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Waste Paper as Promising Feedstock for Production of Biofuel

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Author's contribution

This whole work was carried out by author MI.

Original Research Article

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ABSTRACT

Modern approach to utilization of non-edible biomass is its conversion to glucose, and the following fermentation of the sugar into final bioproducts. Among various biomass types, the waste of office paper is distinguished by increased content of cellulose and negligible content of lignin; therefore it can be a suitable feedstock for bioconversion into valuable bioproducts. In this article, an advanced technology has been proposed for complete utilization of the paper waste by bioconversion. The technology is comprised of the following main steps: (1). Redispersion of the waste paper and then screening of the pulp in order to separate fibers from mineral fillers; (2). Acidification and washing of the fibers to remove the residual calcium carbonate; (3). High-solids enzymatic hydrolysis of the demineralized paper to obtain fermentable sugar - glucose; and (4). Fermentation of the glucose into biofuel. As a result, from 1 ton of the waste office paper about 280L of bioethanol can be produced that have capacity of the heat energy of 1680kWh. Besides, there remain by-products of the processing including about 260kg of residual fibers and about 270kg of mineral fillers that can be used repeatedly in the papermaking. Thus, the waste paper can be utilized completely for production of the valuable bioproduct and recycled paper materials.

Keywords: Waste paper; demineralization; enzymatic hydrolysis; fermentation; bioethanol.

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1. INTRODUCTION

Important area of the modern biotechnology is a conversion of non-edible plant biomass to valuable bioproducts, biofuels and / or biochemicals [1]. These biomasses can involve agricultural residues, natural herbaceous plants, forest residues, industrial and municipal wastes. World pulp and paper industry produces about 300-350 million tons of various types of paper and board. Smaller part of waste paper materials is recycled, while the most of the used materials is thrown out or burned. Plant-based biomasses including paper materials are regarded as abundant, renewable and inexpensive sources of raw-materials that accumulate in the world in huge amounts. For example, the estimated annual accumulation of the biomasses in the US is more than 1 billion tons per year [2].

To produce the bioproducts, the cellulosic component of the biomass is hydrolyzed by cellulolytic enzymes and the obtained glucose is fermented into final bioproducts. However, the various types of the biomass show a high recalcitrance to enzymatic cleavage due to barrier properties of lignin and other admixtures [3-5]. Lignin is an aromatic, rigid and hydrophobic polymer impenetrable for cellulolytic enzymes. In the plant cell wall, lignin layers surrounding the hydrophilic cellulose fibrils prevent these from the enzymatic attack [6,7]. Most types of the waste paper and board (e.g. newspaper, packaging paper, cardboard, corrugated board, coated or impregnated paper and board, etc.) can contain not only lignin, but also additional barrier components such as waxes, fats, rubbers, synthetic polymers and resins, and other hydrophobic substances that prevent the enzymatic cleavage of the paper materials. In order to remove the barrier components and improve the enzymatic digestibility, the biomass samples including paper materials should be pretreated by chemicals at increased temperatures [8,9]. However such pretreatments decrease yield of the feedstock and require additional expenditures of chemicals and energy that raise cost of the final bioproducts [10].

Among various types of the paper wastes, some waste papers (e.g. chemical pulp, napkins, blotting paper, hygiene paper, office paper, etc.) are distinguished by increased content of cellulose and negligible content of lignin and other barrier components. Therefore these feedstocks do not require the high-temperature chemical pretreatment [11]. For example, the bleached office paper, both printing and writing paper, almost does not contain lignin and other barrier admixtures. Moreover, it is a widespread paper type that produced in the world in amounts about of 100 million tons [12]. From third to half of the used paper is recycled, while the residual amount of the paper is thrown out; thus a valuable raw-material is lost. Recently, attempts have been made to use the mixed paper waste or papermaking sludge as biomasses for enzymatic hydrolysis [13,14]. However, variable composition and heterogeneity of such biomasses complicates study the hydrolysis process. More reliable results can be obtained if uses for this purpose the known paper type having stable composition. In this research, a special advanced technology has been proposed for the complete utilization of the used office paper through bioconversion into fermentable sugar with the subsequent production of biofuel.

2. MATERIALS AND METHODS

2.1 Materials

Some types of waste paper of Israel: cardboard, napkins, newspaper, packaging paper, blotting paper and office paper, were used as initial materials. These materials were delivered from Amnir Recycling Ind.

