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Marek STELMACHOWSKI[1]

UTILIZATION OF GLYCEROL, A BY-PRODUCT OF THE TRANSESTRIFICATION PROCESS OF VEGETABLE OILS: A REVIEW

METODY ZAGOSPODAROWANIA GLICERYNY, PRODUKTU UBOCZNEGO Z PROCESU TRANSESTRYFIKACJI OLEJÓW ROŚLINNYCH: PRZEGLĄD LITERATUROWY

Abstract: The use of biodiesel is expected to grow in the future due to the environmental policy of the EU. The increase in the production of biodiesel has resulted in a glut of glycerin that has led to a precipitous market price drop. At present glycerol is in surplus but in the near future could become a waste problem. It may create a barrier for the development of this industry branch and reduce biodiesel applications as well. This glut also indicates that known technologies for the utilization of glycerol have many disadvantages and that their efficiency and profitability are too low. The utilization of waste glycerol may be carried out by feedstock recycling into energy carriers (hydrogen, syngas and methane), or it may be converted into other chemicals (eg, acrolein, epichlorohydrin, ethers, esters and alcohols). As hydrogen is a clean energy carrier, the conversion of glycerol into hydrogen is the best glycerol use. Catalytic steam reforming, aqueous reforming, autothermal reforming, pyrolysis, gasification, photo-conversion and bioconversion of glycerol may be considered to solve the glycerol surplus problem. This analysis indicates that the (aqueous/steam) reforming and/or photocatalytic conversion of glycerol have become the best processes for the utilization of glycerol from an economic and environmental point of view.

Keywords: glycerol, hydrogen, pyrolysis, gasification, bioconversion, photocatalysis, reforming.

Introduction

The limited oil reserves on Earth, the increasing price of a barrel of oil (which is sometimes higher than \$100) and the need to reduce CO_2 emissions resulting from the combustion of fossil fuel have resulted in the search for new technologies that can produce new types of liquid fuels and new additives for traditional liquid fuels. Transesterification of vegetable oils (palm, soybean, rapeseed and many others) is a method of producing biodiesel, which is a mixture of esters (methyl or ethyl) of higher fatty acids (FMEs). Bioethanol (also produced from biomass) and FMEs are the most popular additives in

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traditional fuels. The European Union recommended in the 2003/30/EC Directive that the fraction of biofuels in conventional fuels should at least be 5.75% wt. in 2010 and 20% in 2020 [1]. Therefore, the production of biofuels has recently dramatically increased. Statistical data from different sources differ to a small extent. In 2004, the production of biodiesel in EU countries was approximately 1.93 million tons(Mg), while it amounted to 4.89 million tons in 2006 (in some reports, this value was given as 3.1 million tons). In 2006, it was also predicted that the production of biodiesel in 2012 in the EU countries could be more than 10 million tons [2, 3]. In fact, in 2008, the amount of biodiesel produced was 7.8 million tons [4]. A production of 20.9 million tons has been reported for 2009, and only two countries, Germany and France, produced more than 7.7 million tons. However, the *European Biodiesel Board* (EBB) official statistical data for 2009 were based on the declared capacity of existing processing plants [4]. Thus, the actual amount of biodiesel produced was probably lower. In the USA, the production of biodiesel increased from 0.5 to 250 million gallons(3.79 dm^3) between 1999 and 2006 [5]. Similar results could probably be observed in China, Canada and other countries with high transport fuel demands.

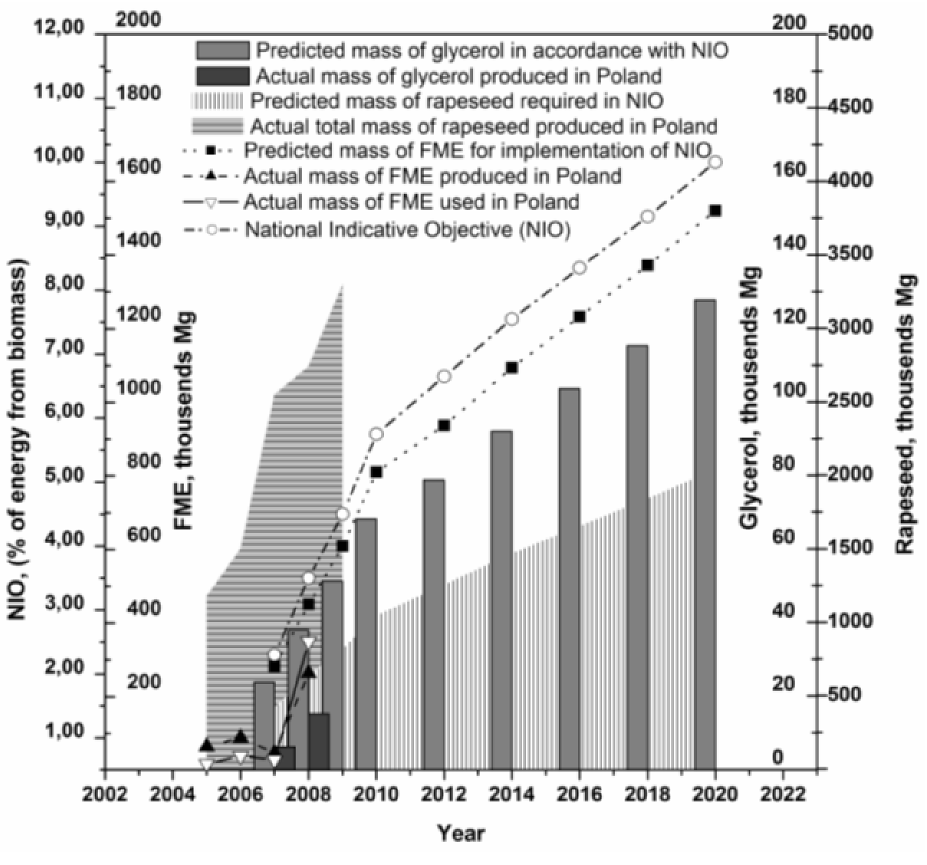

Fig. 1. Predicted and actual production of rapeseed, FMEs and glycerol in Poland in relation to the National Indicative Objective (NIO) [4, 6, 7]

According to EBB estimates, the production capacity of Poland was approximately 0.58 million tons in 2009 [4]. However, the actual production was probably 10 to 20% lower. It is predicted that the annual amount of manufactured FMEs will be around 1.5 million tons in the coming years. Figure 1 represents the actual output growth between 2005 and 2008 and the growth predicted from 2008 to 2020 for rapeseed, bioesters and glycerol. As can be seen, the current fraction of biofuels in transport fuels in Poland is not close to the value required by the EU transport and fuel policies, ie, 5.75%. A value of 5.75% could not be achieved in Poland because the supply of rapeseed oil esters is below 0.6÷0.65 million tons/year [8-10]. There are also significant differences between the objectives set by the EU policies and the results expected by the *National Indicative Objective* (NIO) (especially before 2008) for the fraction of biofuels in the structure of energy consumption in Poland.

The EU environmental policy, which assumes that the combustion of fossil fuels is responsible for climate changes, will be applied in the future even if this assumption has not yet been confirmed; thus the profitability of the policy is undetermined and many researchers have questioned the methodology and quality of the tools used for assessing the effects of fossil fuel combustion. However, from the other side, the increase of the price of an oil barrel and a higher biodiesel demand may increase the profitability of the production of biodiesel. The evaluation of the economic and technological aspects of biodiesel production in Poland and the EU is not simple. It is essential to assess whether:

- it is possible to use the required acreage of agricultural land that is suitable for the cultivation of rapeseed (which in Europe would be the basic raw material for the manufacture of bioesters),
- the acreage of other crops cultivation can be exempt for the cultivation of rapeseed; it is not certain that ethical aspects can be excluded from this assessment; however, as these aspects cannot be quantified, they will be ignored in the rest of the present study.

The following factors have also to be determined:

- the optimal size of the acreage of the rapeseed cultivation,
- the optimal volume of the oil-producing facilities and their distance from the cultivation area to take into account the energy costs related to transport,
- the technology of the transesterification process,
- the optimal scale of the industrial plant of biodiesel production,
- the selection of methods and processes that use the wastes and by-products, which increase the profitability of the whole process.

It should be also taken into account that rapeseed is cultivated seasonally and harvested during the 2-3 months of summer in Europe. The seeds must therefore be stored in a manner that allows the facilities to work for the next 10 to 11 months. Some preliminary analyses regarding Poland's problems were reported by Jerzykiewicz et al [11] and Korytowski and Inwolski [12]. Both groups mentioned issues related to the development of waste and by-products of different technologies. Further economic analyses are indispensable to promote the use of biofuels. These analyses should demonstrate that the production of biofuels is profitable for both the farmers and the processing plants.

Several wastes and by-products are generated during the production of FMEs from rapeseed. A simplified diagram of the whole process is presented in Figure 2.

Until now, the utilization of straw and oilseed cake has not generated significant problems when rapeseed has been cultivated for a traditional use, ie, the manufacturing of edible oil. Straw and oilseed cake have been used for the manufacturing of protein feed and solid fuels (pellets, briquettes) to produce green energy. However, the use of the whole area of agricultural land dedicated to the cultivation of rapeseed to achieve the required fraction of bioesters will result in a large amount of these two by-products, which will be problematic. New techniques have to be developed to efficiently use straw and oilseed cake. For instance, the components could be used to produce amino acids, proteins and fats, among others.

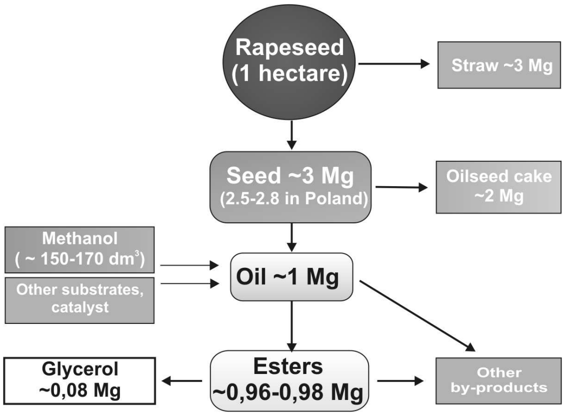

Fig. 2. Simplified diagram of the production of FMEs based on the NBB data

Glycerol, a by-product of the production of bioesters

The most important by-product obtained during oil transesterification is crude glycerol. This phase contains glycerol, unprocessed methanol and smaller amounts of other substrates and by-products. The mass of crude glycerol is equal to approximately 12% wt. of the obtained mass. The content of pure glycerol in the glycerin phase is about 60÷70% wt.

