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# Degradable Bioplastics as an Alternative to Nondegradable Polyolefins

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## Abstract

Urgency is demonstrated concerning the studies focused on the development of processes for producing a new generation of environmentally safe and biodegradable polymeric materials. Basing on the experimental characteristics of the process of synthesizing polyhydroxyalkanoates obtained as the result of pilot plant operation at the Institute of Biophysics of the SB RAS (Krasnoyarsk), there has been a technical and economic analysis of the process performed. Calculation results are presented for the cost price of polyhydroxyalkanoates in the case of different substrate scenarios.

Key words: biopolymers, polyhydroxyalkanoates, degradable bioplastics, cost price of polyhydroxyalkanoates, substrates, synthesis gas

#### INTRODUCTION

Synthetic polymeric materials represent an integral part of modern life, but the application thereof runs into a global environmental problem. These materials are produced from non-renewable resources, and their accumulation leads to environmental pollution. The production volume of synthetic plastics, mainly polyolefins (polyethylene and polypropylene), obtained in the processes of petroleum chemistry and organic synthesis are enormous being by now as much as about 300 million t/year. The consumption of these materials per ca. in the USA, Western Europe and Japan is equal to about 37 kg [1-3], while about 60 % of the plastics is used for packaging and up to 40~%of "packaging" plastics are used for packing food and bottling.

In order to decontaminate the environment from waste plastics, as a rule, one uses dispos-

al procedures. In developed countries, the proportion of wastes those are exposed to recycling does not exceed 15 %.

# SYNTHESIS OF DEGRADABLE BIOPLASTICS. URGENT RESEARCH LINES

Currently, of increasing importance are environmentally safe materials obtained from renewable raw materials such as plant biomass and the products of microbiological synthesis (so-called biopolymers or bioplastics). According to a forecasted increase in the production volume of degradable bioplastics, the share thereof could reach a quarter of the global plastics market. At the present time, however, the mass use of biodegradable polymers is constrained by a relatively high price thereof as to compare with synthetic polymers produced from oil because the latter are 2.5–7 times cheaper than bioplastics [4]. Besides naturally occurring degradable polymers under use (cellulose, starch, *etc.*), a more wide used is found by the polymers of lactic and glycolic acids and polyhydroxyalkanoates (PHA), the polyesters of fatty acid hydroxy derivatives produced by microorganisms [5, 6].

In connection with the fact that the cost of PHA is to a considerable extent dependent on the feedstock, the main direction of research that indicates the strategy of the industrial production of such bioplastics, is currently associated with the potentialities of extending the resource base. For this purpose, under active investigation there are the patterns and efficiency of PHA biosynthesis by known organisms with the attracting of new substrates, searching for new natural-producing strains being continued, transgenic producers able to absorb different substrates, including novel ones are under construction.

For obtaining PHA, in principle, it is possible to involve of various substrates (carbon dioxide and hydrogen, sugars, alcohols, organic acids), the wastes resulting from alcohol, sugar, hydrolysis industries, prom olive and palm oil production, *etc.* [7].

Hydrogen-oxidizing microorganisms are considered nowadays to be the most promising producer of PHA, since they are able to synthesize polymers of different chemical structure on different substrates and with high yield. The source of hydrogen could be presented by water electrolysis, whereas the carbon source could be presented by expander carbon dioxide from biochemical production. An alternative substrate could be presented by synthesis gas as a source of carbon and hydrogen produced *via* the gasification of coal, and oxygen obtained from air separation units.

The consumption of sugars for the formation of PHA theoretically amounts to about 2.5 kg/kg; however, real consumption, for example, that of Chemical Co. ICI (England) amounting up to 3.0-3.3 kg/kg of polymer (economic factor 0.3).

Hydrogen is considered an alternative substrate with respect to sugars, but the explosion hazard thereof and poor solubility inherent in the gaseous substrate are hindering the use of hydrogen in large-scale fermentation processes [8].

The PHA biosynthesis efficiency with hydrogen as an energetic substrate is high; in this case the consumption of substrate for the product formation is minimal. The economic factor for preparing the polymer with the use of hydrogen is equal to 1, whereby the development of this substrate could be promising for the development of the fermentation state of the art [9].

At the present time, the studies concerning the hydrogen as a potential substrate for the biosynthesis of PHA are performed by research teams at the Faculty of Agriculture, the University of Kyushu (Japan) and at the Laboratory Chemoautotrophic Biosynthesis, the Institute of Biophysics of the SB RAS (Krasnoyarsk, Russia). The main problem of organizing the PHA biosynthesis with hydrogen consists in developing of equipment with high gasdynamic characteristics to provide efficient gas transport from the gas phase to the liquid phase. In Japan, there were fermenters developed and investigated with high mass transfer characteristics having the volume mass transfer coefficient with respect to oxygen  $K_{La} = 380 2970 h^{-1}$  [10, 11]. Using this equipment, a high yield of polymer was attained to range from 25 to 60-80 g/L for the productivity with respect to the total biomass ranging from 0.33 to  $1.0 h^{-1}$ . The polymer content in the biomass in this case ranged from 55.7 to 82.1 % [12], which is comparable with the results of the Russian process [13-15].