2.2 Chemical Analysis

The chemical composition of initial and pretreatment biomass samples was determined by conventional methods of chemical analysis [1,15]. The content of ash in the paper samples was determined according to TAPPI standard T211 [16]. The content of holocellulose, consisting of cellulose and hemicelluloses, was measured after complete selective delignification of the biomass with sodium chlorite. The obtained holocellulose sample was hydrolyzed with boiling 1.5% hydrochloric acid for 2h. The content of cellulose was calculated from the dry residue remained after hydrolysis of the holocellulose, while the content of hemicelluloses was measured from weight loss of the hydrolyzed holocellulose sample. Content of lignin was analyzed according to TAPPI standard T222 [17]. Three samples of the same paper kind were tested to calculate an average value and standard deviation. The standard deviation (*SD*) at determination of the percentage of components was ±1%. The percentage of lignin in highly delignified samples was evaluated by Kappa number (*K)* in accordance with TAPPI standard T236: *L(%)=0.13K*; in this case *SD* at determination of the lignin content was ±0.3%.

2.3 Demineralization of the Waste Paper

Presence of mineral fillers (mainly calcite and kaolin) in the waste paper leads to nonproductive adsorption and inhibition of enzymes that hinders enzymatic digestibility of the paper sample [13]. Therefore, the demineralization should be preliminary performed in order to remove the mineral fillers from the paper biomass and also increase the content of cellulose. The initial waste paper was resuspended in water by “Waring” blender at 5000 rpm for 1 min to obtain of 3wt% dispersion. Then the dispersion was screened through 50 mesh sieve under vacuum. The fibers remain on the sieve, while the small particles of the mineral filler penetrate together with water through the sieve and are precipitated on the bottom of a suction flask. This procedure was repeated up to final ash content less than 5wt%. In the case if the filler was calcium carbonate (calcite), the pulp was acidified with 1% hydrochloric acid up to pH=6.0-6.5. Finally, the demineralized pulp was squeezed on the glass filter No1under vacuum to obtain the wet pulp with solid content about 30-40%.

2.4 Enzymatic Hydrolysis

Various types of waste paper were hydrolyzed with a mixture of commercial cellulolytic enzyme – cellulase, Accelerase-1500 (DuPont Ind. Biosciences, USA) and β–glucosidase Novozyme-188 (Novozymes A/S, Denmark). The dose of the cellulase was 15 FPU per 1g of solid sample and of β–glucosidase was 7 CBU per 1g of solid sample. Hydrolysis of the paper samples was carried out in 50-mL polypropylene tubes. The samples containing 1g of the solid matter in 50mM acetate buffer (pH=4.8) were supplemented with the enzyme cocktail. The loading of the paper biomass (*BL*) was from 50 to 200g/L. The tubes closed with covers were placed in a shaker incubator at 50°C and shaken at 150rpm for 24 to 120 hours. Finally, the tubes were centrifuged in order to separate the residual biomass and hydrolyzate. Concentration of the glucose in the hydrolyzate was tested by the HPLC method. The conversion degree of the paper, yield of glucose and some other characteristics were determined.

2.5 Fermentation

The fermentation of the sugar-containing hydrolyzate to produce bioethanol was carried out in a laboratory fermentor "Biostat A Plus" (Sartorius AG) using the yeast of *Saccharomyces cerevisiae* at 35°C for 3 days. Concentration of the yeast was 10g/L. Peptone and some other nutrients were added [18]. Concentration of the generated ethanol was tested by the HPLC method.

2.6 HPLC-Analysis

Concentrations of glucose and ethanol were determined by HPLC-apparatus of Agilent Technologies 1200 Infinity Ser. The Amines HPX-87H column was used. Main conditions of the analysis were: temperature 45°C; mobile phase 0.005 M sulfuric acid; flow rate 0.6ml/min. The sample of hydrolyzate was preliminary filtered through 0.45μm Nylon filter and degassed. Conversion degree (*CD*) of the paper sample and yield of glucose (*Y*) after enzymatic hydrolysis was calculated by the equations:

$$CD\ (\%) = 90\ (C_g/BL) \quad (1)$$

$$Y\ (\%) = 100\ (C_g/BL) \quad (2)$$

Where C_g(g/L) is concentration of glucose; *BL*(g/L) is loading of paper biomass at the enzymatic hydrolysis

Three paper samples were hydrolyzed simultaneously to obtain accurate results. The standard deviation at determination of the glucose yield was ±2%.