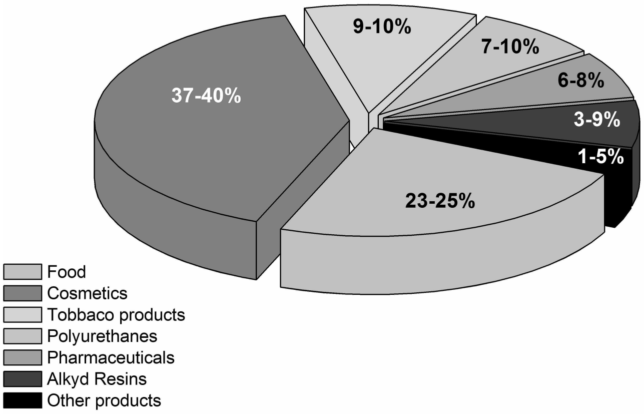

Fig. 3. Traditional glycerol uses with average worldwide values. In Poland, the data are a little different

The estimated worldwide glycerin demand in 2006 was between 93 000 and 95 000 Mg. The demand was slightly higher in subsequent years because of economic growth. The traditional uses of glycerin are shown in Figure 3. The increase of the production of biodiesel and the resulting excessive amount of glycerol produced by the transesterification of oils have led to considerable lower market prices of glycerol. Figure 4 shows the fluctuations of the glycerol price and the correlation of the price with the volume of manufactured glycerol (derived from the production of biodiesel) in Europe between 1996 and 2008. Glycerol prices reached 300÷400 \$/Mg but there were periods when it dropped to 50÷100 \$/Mg.

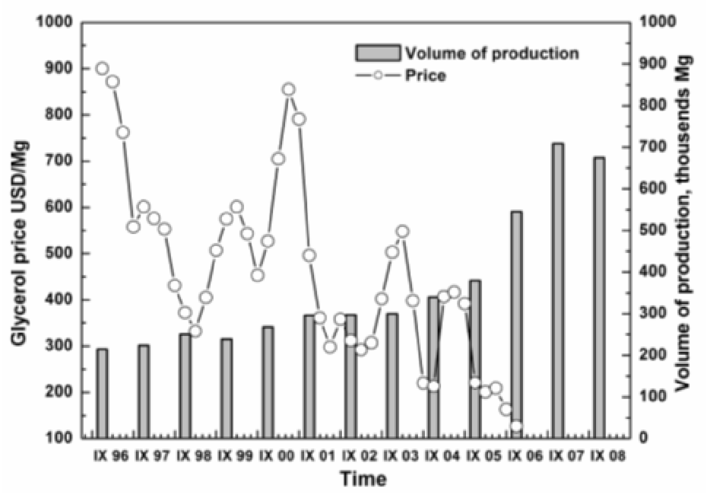

Fig. 4. Fluctuations of the glycerol price in Europe [3, 4, 10]

A further increase in the production of biodiesel and glycerol will result in a further decrease of the glycerol price in the long term. This will also decrease the profitability of the production of rapeseed and bioesters unless new glycerol utilizations are found. The glut of glycerol may slow the development of this industrial branch and reduce the application of biodiesel. This glut also indicates that the technologies using glycerol present many disadvantages and that their efficiency and profitability are too low.

The simplest utilization method of crude glycerol is its combustion, which is an advantageous method as it does not require any purification, which would increase the cost of the method. However, this process is not easy from a technological point of view. The following stoichiometric equation corresponds to the combustion of glycerol:

$$C_3H_5(OH)_3 \quad + 3{,}5O_2 \quad \rightarrow \quad 3CO_2 + \ 4H_2O \ - 1655\,\text{kJ/mol} \qquad (1)$$

The heat of combustion is two times lower than that of fossil fuels but is comparable to the heat of combustion of most types of biomass (eg, wood, straw, oilseed cake, bark, chips, willow and sawdust). The calorific value is lower due to the relatively large amount of water that is obtained. Moreover, water renders the combustion of glycerol very difficult because it leads to the blanketing of the flame at the burners and the formation of large quantities of carbon black. In practice, it is essential to perform co-combustion of glycerol with other liquid fuels using special burners. The co-combustion of the glycerol/glycerol phase and oilseed cake and/or straw has not yet been carried out in a large scale.

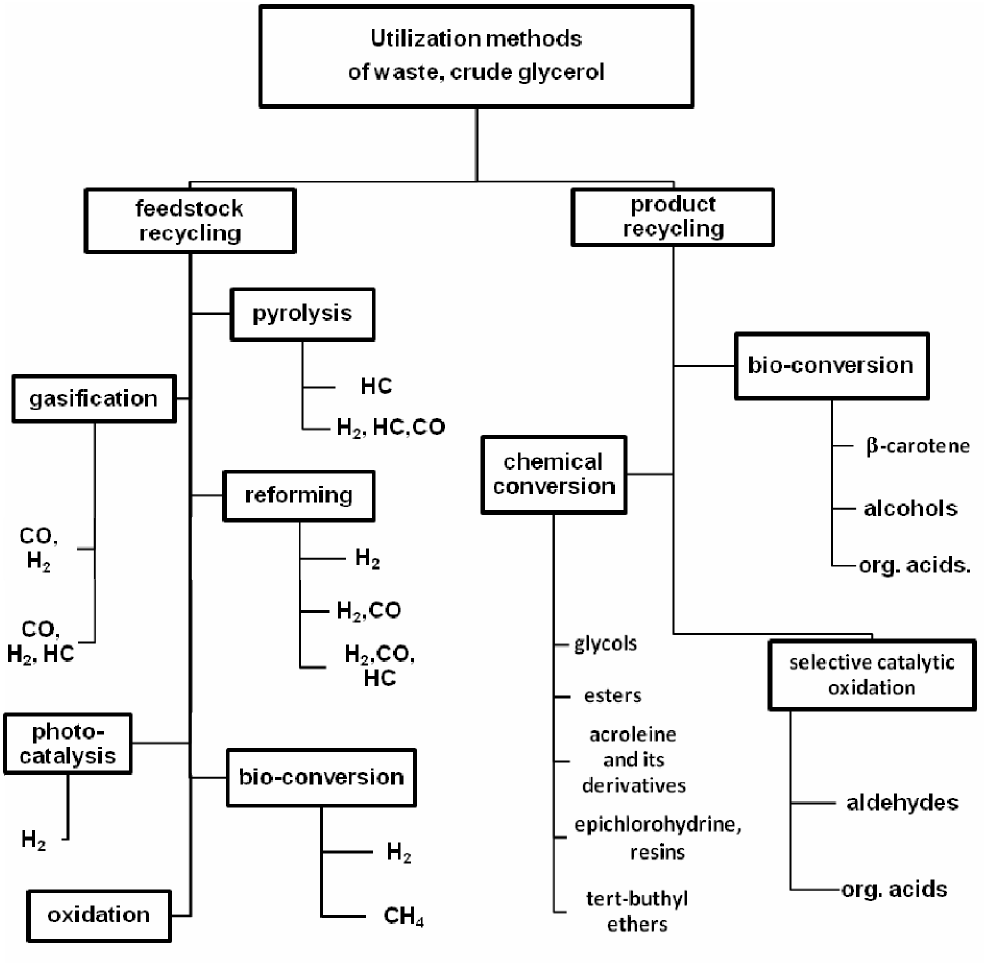

Fig. 5. Methods using waste glycerol obtained by transesterification of vegetable oils

Various methods have been reported in the literature for the utilization of glycerol, some of which have already been implemented on an industrial scale. However, it seems that at least some well-known technologies lead to the manufacturing of traditional products that are usually obtained by other technologies. The technologies that use glycerol may result in a lower profitability for the production of such traditional products.

The methods using waste glycerol can be categorized based either on the obtained products (energy carriers) or the technology. The different technological methods are further discussed in the chapter. Figure 5 gives an overview of different methods using glycerol.

Feedstock recycling of glycerol

Pyrolysis and gasification

Table 1

Products obtained by pyrolysis of glycerol

Fernandez et al [15]						**Valliyappan et al [14]**			
Glycerol having a purity of 99% [40 cm^3/h]						**Glycerol having a purity of 72% [6.5 cm^3/h]**			
Temperature									
800						650	700	750	800
Classical pyrolysis				Pyrolysis in a microwave oven		Conventional pyrolysis (fixed-bed reactor) under a nitrogen atmosphere (60 cm^3/min)			
Product	Catalyst					Without catalyst (glass bead bed (d = 4 mm)			
	Active carbon		Without catalyst	Active carbon					
	BC	CC		BC	CC				
Product yield [% mass]									
Quick coke	1.4	1.7	0.1	3.7	2.4	-			
Liquid	16.8	18.5	21.5	12.7	16.1				
Gas	81.8	79.8	78.4	83.6	81.5	~ 100			
Gas product composition [% vol.]						Gas product composition [% mol]			
H_2	28.9	30.1	22.6	34.6	33.2	54.0	50.0	45.7	44.9
CO	48.7	43.5	51.7	45.9	44.4	17.0	22.1	27.7	48.6
CO_2	1.4	4.8	1.4	1.8	3.8	0.2	0.0	1.1	1.0
CH_4	14.6	16.7	14.4	13.5	13.1	14.2	14.5	14.1	3.3
C_2H_4	4.2	3.3	7.9	2.9	4.4	10.1	9.6	9.1	2.0
C_2H6	1.8	1.3	1.6	1.0	0.6	2.2	2.0	1.5	0.1
C_3H_6	Not analyzed					2.4	1.7	0.8	0.1
H_2 + CO	77.7	73.6	74.3	80.5	77.6	71.0	72.1	73.4	93.5
H_2/CO	0.59	0.69	0.44	0.75	0.75	3.2	2.3	1.6	0.9

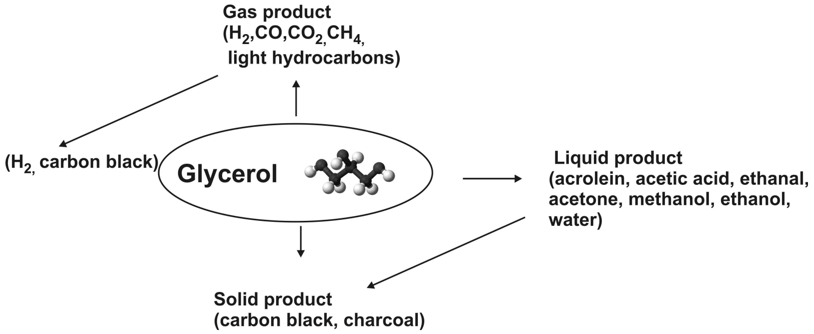

Fig. 6. Reaction pathways and products obtained by pyrolysis of glycerol at atmospheric pressure

Chaudhary and Bhakshi [13], Valliypana et al [14] and Fernandez et al [15], Stein et al, [26] among others, have studied the pyrolysis and gasification of glycerol at 650÷800ºC under ambient pressure. Dou and Dupont investigated the kinetics of the pyrolysis of crude glycerol (from the biorefinery of D1-Oils Ltd., Middlesborough, UK) using thermogravimetry [17]. They designated the kinetic constants for three simple kinetic models and distinguished three stages for the process. Reaction pathway diagram of the process proposed by the authors is presented in Figure 6 and experimental results obtained by Valliypan and Fernadnez are summarized in Table 1.