# PROSPECTS OF ORGANIZING THE PHA PRODUCTION

The researchers of the Institute of Biophysics of the SB RAS carried out a series of fundamental studies concerning the features of degradable PHA synthesis. They found out key factors determining the yields, chemical structure and physicochemical properties of the polymers as well as developed and implemented the processes for the production of polymers with different composition and high yields (up to 80-90 % with respect to the mass of solid dry matter of a cell) on different substrates, having different basic physicochemical properties [16]. For the first time in the world biotechnological practice, the Institute of Biophysics of the SB RAS together with the Institute of Chemistry and Chemical Technology of the SB RAS (Krasnoyarsk) have

#### TABLE 1

Main technical and economic characteristics of PHA production (according to pilot production results)

Characteristics	Fructose	Glucose	Synthesis gas
Proceeds from sales (biopolymer), thousand rub.	14 500.00	14 500.00	14 500.00
Income turnover, thousand rub.	12 111.76	12 035.55	12 004.19
Production costs, thousand rub.	12 032.94	8896.93	6640.56
Balance sheet profit, thousand rub.	78.82	3138.62	5293.89
Income distribution, thousand rub.	63.06	2510.90	5363.63
Commodity product profitability, $\%$	1	22	37
Cost price of 1 kg of polymer, thousand rub.	4.149	3.068	2.29

developed and implemented a process for the synthesis of PHA, basing on synthesis gas obtained from the gasification of KAFEC brown coal and hydrolytic lignin [17, 18].

The operating experience of the first Russian pilot production allowed researchers to perform preliminary technical and economic studies concerning the PHA production process for the three substrate scenarios involving fructose, glucose and synthesis gas. Input data for the calculations were obtained in the course of the pilot production operation at the Institute of Biophysics of the SB RAS, with the productivity amounting up to 50 kg of PHA per year.

In the case of using glucose and fructose the sugar cost amounts to 659 and 150 rub./kg, respectively (at the consumption rate equal to 3 kg/kg of the polymer). For the variant with using the synthesis gas the cost of the substrate is equal to 9 rub./kg (at the consumption rate equal to 8.2 kg/kg of the polymer).

An approximate cost price of PHA ranges within 4.1-2.3 thousand rub./kg. Table 1 demonstrates comparative technical and economic parameters for the pilot production of PHA with the use of various substrates at the expected selling price of the finished product equal to 5000 rub./kg.

It can be seen that the type of substrate exerts a significant effect on the economic characteristics of the production. The most promising variant seems consist in using the synthesis gas since it is characterized by the lowest production costs and the greatest stability (37 % profitability, the cost price of commercial PHA being of 2452 rub./kg.)

Further PHA cost price reduction for a gaseous substrate could be possible in the case when the synthesis gas is not the only and the final product of coal gasification process, being a by-product resulting from the main production (*e.g.*, coke or sorbents) [19].

### REFERENCES

- 1 Fomin V. A., Guzeev V. V., Plast. Massy, 2 (2001) 42.
- 2 Potapov A. G., Parmon V. N., *Ekol. i Promyshl.*, Special issue (2010) 4.
- 3 Scott G. (Ed.), Degradable Polymers. Principles and Application, Kluwer Acad. Publ., Dordrecht, the Netherlands, 2002.
- 4 Shishatskiy O. N., Khlebopros R. G., Volova T. G., Analiz Rynka Bioplastikov i Perspektivy Yego Razvitiya, Krasnoyarsk, 2008.
- 5 Bordes P., Pollet E., Averous L., *Progr. Polymer Sci.*, 34 (2009) 125.
- 6 Popov A., Tara i Upakovka, 3 (2007) 43.
- 7 Volova T. G., Sevastyanov V. I., Shishatskaya E. I., Polioksilkanoaty (POA) – Biorazrushayemye Polimery dlya Meditsiny, in V. I. Shumakov (Ed.), Platina, Krasnoyarsk, 2006.
- 8 Shabanov V.F., Kuznetsov B.N., Shchipko M.L., Volova T.G., Pavlov V.F., Fundamentalnye Osnovy Kompleksnoy Pererabotki Ugley KATEK dlya Polucheniya Energii, Sintez-Gaza i Novykh Materialov s Zadannymi Svoystvami, Nauka, Novosibirsk, 2005.
- 9 Volova T. G., Hydrogen-Based Biosynthesis, Nova Science Publ. Inc., NY, 2009.
- 10 Tanaka K., Ishizaki A., Kanamaru T., Kawano T., Biotechnol. Bioeng., 45 (1994) 268.
- 11 Sugimoto T., Tanaka K., Ishizaki A., Biotechnol. Bioeng., 62 (1999) 625.
- 12 Ishizaki A., Tanaka K., Appl. Microbiol. Biotechnol., 57 (2001) 6.
- 13 Volova T. G., Biosintez na Vodorode, Izd-vo SO RAN, Novosibirsk, 2004.
- 14 Volova T. G., Kalacheva G. S., Altukhova O. V., Mikrobiol., 70 (2001) 745.
- 15 Voynov N. A., Volova T. G., Prikl. Biokhim. Mikrobiol., 39 (2003) 166.
- 16 Volova T. G., Shishatskaya E. I., Biorazrushayemye Polimery: Sintez, Svoystva, Primeneniye, in E. J. Sinski (Ed.), Krasnoyarsk, 2011.
- 17 RU Pat. No. 2051962, 1996.
- 18 RU Pat. No. 2207375, 2003.
- 19 Islamov S. R., Khim. Tv. Topl., 2 (1991) 59.