3. RESULTS AND DISCUSSION

Chemical compositions of the initial and demineralized waste papers were shown in Table 1. The initial samples contained 38 to 81% cellulose, 5 to 15% hemicelluloses (Hemicel), 1 to 21% lignin and 7 to 30% mineral fillers. The most lignified paper samples were waste of cardboard and newspaper. The waste of napkins, newspaper, packaging paper and office paper contained a high amount (20-30%) of mineral fillers.

After demineralization of lignified waste papers the increased content of carbohydrates and also lignin was observed. In contrast to lignified waste, the demineralization of the bleached waste papers, e.g. office paper, leads to increase of content only carbohydrates, mainly of cellulose Table 1, Fig. 1.

Table 1. Chemical composition of the initial (IN) and demineralized (DM) waste paper

Waste paper	Cellulose, %		Hemicel, %		Lignin, %		Minerals, %	
	IN	DM	IN	DM	IN	DM	IN	DM
Cardboard	61	63	12	13	18	19	7	3
Newspaper	38	50	15	18	21	26	19	4
Packaging paper	60	73	11	8	7	12	20	3
Napkins	58	78	6	10	4	5	29	4
Blotting paper	81	84	6	7	4	3	7	3
Office paper	62	87	5	8	1		30	1

To estimate the enzymatic reactivity of the initial and demineralized waste papers, their enzymatic hydrolysis was carried out for 24h at *BL*= 50g/L. The results show that the initial waste samples containing higher amounts of lignin and/or mineral fillers have a low conversion degree, 10-30% Fig. 2. The exception is the waste of initial blotting paper that exhibits a higher conversion degree, about 50%, due to low content of lignin and mineral fillers. Due to the significant influence of the mineral substances on the activity of cellulolytic enzymes, a correlation between the lignin content and the conversion degree of initial paper samples was not found. The squared correlation coefficient for the conversion degree as a function of the lignin content was slight, R^2=0.16; this means there is no correlation. Negative effect of mineral fillers on enzymatic hydrolysis of paper was found also in other studies [13,14]. This effect may be caused by neutralization of acidic buffered medium with the fillers, non-productive adsorption of the enzymes, as well as reduction of cellulose fraction in the paper sample.

The demineralization of the waste papers changes significantly their enzymatic cleavage. For this samples a negative linear correlation between the lignin content and the conversion degree was observed, R^2=0.98 Fig. 3. The waste of bleached office paper having a neglible amount of lignin after demineralization acquires the higher enzymatic digestibility, while the other demineralized samples having more lignin show the lower conversion degree. A negative effect of lignin on enzymatic hydrolysis of cellulose-containing materials is well-known. Lignin is a rigid aromatic, amorphous and hydrophobic polymer built of phenylpropane units, which are cross-linked to each other with a variety of different chemical bonds. Due to this structure lignin is stable to some chemical reagents and cellulolytic enzymes. In the cellulose materials, barrier layers of lignin surrounding hydrophilic cellulose fibrils adsorb the enzymes and protect the cellulose from the enzymatic attack [19,20]. Thus, the removal of lignin enhances the accessibility of the enzymes and improves the conversion of cellulose into glucose.

Annual quantity of the used office paper is a quite high - tens of millions tons; therefore this kind of the waste paper was selected as a preferable feedstock for the further bioconversion and fermentation. Though the wastes of demineralized blotting paper and napkins have also an increased hydrolysability, reserves of these raw-materials are minor in order they can be used as substrates for industrial bioconversion.

As known, the enzymatic hydrolysis at the increased biomass loading is a key to scale up of this process to pilot and industrial production [21]. Use a high biomass loading through its conversion into fermentable sugars and bioproducts is important foremost owing to techno-economical reasons. This approach permits to achieve the high concentration of the sugars and bioproducts that can bring significant economic savings to the bioconversion process, such as reducing capital, decreasing operating cost for hydrolysis and fermentation, as well as minimizing energy consumption for distillation, evaporation and other processes [22].

Therefore, the enzymatic hydrolysis of the demineralized waste of office paper (DOP) at the increased biomass loading has been studied in order to determine the optimal hydrolysis conditions and achieve the maximal yield of the fermentable glucose. Study of the enzymatic hydrolysis of DOP showed that the increase of the biomass loading caused the decrease of conversion degree Fig. 4, probably, due to limited mass transfer of the enzyme. On the other hand, the enzymatic hydrolysis at the increased biomass loading promotes achieving the higher concentration of the fermentable sugar - glucose Fig. 5.