A few reports in the patent literature state that the pyrolysis of glycerol for generation of hydrogen is not the technically and economically most advantageous solution.

Reforming of glycerol

The reforming of glycerol to hydrogen and/or carbon monoxide and hydrocarbons has been widely studied [18-35]. The following stoichiometric equation corresponds to the reforming of glycerol [18]:

$$C_3H_8O + xH_2O + yO_2 \rightarrow aCO_2 + bCO + cH_2O + dH_2 + eCH_4 + \dots\dots \qquad (2)$$

Depending on the heating source and the reagents, the process can be operated as a steam reforming in the gas phase (with or without catalysts) or in the aqueous phase (*aqueous-phase reforming*; APR) and as an autothermal process in the aqueous phase. The most effective catalysts for the reforming of oxygenated hydrocarbons are based on Group VIII metals because these metals generally facilitate the breaking of C–C bonds. Silica or (Al_2O_3)-supported nickel, cobalt, nickel/copper, platinum (and other metals: Rh, Ir, Ru, Zr, Ce, La) are the most commonly used catalysts [18-22].

The steam reforming of glycerol (x > 0, y = 0) is described by the following equation:

$$C_3H_8O_{3(gas)} + 3H_2O_{(gas)} \longleftrightarrow 7H_{2(gas)} + 3CO_{2(gas)} \quad \Delta H_{298} = 345 \ \text{kJ/kmol} \qquad (3)$$

In view of the stoichiometry of the reaction, the maximum amount of hydrogen that can be produced is 7 moles of hydrogen per mole of glycerol. However, as it is an equilibrium reaction, the maximum yield is smaller. Douette et al studied the reforming of pure glycerol and a glycerol phase (from Pacific Biodiesel, Honolulu, HI, USA) in a laboratory-scale tubular reactor using a nickel catalyst [18]. A yield of 4.6 moles of H_2 per mole of glycerol was obtained at 760°C. The drawbacks of this method are high energy inputs and a quick deactivation of the catalysts.

Adhikari et al also performed a comparative thermodynamic analysis and experimental studies [5, 19-21]. The thermodynamic analysis of the process showed that a high temperature (T > 420°C), low pressure (0.1 MPa) and a high ratio of water to glycerol (9:1) led to a high conversion of glycerol into hydrogen (the conversion to methane was minimized and the conversion to coal did not occur). The authors confirm also the essential role of the water gas shift reaction. Other, essential thermodynamic studies of this process were performed also by Kunkes et al [23] and Wang et al [24].

The reforming of glycerol can also take place in the *aqueous phase* (APR). For x = 0, y = 0 and a C:O ratio of 1:1 for organic compounds, the reforming of glycerol is given by the following stoichiometric equation:

$$C_3H_8O_3 \longleftrightarrow 3CO + 4H_2 \qquad (4)$$

Under the above-mentioned conditions, the reaction is accompanied by the water gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{5}$$

The advantages and drawbacks of the method were discussed by Davda et al [25], who performed thermodynamic and kinetic analyses of the conversion of oxygen derivatives into hydrogen and/or alkanes. Several metals supported on various materials were investigated to optimize the yield and selectivity of the hydrogen production. It was claimed that catalysts based on Pt and Ni-Sn alloys are the most promising materials for hydrogen production and that the catalytic activity of metals is Pt ~ Ni > Ru > Rh ~ Pd > Ir. The selectivity depends on various factors such as the nature of the catalytically active metal, the support, the pH of the solution, the feed and the process conditions. Davda et al also proved that the method can be highly efficient. In their opinion, the reforming reaction under APR conditions:

- reduces the amount of energy required, the substrates and products do not need to be vaporized,
- makes the process more safe because the products are non-toxic and non-flammable,
- can lead to decreased CO production and increased hydrogen production because the water gas shift reaction is favorable in the process conditions,
- hydrogen and CO can be easily and effectively purified using membrane technologies because the pressure of the effluent gas is high (1.5÷5 MPa),
- is performed at temperatures that minimize undesirable reactions,
- gives the possibility of performing the process in a single step at low temperature.

Wen et al also investigated the reforming of glycerol in the aqueous phase [26]. They investigated the activity and stability of catalysts that are based on Pt, Ni, Co or Cu zeolites. They also investigated the effects of the process conditions, catalyst type and catalyst support on the production of hydrogen. Some of the obtained results are presented in Table 2.

Table 2

Conversion of glycerol into hydrogen under APR conditions [26]

Catalyst	**Carbon conversion**	**Product composition**				**Productivity**
		H_2	**CO_2**	**CO**	**Alkanes**	
	[%]	**[% mol]**				**mmol/[min $g_{cat.}$]**
Pt/Al_2O_3	18.9	69.8	24.5	0.05	5.8	572.2
Pt/SiO_2	10.8	71.8	25.8	0.06	2.3	369.4
Pt/act. carbon	17.2	69.6	27.1	0.08	3.1	307.7
Pt/MgO	13.8	79.9	18.2	0.10	1.9	431.9
Pt/HUSY	22.0	71.8	21.4	0.07	6.8	337.0
Pt/SAPO-11	13.3	72.8	24.4	0.09	2.6	222.1

In several articles, [5, 21, 24, 27-32], comparative thermodynamic analyses were performed. In most cases, it was concluded that it is necessary to purify the crude glycerol (glycerol phase) before using it in the process. It seems that a further and more detailed discussion of all the methods of conversion of glycerol to hydrogen will be presented.

In April 2009, the Linde Group announced the construction of a demonstration plant for the conversion of glycerol for mid-2010. However, the method and technology that would be used for the conversion of glycerol were not revealed. In other words, it is unclear whether a low-temperature pyrolysis (400÷600°C) to liquid products, a high-temperature pyrolysis to gaseous products or a steam reforming (under APR conditions) to hydrogen will be performed.

Processes (eg, reforming and oxidation) performed in supercritical water have been perceived as very interesting. Adhikari et al [20], Byrdet al [33], Xu et al [34] and Chainkala et al [35] have experimentally studied such processes. The product obtained in these processes consists of hydrogen, carbon dioxide and methane. It is noteworthy that the process conditions are rather drastic in this case (T > 420°C, P > 24 MPa). This will certainly limit the applicability of the technology at a large industrial scale for economic reasons.

Photocatalysis as a method to convert glycerol into hydrogen

The idea of using a photocatalytic process for the conversion of glycerol is based on results obtained for the degradation of organic pollutants in wastewater and the conversion of alcohols (eg, ethanol) into hydrogen. Patsoury et al, Kondarides et al, Veykios et al and Strataki et al [36-38] have reported results obtained during the degradation of organic pollutants, ie, simple organic alcohols, organic acids and aldehydes. The results indicated that glycerol, can be converted into hydrogen in the presence of photocatalysts under mild conditions. The reaction is given by eq. (9):

$$C_3H_8O_{3(\text{liquid})} + 3H_2O_{(\text{liquid})} \rightarrow 7H_{2(\text{gas})} + 3CO_{2(\text{gas})} \tag{9}$$

It is endothermic and proceeds under ambient conditions. The energy is obtained from electromagnetic radiation. Specifically, in the laboratory, the energy source is a lamp, eg, a mercury lamp (for UV) or a xenon lamp (simulating sunlight). The catalysts for the reaction are based on the most widely used photocatalyst, TiO_2, which is mainly modified with gold, palladium, platinum or copper. Different laboratory reactors were used in the investigations. Tank batch photoreactors with a stirrer and in which the catalyst was suspended in a liquid (glycerol solution in water) were mainly used.

Table 3

Comparison of the results of photoconversion of glycerol to hydrogen

	[43]	[40]	[41]	[42]	[39]
Photoreactor/vol. of solution	250 cm^3 Pyrex	~200 cm^3 of solution	100 cm^3 of solution	200 cm^3 of solution	60 cm^3 of solution
Lamp/power [W]	Hg/125	Xe-arc/250	Hg/250	Xe-arc/250	Xe-arc/300 Xe-arc/450
Catalyst/metal content	CuO_x/TiO_2 (2.5% Cu)	Pt/TiO_2 (0.5÷5% Pt)	Pt/TiO_2 (-)	Pd/TiO_2 (0.5% Pd)	Pt/TiO_2 (0.5% Pt)
Temperature [°C]	20	40÷80	ambient	ambient	40
Glycerol concentration	1 M	0÷1 M	0.75÷4.0 mM	50 vol %	0.0÷1.1 M
Gas environment	Argon flow	Argon flow	-	Argon flow	Argon flow
H_2 Yield	0.5÷1.05 mmol/[$g_{cat.}$· h]	Max. 1.5 mmol/[$g_{cat.}$· h]	Max. 0.3 [mmol/h]	Max. 0.22 [mmol/h]	Max. 0.2 [mmol/h]

Kondarides et al, Kondaridiesand & Daskalaki, Li and others [39-41] studied the decomposition of water with simultaneous oxidation of various organic substances (ie, ethanol, glycerol, and sugars) at ambient temperature and under atmospheric pressure in the presence of a Pt/TiO_2 catalyst. Their main goal was to determine the influence of various process parameters on the efficiency of the process. Bowker et al conducted experiments on the decomposition of glycerol to produce hydrogen with a TiO_2 catalyst modified with palladium and gold [42]. Bowker et al also presented their own proposal of a six-stage model for the mechanism of the photocatalytic conversion process. Gombac et al performed a comparative study of the photocatalytic conversion of ethanol and glycerol into hydrogen using a CuO_x/TiO_2 catalyst [43]. The influence of the catalyst preparation and the nature of the copper ions that are present on the surface of the TiO_2 catalyst were also investigated.

Wu et al investigated the role of copper (in various forms) in the photocatalytic conversion of glycerol into hydrogen in the presence of a CuO_x/TiO_2 catalyst [44]. They found that high concentrations of Cu(I) led to higher yields of hydrogen than Cu(0). The inhibitory role of Cu(II), initially reported by Li et al, was confirmed. Table 3 summarizes all the results obtained by the different groups.

A new generation of titanium semiconductors with a photocatalytic activity that includes the visible spectrum ($\lambda > 400$ nm) is currently being developed. With these catalysts, the energy inputs are reduced. Photocatalysts that are active over the entire visible spectrum are obtained by different preparation methods [45]:

(A) modification of by addition to a basic support noble or other metalsa (Anpo, [46]),
(B) preparation of reduced forms of TiO_{2-x} (Nakamura et al [47]),
(C) sensibilization of TiO_2 using dyes (Chatterjee, Mahata [48]),
(D) sensibilization of TiO_2 with semiconductors (Hirai et al [49]),
(E) doping of a base catalyst with a non-metal (N, S, C, B, P, F, I) [50-53],
(F) doping of a catalyst with luminescent substances (Feng [54]).

The recovery process of spent catalysts from the solutions may limit the use of heterogeneous photocatalysis in industrial processes. Immobilization of the catalyst in the reactor and/or separation of the catalyst particles from the purified liquid are required before disposal of the solution [55]. By solving this problems the method could be used for the treatment of glycerol waste in an efficient manner.

