

Table 3 shows that the treatment with 10% LPP water solution leads to a six-fold increase in the number of sprouted potato tubers as against control tubers. The use of more concentrated solutions (1:1) and (1:0) has led to a dramatic inhibition of potato sprouting.

  

In order to produce etiolated tuberous cuttings, the tubers of potatoes *Udacha* were placed in a dark chamber until the sprouts were 6 to 8 cm long and 0.5 cm in diameter. Then they were separated from tubers and, by 30 pieces each, were placed in cultivation media. Control sprouts were planted in vessels filled with water, while the experiment sprouts were placed in vessels filled with LPP solutions. The vessels were placed in a luminostat with a light-darkness mode set to 12:12 hours. In 15 days, the cuttings that had formed a developed root system were counted. The results are presented in Table 4.

**Table 4. The effect of LPP on the formation of root system of etiolated tuberous cuttings**

| Variant of the experiment | Number of etiolated cuttings that formed roots, % |
|---|---|
| Control tubers (planted in water) | 20 |
| Experiment tubers (planted in undiluted LPP) | 4 |
| Experiment tubers (planted in 1:10 LPP water solution) | 80 |

Table 4 shows that the placement of tubers into 10% LPP water solution leads to a four-fold increase in the number of etiolated cuttings that have formed root system, as against control cuttings. The cultivation tubers in the undiluted LPP medium resulted in a sharp inhibition of the root formation (five-fold decrease as against control sprouts).

### 3.2.3 Wheat and pea

Germination of *Inna* wheat seeds and *Sakharny* pea has been studied as follows. The wheat and pea seeds were placed in a growing medium. Control seeds were planted in sand moistened with water, while experiment seeds were planted in sand moistened with original undiluted LPP and (1:10) LPP water solution. The results are shown in Table 5.

**Table 5. The effect of treatment with undiluted LPP and (1:10) LPP solution on the germination of wheat and pea seeds.**

| Variant of the experiment | Number of sprouted wheat seeds, (%) | Number of sprouted pea seeds, (%) |
|---|---|---|
| Control seeds (planted in sand moistened with water) | 40 | 25 |
| Experiment seeds (planted in sand moistened with (1:10) LPP solution) | 70 | 45 |
| Experiment seeds (planted in sand moistened with undiluted LPP) | 20 | 10 |

  

Table 5 shows that the treatment with 10% LPP solution leads to a 1.75 increase in the number of wheat germs and 1.8 increase in the number of pea seedlings, as against control seeds. The use of original LPP without dilution has led to a sharp inhibition of seed germination in both examined cultures.

## 4. CONCLUSIONS

Thus, the data obtained show that neutralized to pH 6 liquid water-soluble products resulted from catalytic oxidative processing of plant biomass can be used in agriculture for a growth stimulation.

It is known, growth stimulation or inhibition properties of most growth regulators are determined by the concentrations used. In our experiments, the maximum stimulation effect on the germination and subsequent development of plants was obtained in diluted solutions using 1:10 and 1:20 solutions of LPP diluted with tap water. The use of more concentrated LPP solutions — 1:5 and 1:1 — has led to inhibition of both seed germination and further development of plants. This latter effect also appears important, as long as more concentrated LPP solutions can be used for the treatment of vegetable crops and plant intended for long-term storage. It is well understood for potato tuber treatment: the acceleration of potato tuber germination occurs at low doses (10%) LPP, and inhibition of germination at higher LPP concentrations (>50%), which is useful for a long storage of potatoes.

Thus, the application of catalytic oxidative treatment of waste biomass facilitates the solution of two problems: the utilization of agricultural wastes and the improvement of the agricultural, and greenhouse soils by returning to the soil the chemicals needed by the plants.

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