An additional problem connected with the enzymatic hydrolysis at the high-solids loading of the biomass is diminution of the volume of the sugar solution (hydrolyzate) owing to its absorption and retention by residual non-hydrolyzed biomass [21].

To find the optimal conditions of enzymatic hydrolysis and namely, the optimal loading of the biomass and hydrolysis time, the amount of glucose (*P,* g per 1L of the initial liquid medium) had been determined: $P=C_g \times V_a$, where C_g(g/L) is concentration of the glucose in hydrolyzate V_a (L/L is its relative available volume*)* of the hydrolyzate.

At certain hydrolysis time (e.g. 48h), with increasing of the biomass loading *(BL)* concentration of the hydrolyzate increases, while the available volume declines. As a result function *P=F(BL)* has extremum Fig. 6.

Prolongation of the hydrolysis process promotes rise the extremum *P*-value up to achievement its maximal magnitude Fig. 7.

Determination of the maximal glucose amount, $\boldsymbol{P_m}$, allows to find the following optimal conditions of enzymatic hydrolysis of the sample, and namely: optimal biomass loading $\boldsymbol{BL_o}$=150g/L and optimal hydrolysis time $\boldsymbol{t_o}$=96h (4 days). As a result, the following maximal features of the enzymatic digestibility were obtained Table 2.

After yeast fermentation of the hydrolyzate having maximal concentration of glucose ($C_{g,m}$=105g/L), about 50g of the bioethanol from 1L of the hydrolyzate can be produced Table 2. This amount corresponds to yield of 400L of bioethanol from 1 ton of the demineralized paper or about of 280L of bioethanol from 1 ton of initial paper waste.

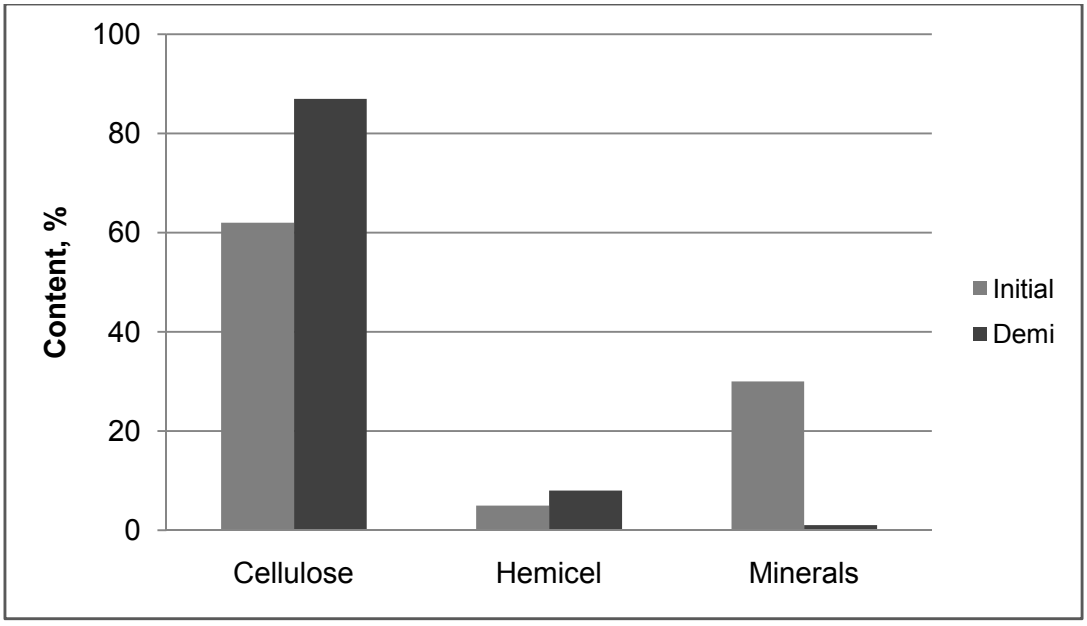

Fig. 1. Change of chemical composition of the waste office paper after demineralization (Demi)