Biochemical conversion of glycerol into energetic raw materials

Sabourin-Provost and Hallenbeck studied the photofermentation of a crude glycerol fraction into hydrogen in the presence of *Rhodopseudomonas palustris* bacteria (*CGA009, wild-type; CGA750, NIF-*) [56]. Six moles of hydrogen were obtained per mole of glycerol. The presented results are only preliminary. Seifert and Waligorska et al studied a periodic glycerol fermentation in which the main product was hydrogen [57]. A glycerol conversion of about 75% was achieved, and 0.41 moles of hydrogen per mole of glycerol were obtained; the maximum rate of hydrogen production was 0.15 g $H_2/(dm^3\ h)$. It was also found that the addition of glycerol increased the production of biogas (methane) during the biodegradation/fermentation of organic wastes. Siles Lopez et al conducted one of the best studies on the anaerobic bioconversion of glycerol into biogas (methane was a main component) [58]. Using an aqueous solution of glycerol and sewage sludge as the raw material, they achieved a conversion of almost 100% of the stock (ie, the organic loading). The methane yield amounted to nearly 0.14 kmol of CH_4/kg of reacted glycerol under ambient conditions. This result is better than that obtained for the conversion of glycerol into hydrogen; additionally, the reaction rate was higher. The bioconversion of glycerol (and organic wastes) into hydrogen has only been studied in the laboratory. The applicability of the method to industrial processes has not yet been evaluated.

Product recycling of glycerol

Selective catalytic oxidation

As can be seen in Figure 5, not a large number of products can be obtained by selective oxidation of glycerol. Demirel et al have investigated the oxidation of glycerol in the liquid phase and in the presence of a catalyst and compared their results with those reported in the literature [59, 60]. The effects of the catalyst particle size, temperature, pressure and concentration of NaOH in the solution on the selectivity (to glycolic acid, tartronic acid and other products) and the reaction rate were investigated. The maximum glycerol conversion that was obtained was ~50%. Studies performed with other catalysts have also been reported. Thus, Srivastava et al have investigated the kinetics of the oxidation of glycerol in the presence of a ruthenium catalyst [61]. Bianchi et al evaluated the selective catalytic oxidation in the presence of mono- and bimetallic catalysts [62]. Ketchi et al and Demirel studied the activity of carbon-supported catalysts and of a bimetal AuPd catalyst in the oxidation of glycerol and carbon monoxide [63]. Liang et al [64] and Prati et al [65] investigated the same reaction in the presence of a platinum catalyst and a gold catalyst (in the form of nanoparticles), which was supported on either activated carbon or TiO_2, respectively. On the other hand, Zope and Davis studied the influence of process parameters on the oxidation of glycerol with molecular oxygen in the liquid phase and in the presence of a Au/TiO_2 catalyst [66]. The reaction in the presence of mono- or bimetallic catalysts based on noble metals was supported) on activated carbon or TiO_2 occurs at a relatively low temperature and with a conversion of up to 50%.

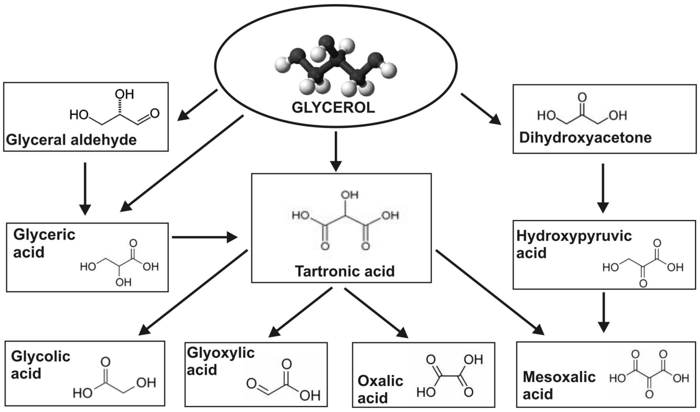

Fig. 5. Possible reaction pathways and products obtained by selective catalytic oxidation of glycerol

Chemical conversion of glycerol into other chemical products

Most scientific studies focused on the possible manufacturing of useful products and semi-products that are different from those obtained by oxidation or reforming of glycerol. Modifications of known processes and new methods have thus been proposed.

Zheng et al reviewed the different methods [67]. The following products can be obtained:

- acrolein (CH_2=CH-CHO) obtained by dehydrogenation,

- 1,3-dichloro-2-propanol ($C_3H_6Cl_2O$) and epichlorohydrin (C_3H_5ClO) obtained by chlorination,
- *tert*-butanol ethers, tri-*tert*-butyl ethers and di-*tert*-butyl ethers obtained by etherification,
- monoacylglycerol and diacylglycerol obtained by esterification,
- 1,2-propanediol and 1,3-propanediol obtained by reduction.

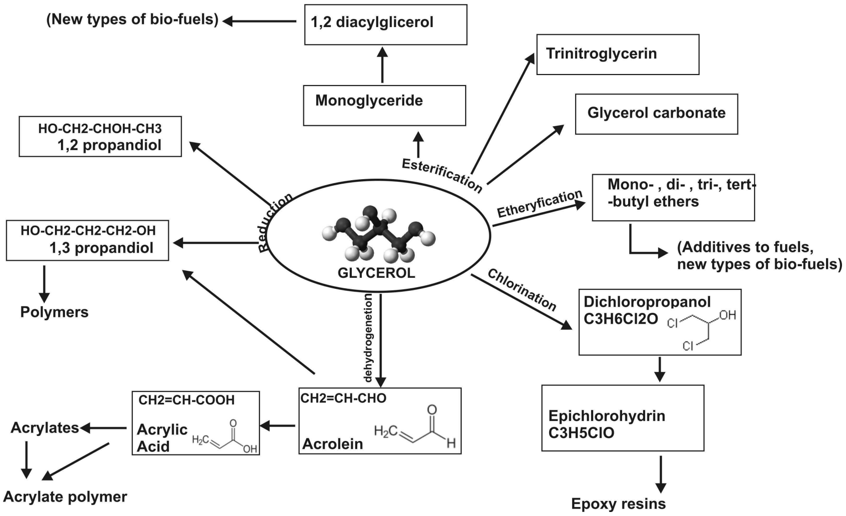

Fig. 6. Methods of conversion of glycerol into useful products (excluding selective oxidation)

Figure 6 summarizes the different possible reaction pathways and products. Most of the studies focused on the dehydration of glycerol into acrolein (eg, Corma et al [68]), the synthesis of alcohols, particularly 1,2-propanediol (eg, Guo et al [69]), and the production of additives for fuels (eg, Frusteri et al [70]). The yield, selectivity and glycerol conversion are very different for different products, as discussed below. Watanabe et al reported the results of the synthesis of acrolein from [71]; a glycerol conversion of 90% and selectivity for acrolein of 80% were achieved. Tsukuda et al also studied the synthesis of acrolein from glycerol [72]. The aim of the study was to optimize the composition of the catalyst. The best results were obtained with the highest temperature and a Q10-SIW-30 ($H_4SiW_{12}O_{40}$•$24H_2O$) catalyst. A glycerol conversion of almost 100% and selectivity for glycerol of over 85% were achieved. Kijenski et al from the *Industrial Chemistry Research Institute* (ICRI) in Warsaw (Poland) studied the dehydration of glycerol in a fixed-bed flow reactor in the presence of various catalysts: Al_2O_3, SiO_2, Al_2O_3, TiO_2 and the same compounds impregnated with H_2SO_4, H_3PO_4 and $H_3Mo_{12}O_{40}P$ [73]. The conversion to acrolein and allyl alcohol was the highest: it was 58 mol% between 300 and 320ºC. Corma et al also studied the conversion of glycerol to acrolein in two different reactors: a fluidized bed reactor similar to an FCC and a fixed-bed reactor [68]. It was found that lower temperatures favor the conversion into acrolein (yield of 55 to 62%) and higher temperatures favor the conversion into acetaldehyde. Atia et al investigated and discussed the conversion of glycerol into acrolein in the presence of various catalysts of formula $[X^{n+}Y_{12}O_{40}]^{8-n}$•$xH_2O$

(where X ≡ P, Si, B, Y ≡ Mo, W, V and "n" is the oxidation number of X) [74]. With all catalysts, acrolein was the main product; the selectivity for acrolein was 75% at 275°C for X ≡ Si and Y ≡ W. Suprun et al studied the influence of acid catalysts on the selectivity of the dehydration reaction of glycerol to acrolein [75]. The highest yield of acrolein (ie, 72%) was obtained for the zeolite SAPO-34. Ulgen and Hoeldrich studied the dehydration of glycerol into acrolein on a WO_3/ZrO_2 catalyst [76]. The highest selectivity was ~75% with a total conversion of glycerol. Kim et al investigated the same reaction using zeolites as catalysts [77]. The results were similar to those previously discussed. Wei and Suppes obtained acrolein in 67% yield with a glycerol conversion of 99% and a selectivity of 84% [78].

Frusteri et al prepared fuel additives by etherification of glycerol with *tert*-butyl alcohol [70]. Both the glycerol conversion and the selectivity were high and exceeded 93%. Kijenski et al also studied the conversion of glycerol into its *tert*-butyl ether derivative [79]. A glycerol conversion of 50% was achieved and a high selectivity to ethers was obtained for long reaction times.

Guo et al investigated the reduction of glycerol into 1,2-propanediol with a bifunctional Co/MgO catalyst [69]. The maximum glycerol conversion was about 55% and the selectivity for the desired product did not exceed 42%. Akiyama et al also studied the conversion of glycerol into 1,2-propanediol (1,2-PDO) [80]. A glycerol conversion of 100% was obtained with copper catalysts (Cu/Al_2O_3). A selectivity of 75% was obtained at 190÷200ºC and under a partial hydrogen pressure of 0.1 MPa. Huang et al investigated the conversion of glycerol into 1,3-propanediol (1,3-PDO). The main goal of this study was to demonstrate that the conversion of glycerol into the desired products occurred in one step. The obtained results confirmed the hypothesis [81]. Similar studies were carried out by Alhanashi et al [82] and Ma and He [83].

Luo et al studied the direct chlorination of glycerol to form 1,3-dichloropropanol (DCP), which is a raw material in the production of epichlorohydrin [84]. The goal of the study was to model the reaction kinetics. A very high glycerol conversion (at T = 90÷110ºC) was obtained. The direct chlorination of glycerol (by gaseous hydrogen chloride) to form DCP was also investigated by Song et al in a batch reactor [85]. The conversion of glycerol was close to 100% and the selectivity to DCP was ~90%. Santacesaria et al also investigated the chlorination of glycerol with gaseous hydrogen chloride under various conditions [86]. 1.3-dichlorohydrine was obtained in more than 95 mol %.