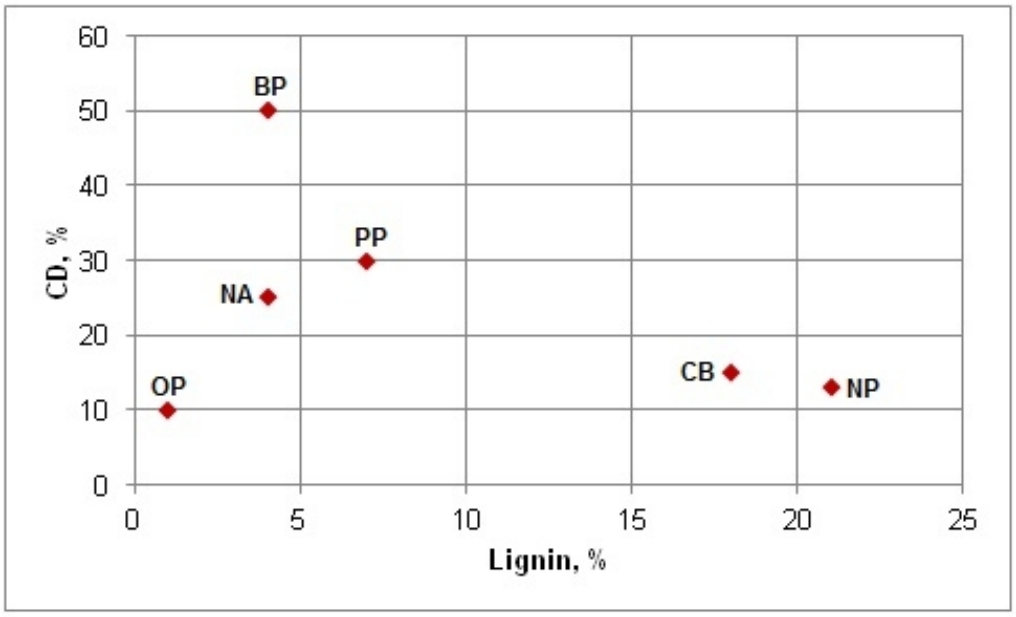

Fig. 2. Conversion degree of the initial waste samples: office paper (OP), blotting paper (BP), napkins (NA), packaging paper (PP), cardboard (CB) and newspaper (NP), having various content of lignin after enzymatic hydrolysis for 24h at *BL*= 50g/L

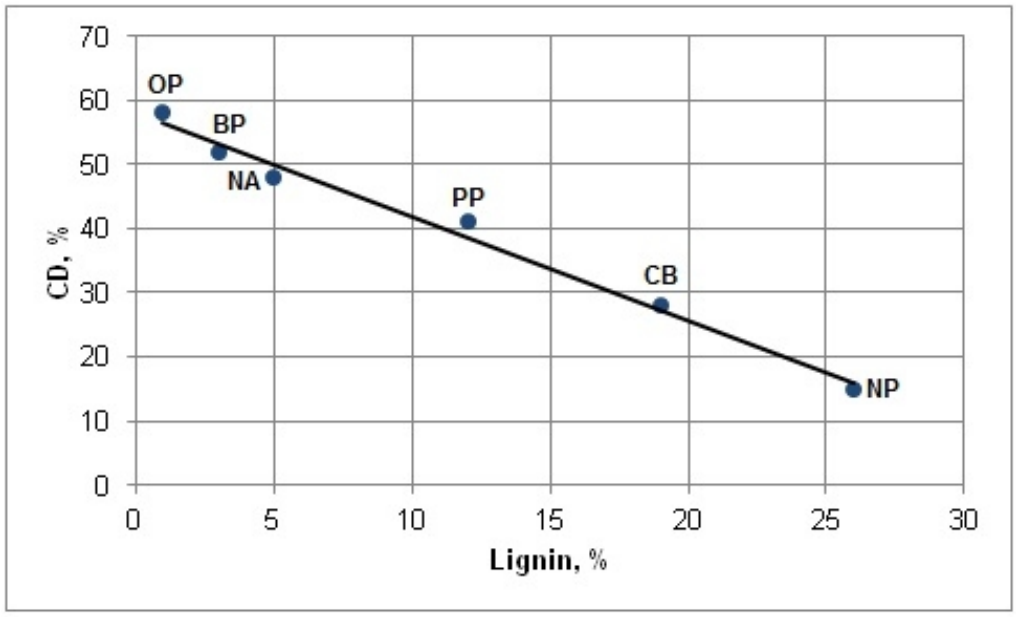

Fig. 3. Conversion degree of the demineralized waste samples: office paper (OP), blotting paper (BP), napkins (NA), packaging paper (PP), cardboard (CB) and newspaper (NP), having various content of lignin after enzymatic hydrolysis for 24h at *BL*=50g/L

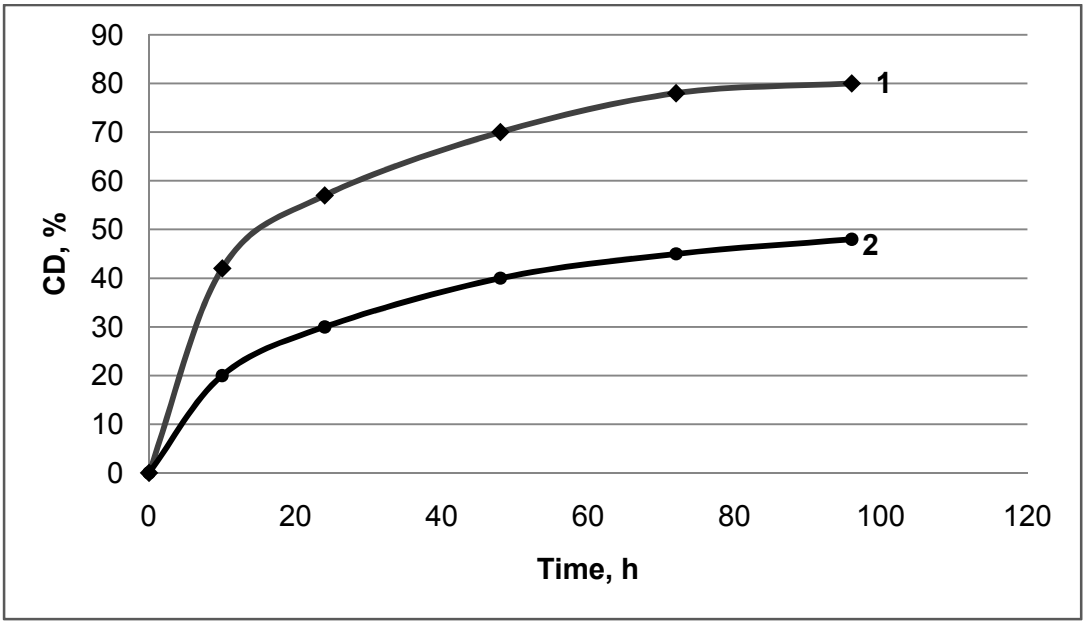

Fig. 4. Conversion degree of DOP after enzymatic hydrolysis at the different biomass loading: 50g/L (1), and 200g/L (2)