Sakthivel et al reported the esterification of glycerol with lauric acid (dodecane acid) in supercritical carbon dioxide and in the presence of catalysts based on a selected group of molecular sieves [87]. A high glycerol conversion and a high global selectivity to three esters of lauric acid were achieved. However, the conditions used (10 MPa, 150°C, reaction time = 18 h) would be problematic on a larger scale.

Maris et al studied theoretically and experimentally the hydrogenolysis of glycerol to ethyl and propyl glycols in the presence of bimetallic, bifunctional $PtRu/C_{act}$ and $AuRu/C_{act}$ catalysts [88]. The study focused primarily on the role of the catalysts. More detailed results were obtained by Feng et al in the presence of a ruthenium catalyst [89]. Feng used a partial hydrogen pressure of 5 MPa, a temperature of 180°C, a glycerol concentration in water of 20% wt. and a reaction time of 12 h. The glycerol conversion was 90.1%, the selectivity for 1,2-propanediol was 20.6% and that for ethylene glycol 41.3%. The same reaction was also studied by Marinoiu et al [90] and Chiu et al [91]. They focused on the optimization of process parameters such as the glycerol concentration, pressure, temperature and residence time to obtain a selectivity for propylene glycol that was greater than 90%.

The evaluation and assessment of methods for the conversion of waste glycerol to other chemicals is relatively difficult. On one hand, product recycling of glycerol should be favored as it leads to useful substances, allow to keep elements and effective (or primary) energy in the global world cycles and prevent the uncontrolled dispersion of waste energy. Therefore, this type of waste management method is the best way to control and prevent environmental pollution and is the best instrument of environmental policy. On the other hand, the application of the aforementioned methods in the recycling of glycerol is limited by, many essential factors:

- the process conditions (eg, high pressure and high temperature),
- the low selectivity and therefore a large range of products,
- the low glycerol conversion (in many cases),
- necessity of maintaining of the process conditions in a small range of variability and purification of the input material.

The application of the methods will also be limited by the market profile of the obtained products, which are often obtained with other technologies. Thus, a thorough market and economic analysis must be conducted.

Biochemical conversion of glycerol into other products

The conversion of glycerol into other useful chemicals using microorganisms has also been investigated. Examples of such investigation include:

- *The use of glycerol as a carbon source for the production of β-carotene.* Mantzouridou, Naziri and Tsimidou replaced glucose with glycerol in the production of β-carotene in the presence of *Blakeslea trispora* [92]. The use of a crude glycerol phase instead of pure glycerol did not inhibit the reaction.
- *Microbiological conversion of glycerin to 1,3-propanediol.* Deckwer has shown that glycerol can be converted into 1,3-propanediol with *Klebsiella* and *Citrobacter Clostridia* by fermentation [93]. The costs and feasibility of the process were also assessed from an industrial point of view.
- *The use of glycerol as a source of organic carbon in the fermentation processes.* Celik et al investigated by fermentation [94] the synthesis of various other organic compounds (organic acids of high molecular weights) using microorganisms.
- Athalye et al [95] and Yu et al [96] proposed the conversion of glycerol into ethanol using *Saccharomyces cerevisiae*.

The results indicate that the methods are industrially feasible. However, it must be considered that biochemical reactions are usually slow. This means that even though the process conditions are good, the kinetics of the process will result in large bioreactors. It is still very difficult to realistically assess the bioconversion of crude glycerol into useful products because not enough studies have been completed.

Conclusions

The production of ecological fuel components (bioesters, bioethanol) that are manufactured from biomass and that are additives for traditional motor fuels (which are obtained from fossil fuels) has recently drastically increased due to the EU environmental policy. For instance, the production of FMEs has been increased by at least ten-fold over the past five years. The EU environmental policy is based on:

- the growing need for independence, even partially, from external energy sources and
- the assumption that carbon dioxide (from anthropogenic sources, especially those produced during the combustion of fossil fuels) is responsible for the increase in air temperature and climate changes.

The above-mentioned assumption has not been scientifically proven (eg, on the basic of thermodynamic considerations and/or energy balances calculations) and is not economically justified. Nevertheless, it seems that there is no return from once established way.

Excellent methods for the production of FMEs and utilization of all of the by-products and wastes (eg, straw, oilseed cake and crude glycerol) that are generated during the production process are therefore required. The methods should be profitable at all stages of the process: during the cultivation of rapeseed (agriculture), in the oil industry (pressing of the oil and its transesterification) and during the production of fuels (for the petroleum industry). This will only be the case if all wastes and by-products are converted into useful materials. At present, straw and oilseed cake are either combusted or used as fodder or fodder ingredients with sufficient profitability. However, the utilization of crude glycerol that is generated during transesterification remains problematic.

Based on the articles reviewed and discussed herein, it may be stated that the well-known and available technologies of the utilization of glycerol and the obtained products decreased profitability of such processes because of the huge amounts of glycerol that are produced. These large amounts have resulted in a dramatic drop of the glycerol price on the market, which means that the traditional products obtained from glycerol has met with the barrier of limited demand. There are only a limited number of patent and scientific publications on the new conversion methods of glycerol into useful products or energy carriers. The investigations of innovative technologies are in most cases in the preliminary phase of research. Thus, the situation is economically difficult in European countries because they need new advanced methods of using glycerol that are not only industrially feasible but also profitable. These methods should allow the production of chemical products from a low-cost material, ie, glycerol. The apparatus used must also be inexpensive, and a market and economic analysis must first be performed.

Currently, the most feasible and promising methods are the conversion processes of glycerol into acrolein, epichlorhydrin, ethers, alcohols and esters. However, the demand for the obtained products might reach a limit too.

It is therefore also necessary to develop new methods for the conversion of raw bio-wastes into energy carriers, ie, third-generation biofuels by various technologies based on feedstock recycling. Such methods have not really been developed yet; current methods do not have optimal economic and technological parameters, which cause a progressive price drop of glycerol that has been observed on world markets. However, it seems, that the conversion of glycerol into hydrogen (or synthesis gas) is the most promising method, as the market for hydrogen (syn-gas) should be unlimited in the future. The question is, which of the investigated and developed processes and technologies may be the most profitable one?

Good process parameters have not yet been found for the gasification and pyrolysis of glycerol (to synthesis gas and/or hydrogen and hydrocarbons). The most-investigated method is the reforming of glycerol into hydrogen. Several types of reactions have been proposed: steam reforming, reforming in the *aqueous phase* (APR), autothermal reforming and decomposition in supercritical water. It seems that the most promising reactions are those that utilize steam reforming and/or APR. Supercritical conditions may not be suitable for economic reasons. The bioconversion and photoconversion of glycerin into hydrogen are still at a preliminary stage.

To properly assess a method, the following two points should be considered:

First, the method should have little impact on the environment. The least energy-consuming methods, ie the bioconversion and photoconversion of glycerin, are the most environmentally friendly methods.

Second, the process parameters, ie, the temperature, pressure, reaction rate and hydrogen yield and selectivity must be considered. These parameters affect the reaction time and plant size and thus the profitability of the method. Methods involving high pressures and temperatures (based on chemical reactions well known in other industries, such as steam reforming) are often characterized by higher reaction rates. Low-pressure methods occurring at ambient temperature in the presence of microorganisms (bioconversion) or photocatalysts (photoconversion) are characterized by significantly lower reaction rates (larger reactor volumes and longer residence time). Based on the reaction stoichiometry and equilibrium conditions, glycerol yield and conversion will be similar for both groups. Energy inputs will obviously be lower for low-pressure methods due to the use of radiation energy, ie, solar or artificial of xenon lamps. Thus, these methods may eventually become profitable if new, more efficient photocatalysts are found (in terms of energy used and reaction rate). Expensive methods that are performed at high pressure and temperature (eg, oxidation or reforming in supercritical conditions) are less profitable because operating costs should be low and the raw product and final products are cheap. As mentioned earlier, the photoconversion and bioconversion of glycerol have not been extensively studied. It is therefore difficult to assess the competitiveness of this technique with traditional methods (eg, reforming), which are characterized by high reaction rate and great industrial experience in exploiting of them.The optimization of the composition of the catalysts for photoconversion, the proper selection of microorganisms for bioconversion and the determination of the optimal process conditions for photocatalysis and bioconversion are necessary and currently investigated in many universities and R&D institutes. The profitability of the production of biofuels depends on the management of the wastes and by-products produced during full life cycle of them.

The development of new methods for the conversion of glycerol into energy, energy carriers and other useful products is funded by all European countries, indicating its importance. In 2008, three projects on the utilization of waste glycerol were started in the 7th Framework Programme [97].

1. *Sustainable and integrated production of liquid biofuels, bioenergy and green chemicals from glycerol in biorefineries* (GLYFINERY), 7th FWP (Seventh Framework Programme), Research area: ENERGY-2007-3.3-02 New uses for glycerol in biorefineries, Coordinator TECHNICAL UNIVERSITY OF DENMARK
2. *Reforming of crude glycerol in supercritical water to produce methanol for re-use in biodiesel plants* (SUPER METHANOL), Coordinator ENSCHEDE NETHERLANDS, The overall project objective is to produce methanol from crude glycerol, and re-use the methanol in the biodiesel plant.

3. *Integrated bioconversion of glycerol into value-added products and biogas at pilot plant scale* (PROPANERGY), Coordinator TECHNISCHE UNIVERSITET HAMBURG-GERMANY, This proposal aims at developing an integrated bioprocess to convert technical glycerol from biodiesel production into biogas and two value-added products 1,3-propanediol (PDO) and fertilizer in a biorefinery approach.

Unfortunately, fundamental gap in the assessment of the fundamental decisions about increasing of the fraction of biofuels in the global mass of energy carriers as well in the research and development of the described processes can be observed. No real thermodynamic analysis (made for instance on the basis of energy (exergy) calculations) and no energy balances for individual national economies and individual industrial process (in which biofuels are manufactured) have been made to confirm the assumptions on which the implemented environmental policy is based. An exergy analysis of the methods and a realistic assessment of the life cycles of fuels (traditionally produced from biomass) would determine the energy efficiency and environmental impact of the methods and products. It is obvious that the ecological profit of the implementation of biofuels (bioesters, bioethanol) can only be properly assessed if the energy and ecological balances take into account the environmental and production aspects of the necessary materials (eg, fertilizer for rapeseed production), the biofuel production (including the transport of seeds, oils and esters) and the management and utilization of wastes and/or by-products (straw, oilseed cake, glycerol, etc.). An environmental and ecological evaluation has been made for the products, but all important aspects have not been considered.