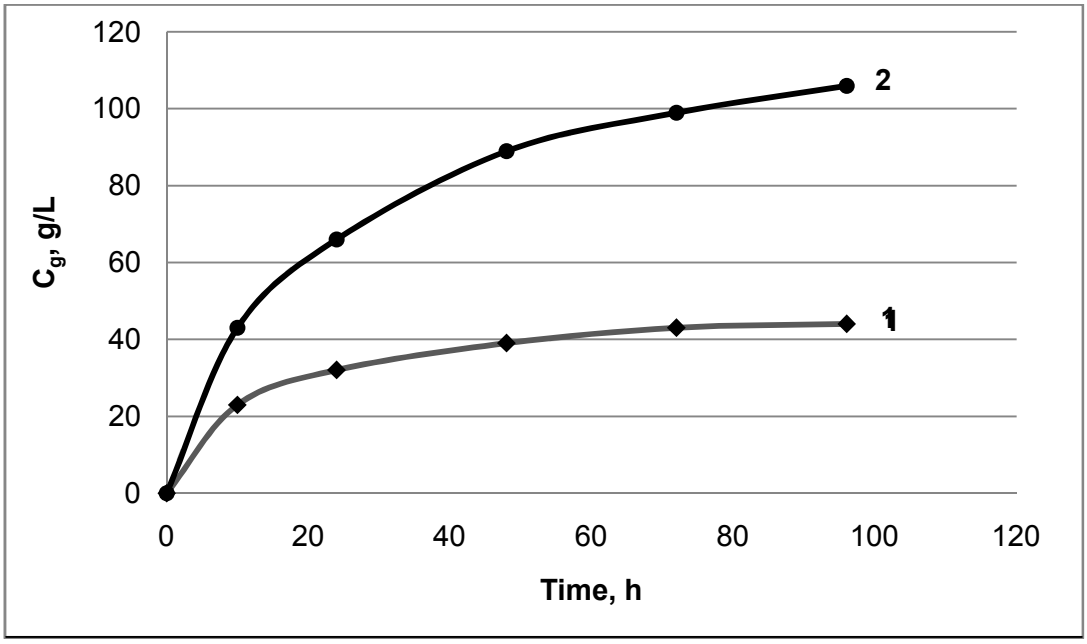

Fig. 5. Concentration of glucose (C_g) after enzymatic hydrolysis of DOP at the different biomass loading: 50g/L (1) and 200g/L (2)

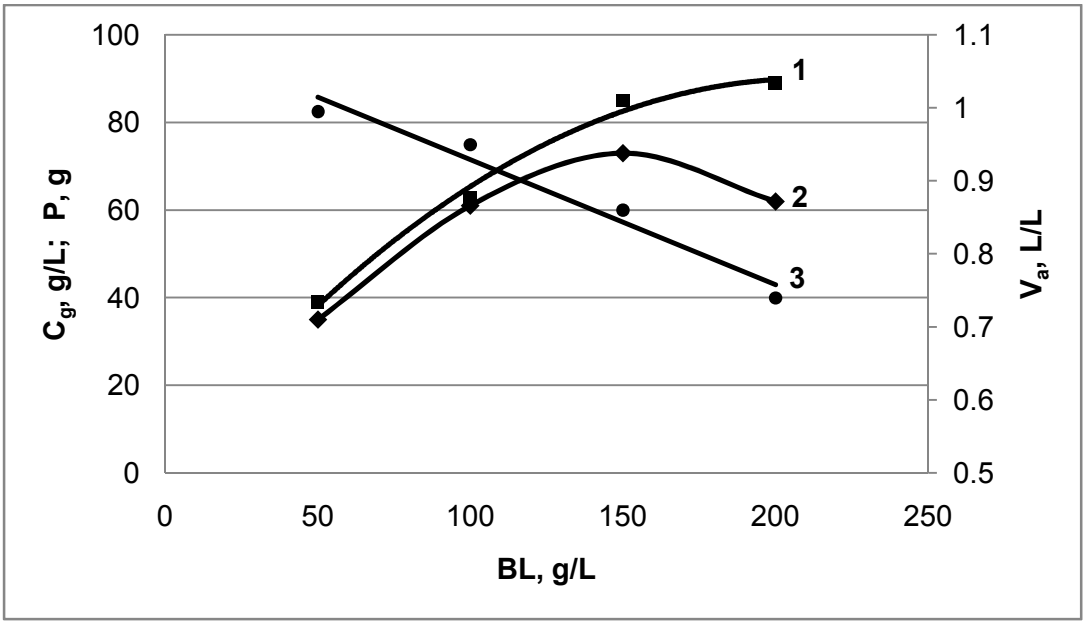

Fig. 6. Dependence of the glucose concentration (1), glucose amount (2) and available volume of hydrolyzate (3) on the biomass loading (BL) at enzymatic hydrolysis of DOP during 48h

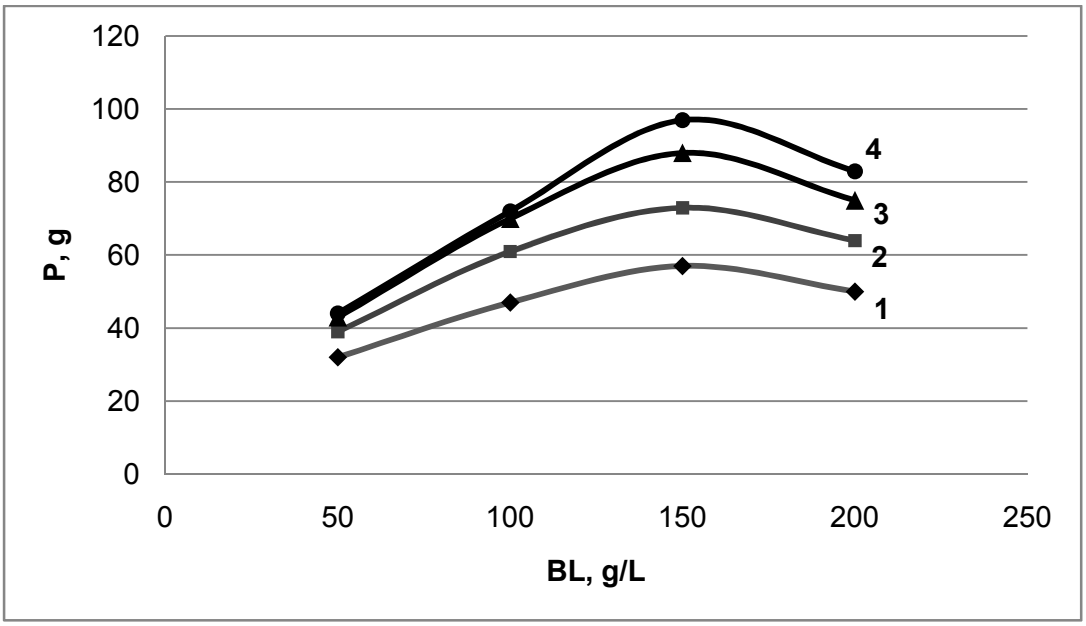

Fig. 7. Dependence of the glucose amount (P) on the biomass loading (BL) after enzymatic hydrolysis of DOP during 24h (1), 48h (2), 72h (3), and 96-120h (4)

Table 2. Maximal features of the enzymatic digestibility of the demineralized waste of office paper

Maximal features	Value
Conversion degree (%)	63
Yield of glucose (%)	67
Concentration of glucose (g/L)	105
Available volume of hydrolyzate (vol.%)	92
Yield of bioethanol (g/L)	50

The remained by-products of the processing - mineral fillers and residual fibers, can be used repeatedly in the papermaking Fig. 8. Thus, the proposed technology permits the complete utilization of the waste paper.

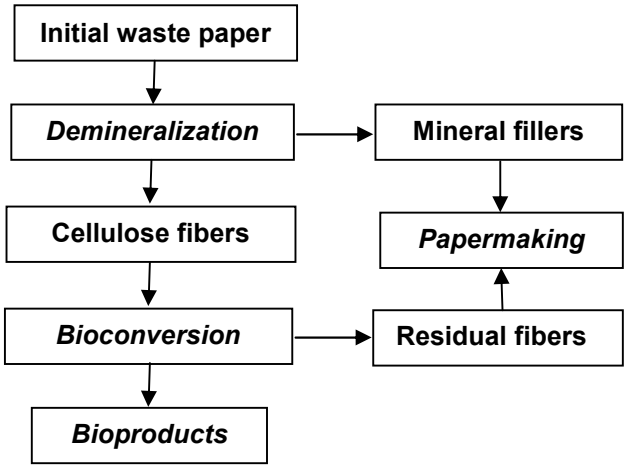

Fig. 8. Scheme of utilization of residual by-products (fillers and fibers) of the waste paper processing

4. CONCLUSION

Presence of calcium carbonate in the waste of office paper hinders its enzymatic conversion because this basic mineral filler neutralizes the acidic buffer required for the effective enzymatic hydrolysis. Therefore, a special technology was developed and performed to remove the mineral fillers from the paper biomass and increase content of cellulose. The demineralized office paper exhibited an increased digestibility under effect of cellulolytic enzyme. The optimal hydrolysis conditions were found and namely: dose of the enzyme 15 FPU per g of solid sample, optimal biomass loading 150g/L, optimal hydrolysis time 4 days. As a result, the maximal features of the enzymatic digestibility were obtained. After fermentation of the hydrolyzate at the optimal conditions, from 1 ton of the demineralized about 400L of bioethanol pulp can be produced. This volume corresponds to 280L of bioethanol per 1 ton of the initial waste paper. Taking into consideration that the net calorific value of ethanol is 6kWh/L, combustion of 280L of the biofuel can provide the heat energy of 1680kWh. Besides, there remain by-products of the processing including about 260kg of residual fibers and about 270kg of mineral fillers that can be used repeatedly in the

papermaking. Thus, the waste paper can be utilized completely for production of the valuable bioproduct and recycled paper materials.

CONSENT

Author declares that this publication does not apply to medicine and treatment of patients. Therefore, it not required consent from the patient (or other approved parties) for publication of this case report and accompanying images.

ETHICAL APPROVAL

This study does not involve in dealing with animal subjects, animal experiments and the human subjects.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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