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METODY ZAGOSPODAROWANIA GLICERYNY, PRODUKTU UBOCZNEGO Z PROCESU TRANSESTRYFIKACJI OLEJÓW ROŚLINNYCH: PRZEGLĄD LITERATUROWY

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Abstrakt: Biodiesel (mieszanina estrów metylowych lub etylowych wyższych kwasów tłuszczowych), produkowany w procesie transestryfikacji olejów roślinnych, jest najpopularniejszym produktem, pochodzącym z biomasy, dodawanym do tradycyjnych paliw płynnych wytwarzanych z ropy. Jego produkcja w ostatnich latach szybko rośnie, co wynika z aktualnej polityki ochrony środowiska dążącej do ograniczenie emisji ditlenku węgla pochodzącego ze spalania paliw kopalnych. W procesie transestryfikacji powstaje szereg ubocznych produktów. Najważniejszym i powstającym w największej ilości produktem ubocznym (w samym procesie transestryfikacji) jest gliceryna. Duży wzrost ilości produkowanego biodiesla w ostatnich latach spowodował wytworzenie odpowiednio dużej ilości gliceryny, co bardzo zachwiało rynkiem gliceryny, wywołując duży spadek jej ceny. Fakt ten może stanowić pewną barierę rozwoju tej gałęzi przemysłu i ograniczyć dalszy wzrost udziału biodiesla w bilansie paliw silnikowych. Wskazuje to także, że dotychczas proponowane metody nie są wystarczająco efektywne technologicznie i ekonomicznie. Istnieją dwie podstawowe możliwości działania: (1) wykorzystanie gliceryny jako surowca do produkcji innych substancji chemicznych i (2) wykorzystanie jej energetyczne, w tym szczególnie do wytwarzania wodoru. Recykling produktowy jest najkorzystniejszą metodą zagospodarowania produktów ubocznych i odpadów. Jednakże, wykorzystanie gliceryny do wytwarzania innych produktów i półproduktów chemicznych może mieć ograniczone zastosowanie ze względu na to, że rynek tych produktów może się spotkać również z barierą popytu oraz ze względu na uzyskiwane niskie selektywności dla tych produktów. Analiza literatury wskazuje, że recykling surowcowy, w tym szczególnie proces konwersji gliceryny do wodoru, jest dobrą alternatywą, ponieważ rynek na wodór będzie w przyszłości praktycznie nieograniczony. Jeżeli instalacje przemysłowe będą ekonomiczne i proste w eksploatacji, ten sposób będzie prawdopodobnie rozwiązaniem optymalnym.

Słowa kluczowe: gliceryna, wodór, piroliza, zgazowanie, reforming, biokonwersja, fotokataliza, produkcja wodoru

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BIOBUTANOL - PRODUCTION AND PURIFICATION METHODS

BIOBUTANOL - METODY WYTWARZANIA I OCZYSZCZANIA

Abstract: The prospective of depletion of natural resources, petroleum products and rising prices of raw materials tend to look for fuels from renewable energy sources and biofuels. The focus so far has been put on bioethanol due to the availability of raw materials for its production and well-developed methods for isolation and purification. Butyl alcohol - biobutanol can be regarded as a potential biofuel. Biobutanol is a very attractive energy source because - as opposed to bioethanol - is non-hygroscopic, does not cause corrosion and has a higher calorific value. Production of butanol may be made by a fermentation process called ABE (*acetone*, *butanol*, *ethanol*), carried out mostly by bacteria *Clostridium acetobutylicum.* The basic problem of wider use of biobutanol depends on its production with sufficient efficiency and this in turn is limited by separation of butanol from fermentation broth. The distillation process is not applicable. The classical extraction requires the use of a flammable or toxic liquid. For separation and purification of biobutanol it is proposed to apply ionic liquids. Use of ionic liquids for the extraction of butanol (to remove from the fermentation environment) can be achieved either through direct application of the liquid in the bioreactor and separation of butanol outside of bioreactor or directing fermentation broth outside the bioreactor and separation of butanol in the membrane contractor.

Keywords: biobutanol, renewable energy sources, ionic liquids

Production of butanol by the anaerobic fermentation is one of the oldest industrial method for obtaining this organic solvent [1]. In the early 20th century interest in butanol resulted from an inadequate level of supply of natural rubber and increase of its market price. At that time, butanol was used as one of raw material for the production of butadiene being a raw material for synthetic rubber production. Currently, butanol is considered as an alternative biofuel.

Butanol is a colourless, flammable alcohol. It is widely used in industry, among others, applied as a solvent. It arouses particular interest due to the role it can play in the future as a biofuel. It is expected that production biobutanol can reduce consumption of oil and natural gas by the automobile industry and reduce emissions of harmful gases into the atmosphere [2, 3].

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The petrochemical industry uses alcohols, mainly ethanol as a fuel additive, improving its quality. Research results show that the use of butanol for this purpose is much more useful than the application of ethanol. Butanol has a high calorific value, which is 29.2 MJ/dm^3 (melting point –89.5°C, boiling point 117.2°C, flash point 36°C, the self-ignition 340°C). Furthermore, it also has a relatively low heat of vaporization, and is less corrosive than ethanol. All these features enhance its usefulness both as an additive to gasoline, as well as biofuels. Currently, butanol is used only as an additive to gasoline because there is no engine working exclusively on this alcohol. However, intensive research is carried out in this direction. [2-4]. Table 1 gives the basic properties of butanol as a fuel in comparison with the other liquid biofuels.

Table 1

Properties of butanol and other biofuels [5]

Fuel	**Combustion energy [MJ/dm^3]**	**Evaporation heat [MJ/kg]**	**RON Research Octane Number**	**MON Motor Octane Number**
Petrol	32	0.36	91÷99	81÷89
Butanol	29.2	0.43	96	78
Ethanol	19.6	0.92	130	96
Methanol	16	1.2	136	104

The process of biobutanol production

Butanol can be obtained using several chemical technologies. It is also possible to produce butanol in the process of fermentation by means of bacteria of the genus *Clostridium*. This process occurs under anaerobic conditions, and butanol as one of the products - called biobutanol [2, 6].

The most popular bacteria species used for fermentation is *Clostridium acetobutylicum*. Such fermentation is so called ABE (*acetone-butanol-ethanol*), due to the names of the main products of this process, the typical ratio of these compounds being 3:6:1. The final concentration of butanol is about 3% [2, 7].

In the course of industrial production of biobutanol, using a fermentation process one must take into account three factors, evaluation of the process profitability: the cost of raw material and its pretreatment, a relatively small amount of product obtained, its significant toxicity, cost of product recovery from fermentation broth. *Clostridium acetobutylicum* belongs to the amylolytic bacteria; therefore a good substrate for production of butanol for these bacteria is starch. Nevertheless, the use for the fermentation crop products is not very economical; primarily because of too high price due to demand for these products from food industries. Therefore, for the production of butanol there are commonly used agricultural wastes for example: straw, leaves, grass, spoiled grain and fruits etc which are much more profitable from an economic point of view. One looks for other sources of plant biomass, which production does not require a lot of work and costs (eg algae culture) [2, 8, 9].

Modern research on the production process of biobutanol focuses on finding the best kind of substrate for fermentation process and for efficient strain of bacteria. Potentially, one can use all the waste containing monosaccharide, and polysaccharides and waste glycerol. Analogously, the biomass of algae is one example of such a substrate. Algae culture does not require intensive labour and high costs. Some of the micro-algae contain relatively high percentage of sugars in dry matter, such as *Chlorella* contains about 30÷40% of sugars, which greatly increases their usefulness in the production of biobutanol.

There is also carried out research on the genetic modification the bacteria *Clostridium acetobutylicum* and *Clostridium beijerinckii* in order to increase the resistance of bacteria to the concentration of butanol in the fermentation broth.

Methods for removal of butanol from the broth

The method eliminates the toxic effect of butanol on bacterial cells is a systematic removal of this compound from the fermentation broth. The traditional method of product recovery is distillation. As butanol has a higher boiling point than water, therefore, this process consumes much energy, and therefore it increases the cost of the whole process, especially at low concentration of butanol in the broth. Distillation is a process energetically and economically unfeasible, as the boiling point of water is lower than the maximum concentration of butanol and butanol fermentation broth is 3% by weight. This leads to low productivity and high costs of separation and purification of butanol [10, 11]. Therefore, currently other methods are used such as adsorption, membrane pertraction, extraction, pervaporation, reverse osmosis or "gas stripping" [12]. Particularly, much attention is paid to the method of pervaporation, which is potentially promising way to recover butanol from fermentation broth, as it allows separation and concentration of the product during a single process.

Butanol recovery by adsorption

Adsorption is investigated in the butanol separation from fermentation broth but the capacity of adsorbent is very low and cannot be used on industrial or semi - industrial plant. A variety of materials can be used as adsorbents for butanol recovery, but silicalite is the one used most often. Silicalite, a form of silica with a zeolite-like structure and hydrophobic properties, can selectively adsorb small organic molecule like C1–C5 alcohols from dilute aqueous solutions. Removal of butanol from fermentation broth by adsorption from the liquid phase can be used only in laboratory scale. This follows from the small-capacity of adsorbents for butanol. For this reason, the separation process is not suitable on an industrial or semi-technical scale.

Butanol recovery by membrane reactor

One of options of butanol removal is to use methods of immobilization of microorganisms in the membrane or the use of membrane reactors. For example, in the capillary membranes (hollow fiber) the increase in efficiency from 0.39 $g/dm^3/h$ to 15.8 $g/dm^3/h$ was attained. On industrial scale cell immobilized technique gives more disadvantages like poor mechanical strength and increase mass transfer resistance. Also, leakage of cells from the matrices is a frequent problem.

Butanol recovery by gas stripping

Among various recovery techniques, gas stripping is a promising technique that can be applied to butanol recovery during ABE fermentation [7, 13, 14]. Separation of volatile compounds can be obtained by lowering the pressure, heat or the use of inert gas. In many practical applications, a combination of these techniques is applied. By introducing the solution into the column in countercurrent to the gas (inert) one achieves the separation of specific components. In this case they are butanol, ethanol and acetone.

Butanol recovery by pervaporation

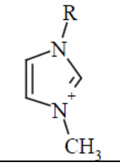
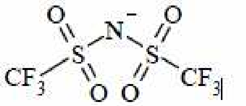
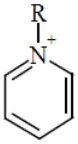
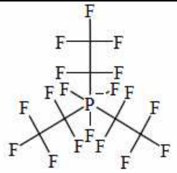
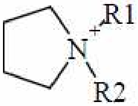
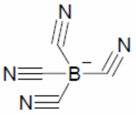
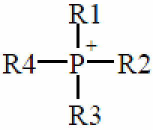
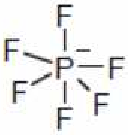
Pervaporation is one of the promising techniques for the removal of toxic substances for *Clostridium acetobutylicum* such as butanol, ethanol and acetone. This method involves the selective transport by diffusion of some components thrugh a membrane. A vacuum applied to the side of permeate. The permeated vapours should be condensed on low pressure side. Membrane in this case ought to be a hydrophobic polymer since transportation of organic components from the fermentation broth is preferred. Polydimethylsiloxane membranes and silicon rubber sheets are generally used for the pervaporation process. The drawback of the method can be high costs to produce low pressure at low pressure side of the membrane. Selection of a suitable polymer forming the active part of the membrane is a crucial issue in this case.

Application of ionic liquids

Release of butanol from fermentation broth is a very difficult technical problem. The extraction process using conventional solvents may be useful, but requires the use of solvents which are often volatile, toxic and dangerous.

Table 2

List of cations and ions in ionic liquids, IL

Cation	Anion
	
	
	
	

In recent years one may observe a growing interest in ionic liquids, IL as non-volatile, environmentally friendly solvents for various chemical processes. Ionic liquids can provide a solution in the case of butanol extraction from fermentation broth. Ionic liquids are organic salts present in the liquid state at room conditions, have very low vapour pressure and low solubility in water. Hence, IL is valuable solvent in the extraction process from aqueous solutions [15].

The following combinations of cations and anions constituting the IL are shown in Table 2. They are promising, due to the properties as a liquid extraction, in the system water - butanol - IL.

Combinations of cations and anions give 16 different IL. In addition, the substitution of the corresponding radical in the structure of cations allows obtaining several times more IL that can be taken into account in designing a suitable ionic liquid to test the extraction process. Studies on the properties of ionic liquids and in particular their possible extraction is currently undertaken and the results of experiments are reported in the literature [15-17].

The use of ionic liquids for the extraction of butanol (to remove from the environment fermentation) can be realized through direct application of the liquid in the bioreactor, and the separation of butanol outside the bioreactor. The diagram of such a solution is shown in Figure 1. Fermentation broth with the addition of the ionic liquid is introduced into the bioreactor. Selected IL should be verified if it is not toxic to the bacterium *Clostridium acetobutylicum*. As a result of contact of the IL with broth the extraction of biobutanol take place simultaneously with other metabolic products such as ethanol and acetone.

Due to the extremely low solubility of IL in water the fraction of the extract constitutes a separate phase, which must be derived from the environment of bioconversion and enter evaporator where the ingredients are extracted and will be distilled. Regenerated ionic liquid after a suitable cooling is recycled to the fermentation tank. Removal of bioconversion products makes further progress towards the transformation of raw materials into biobutanol.

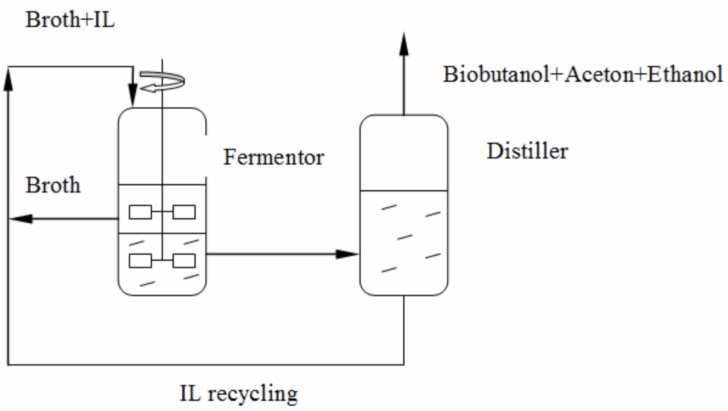


Fig. 1. Application of the IL *in situ* in the bioreactor

Another option is the use of ionic liquids removal of fermentation broth outside the bioreactor and the separation of butanol in the membrane contractor.

Conclusions

1. Biochemical method for obtaining biobutanol is more efficient and less costly in comparison with the methods of chemical synthesis. The basic problem that arises in the application of biochemical methods is a low concentration of biobutanol fermentation broth resulting from the toxic properties of the metabolic products of the bacteria *Clostridium acetobutylicum*
2. The metabolic engineering of different than *Clostridium* bacteria for butanol production is probably the most promising strategy for butanol biosynthesis [18].
3. A promising method of biobutanol separation from the fermentation broth is the use of ionic liquids. The following options are promising for their practical application: the use of IL *in situ*, or extraction with the application of membrane contractors.
4. Use the biobutanol in industry causes a positive ecological effect. Biobutanol as a fuel additive is a better component for hydrocarbon fuels in relation to other alcohols. Its application would result in reductions of greenhouse gas emissions.

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BIOBUTANOL - METODY WYTWARZANIA I OCZYSZCZANIA

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Abstrakt: Perspektywa wyczerpania naturalnych zasobów produktów ropopochodnych oraz rosnące ceny tych surowców skłaniają do poszukiwania paliw z odnawialnych źródeł energii, czyli biopaliw. Główna uwaga do tej pory skupiona była na bioetanolu ze względu na dostępność surowców do jego wytwarzania i dobrze opracowane metody wydzielania i oczyszczania. Alkohol butylowy (biobutanol) może być traktowany jako potencjalne biopaliwo. Biobutanol jest bardzo atrakcyjnym źródłem energii, gdyż - w przeciwieństwie do bioetanolu - jest niehigroskopijny, nie powoduje korozji i ma większą wartość opalową. Produkcja butanolu może odbywać się w procesie fermentacji zwanej ABE (*aceton*, *butanol*, *etanol*), przeprowadzanej najczęściej przez bakterie *Clostridium acetobutylicum*. Podstawowy problem szerszego wykorzystania biobutanolu leży w jego wytwarzaniu z odpowiednią wydajnością, a ta z kolei jest limitowana wydzielaniem butanolu z brzeczki fermentacyjnej. Proces destylacji nie jest w tym przypadku możliwy do realizacji. Klasyczna ekstrakcja wymaga zastosowania cieczy albo palnych, albo toksycznych. W celu wydzielania i oczyszczania biobutanolu proponuje się zastosowanie cieczy jonowych IL. Wykorzystanie cieczy jonowych do ekstrakcji butanolu (usuwania ze środowiska fermentacji) może być zrealizowane albo poprzez bezpośrednie zastosowanie cieczy w bioreaktorze i oddzielenie butanolu na zewnątrz bioreaktora, albo poprzez wyprowadzenie brzeczki fermentacyjnej na zewnątrz bioreaktora i oddzielanie butanolu w kontraktorze membranowym.

Słowa kluczowe: biobutanol, odnawialne źródło energii, ciecze jonowe

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MODERN METHODS OF THERMOCHEMICAL BIOMASS CONVERSION INTO GAS, LIQUID AND SOLID FUELS

NOWOCZESNE METODY TERMOCHEMICZNEJ KONWERSJI BIOMASY W PALIWA GAZOWE, CIEKŁE I STAŁE

Abstract: Biomass utilization through direct- or co-combustion with coal, based on coal, hydrogen and oxygen compounds' chemical energy conversion into heat in boilers, is simultaneously the cheapest and - according to experts - economically least effective solution. In case of heat and electricity production in cogeneration process in biomass fueled heat and power stations (wood, straw, energetic plants, RDF etc), investment costs are little higher, but considering fluidized combustion, combined heat and power (CHP) cogeneration systems, combined heating cooling and power generation (CHCP) trigeneration systems, ORC systems etc. the efficiency increases as well as the economical and ecological effects improve. Therefore, the most effective economical, and technical alike, methods of biomass conversion are: partial oxidation, gasification, thermal decomposition (pyrolisis) and biocarbonization processes. This paper includes review of present modern technologies taking advantage of these processes in gas, liquid and solid fuels production.

Keywords: biomass conversion, pyrolysis, fuels

The utilization of biomass for heat production in direct or co-firing processes is economically the least profitable manner of converting chemical energy into useful energy. A more effective way is conversion conducted in cogeneration and trigeneration systems, because of their superior proficiency. However, conversion into liquid or gas biofuels is the most profitable method. Figures 1 and 2 presents all biomass conversion methods - into thermal and electrical energy as well as into solid, liquid and gas biofuels [1, 2].

Thermal decomposition of biomass

Thermal decomposition of biomass, which is an anaerobic-atmosphere, endothermic process, leads to arise of three products:

- biocarbonate - charcoal while from decomposition of wood,

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- oil - which is an hydrocarbons mixture,
- gas - also an hydrocarbons mixture, but gaseous, with caloric value ca 12 MJ/kg.

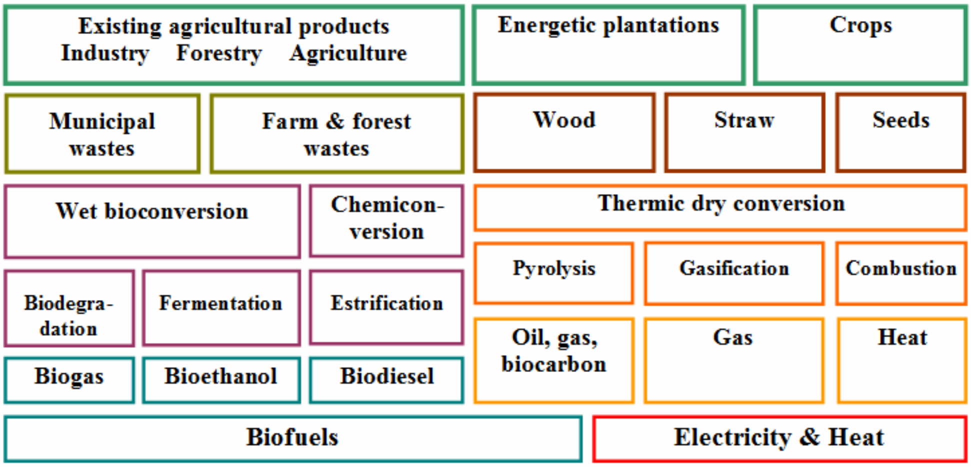

Fig. 1. Sources and types of biomass and methods of their conversion [2]

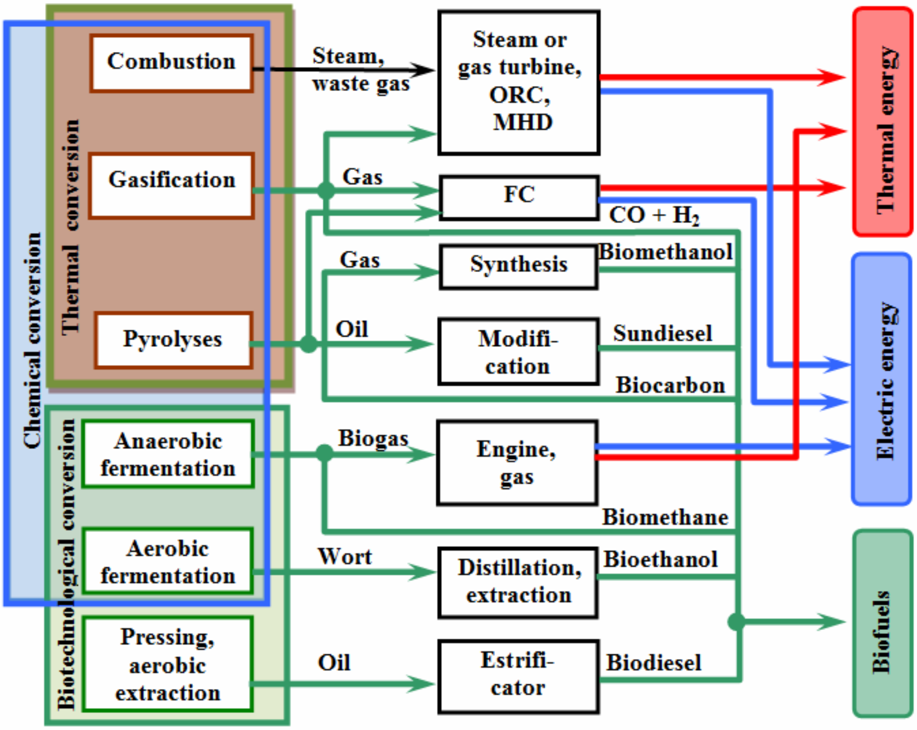

Fig. 2. Review of biomass conversion methods into useful electrical, thermal energy and into solid, gas and liquid biofuels

Its composition depends on temperature of biomass decomposition and so, eg for temperature 482°C/926°C in percentage (by volume) it is following: 5.56/32.48 H_2, 12.34/10.45 CH_4, 33.50/35.25 CO, 3.03/1.07 C_2H_6, 0.71/2.43 C_2H_2. Inflammable gasses are present in this mixture in an amount of 54.97% for temperature 482°C or 81.68% for 926°C [3].

Proportions of gasses, oil and biocarbonate in degradation products depend on accession rate of temperature, decomposition time, temperatures and pressure. At a fast thermal decomposition process rate, over 65% of biomass becomes gas (gasification), at an average rate - over 70% of biomass transforms into oil (pyrolysis) and it is possible to receive over 35% of biocarbonate (biocarbonisation) at slow decomposition rate. As it turns out, one more factor has an influence on thermal decomposition of biomass, namely catalyst.

In a technology used by Alphakat GmbH, a company in Buttenheim near Nürnberg, thanks to Al-Si zeolite addition into biomass (carbon, straw and deposits from sewage-treatment plant of municipal) during thermal decomposition process, it became possible to shift the direction of reaction into receiving more liquid products, at the cost of smaller amounts of gaseous and solid products.

Thermal decomposition of biomass starts at as low as 200°C, while the overhead value of temperature is not limited (it can even be as high as plasma temperature). The final products are charcoal and pyrolytical gasses. In room temperature, ca 30% (by weight) of pyrolitical gasses are condensed in form of a mixture of oil, alcohol, hydrocarbons and other organic compounds.

Gasification

Taking into account the installation reliability, the temperature of gasification and partial pyrolysis should not surpass 950°C. This temperature is adjusted by inserting certain amount of water steam into the gasificator, which endothermically reacts with the residue left after the pyrolysis process - the charcoal:

$$2\,(CH_2O)_n + n\,O_2 \rightarrow 2n\,CO + 2n\,H_2O \tag{1}$$

$$m\,C + m\,H_2O \rightarrow m\,CO + m\,H_2 \tag{2}$$

Produced gas includes a mixture of primary pyrolytical and water gas and its caloric value grows ca 50% higher and is now at a level of ca 11 MJ/kg [3]. Gasification process is conducted in closed ordinary reactors or in reactors with a fluidal field. Received gas, mainly hydrogen and carbon oxide, can be burned in the steam boiler, and the produced steam may supply turbines in a thermal power plant. In a different scenario, it is possible to employ gas from biomass directly in the gas turbine and to receive 1450 kW·h of electrical energy from one tone of biomass e.g. wood (calorific value 16.2 MJ/kg). Gas received from biomass gasification can also be converted into electric power directly in fuel cells. Gasificators with solid packing are applied at forces from about ca 1.5 MW at co-current match, and ca 2.5 MW in countercurrent gasification process. Fluidal reactors can process up to ca 15 Gg/h of dry biomass, creating power from 25 MW up to ca 100 MW.

Thermal biodegradation jointed with hydrogenation

It is also a pressurized oxygen-free biomass gasification process, but lead in such a manner that the final product contains as large amount of liquid hydrocarbons as possible.

The reaction is carried out in two stages. During the first period, synthesis gas emerges, which than reduces biomass into liquid hydrocarbons:

$$(CH_2O)_n \rightarrow n\ CO + n\ H_2 \qquad (3)$$

$$2\ (CH_2O)_n + H_2 \rightarrow C_nH_{(2n+2)} + n\ CO + n\ H_2O \qquad (4)$$

It is also possible to obtain the hydrogen for hydrogenation through hydrothermal gasification of wet biomass in approximately-critical water conditions ($T_c = 374.15$°C, $p_c = 22.14$ MPa). The reaction is following:

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 12\ H_2 \quad \text{for glucose} \qquad (5)$$

$$C_6H_{10}O_5 + 7\ H_2O \rightarrow 6\ CO_2 + 12\ H_2 \quad \text{for cellulose} \qquad (6)$$

During hydrothermal gasification process, hydrogen, carbon oxide and considerable amounts of methane and superior hydrocarbons are produced. There are two methods to carry out this transformation:

- low-temperature T = 350÷600°C with ZrO_2 catalyst,
- medium-temperature T = 500÷800°C with KOH, $KHCO_3$, K_2CO_3 catalysts.

Conversion of biomass into liquid biofuels is, according to specialists [4], most economically reasonable. In their statement, profits obtained from biomass conversion into heat, electricity or liquid fuels are equal to:

$$\text{heat} : \text{electrical energy} : \text{liquid fuel} = 1 : 3 : 9 \qquad (7)$$

Thus far, the price of fuels was not the motor driving the search for new technologies. Presently, when situation has changed and the meaning of biofuels has increased, it is possible to forecast a raise of interest in biofuel production through biomass thermal biodegradation.

Biomass pyrolysis

Pyrolytic thermal biomass decomposition is a complex process in which primary simultaneous reactions occur: dehydration, isomerization, aromatization, carbonization, oxidation and other. Secondary reactions also occur eg thermal water decomposition into synthesis gas, cracking, condensation etc. Depending on technological parameters of the process, mainly temperature and its rise rate, the following products emerge: water steam, carbon oxides, aliphatic and aromatic hydrocarbons, tars, polymers, hydrogen and carbon. Table 1 presents the variability of composition and individual components participation in products of pyrolytic wood decomposition in the function of temperature.

Table 1

Composition of gas gather from free distillation of dry biomass (timber) in function of temperature

Process	**Temp.**	**H_2**	**CO**	**CO_2**	**HC**
	[°C]	**[% mol]**			
Dehydration	155÷200	0.0	30.5	68.0	2.0
Carbon oxides (oxidation)	200÷280	0.2	30.5	66.5	3.3
Hydrocarbons emerge (HC)	280÷380	5.5	20.5	35.5	36.6
Production of hydrocarbons	380÷500	7.5	12.3	31.5	48.7
Dissociation	500÷700	48.7	24.5	12.2	20.4
Emerge of hydrogen	700÷900	80.7	9.6	0.4	8.7

Biomass biocarbonization

Energy plantations and other biomass sources must be placed in a radius of 100 km from energy adaptive plant. Because of big cubature and small specific gravity, transport of biomass through far distances is unprofitable. A certain solution of this problem is biomass conversion into biocarbon, which is pure charcoal and in which concentration of energy is considerably greater than in biomass. Indeed, density of such carbon is not equal to hard coal, but coverage of its profitable transport range for thermal power plants is still contained within Polish territory.

Biocarbon, just as charcoal, is received during biomass warming without access of air. It is possible to carry out this process in closed reactors with overcoat heating

$$(CH_2O)n \rightarrow n\,C + n\,H_2O \qquad (8)$$

First attempts at starting-up a commercial Polish installation of biocarbon production in Wodynia near Elbląg have ended in a failure [5]. An accomplished installation, manufactured by the same planners in Sedziszow is presented in Figure 3 [6-8]. It remains to be seen whether experience gained in Wodynia will prove useful.

Fig. 3. Installation of BIOwęgiel® (biocarbon) production in Sedziszow (under construction) [6-8]

Additional advantages of biocarbon as a fuel are as follows: capability of incinerating in a traditional carbon boiler, without necessity of modernization, lack of sulfur in it and a possibility of obtaining a green energy certificate and additional profit from increment emissions trading (according to CO_2 limitation emission programme).

Pyrolytic RDF recycling installation

An example of flash-type pyrolysis is a vacuous installation for conversion inflammable fractions of waste materials called RDF (Fig. 4) [9, 10]. From 1 kg of waste it is possible to receive ca 0.23 kg of recovered fine-grained carbon at temperature t = 760ºC and gas mixture of hydrocarbons at temperature t = 510ºC. Liquid fuel was obtained after fast cooling to ca 80ºC, in order not allow a reaction with carbon to occur.

After multistage cleaning-up the gas was transferred for industrial utilization. Part of it was turned back to sustain the pyrolysis process. The final effect of RDF pyrolysis was: ca 10% (by weight) of water, 20% of carbon, 30% of gas and 40% of liquid fuel. Recycling efficiency of carbon production at calorific value 20.9 MJ/kg and ca 30% contents of ash, equals ca 7.5%, in dry mass calculation. In case of liquid fuel, the equivalent values were following: calorific value - 24.4 MJ/kg, contents of ash from 0.2 to 0.4% and production efficiency - 22.5% by weight.

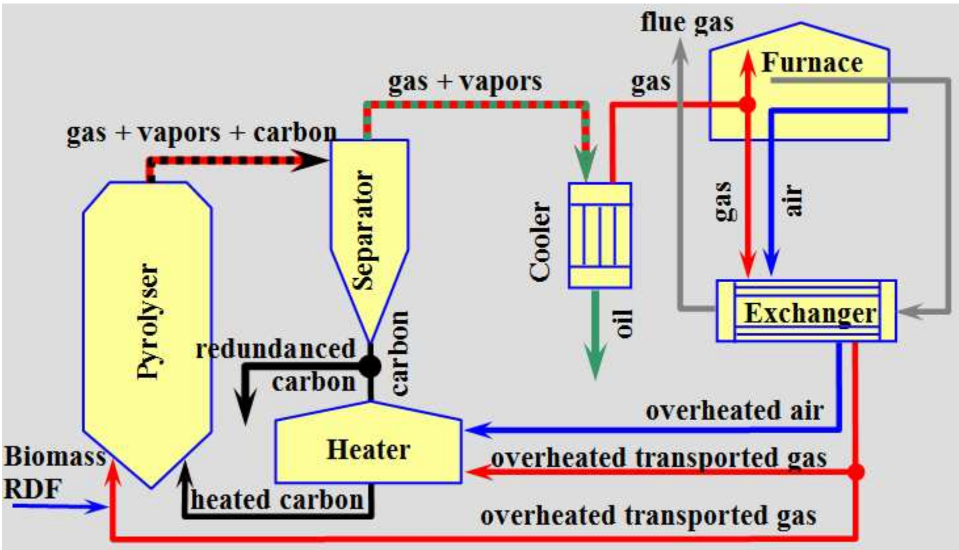

Fig. 4. Scheme of technological line of RDF pyrolytic conversion into liquid fuels

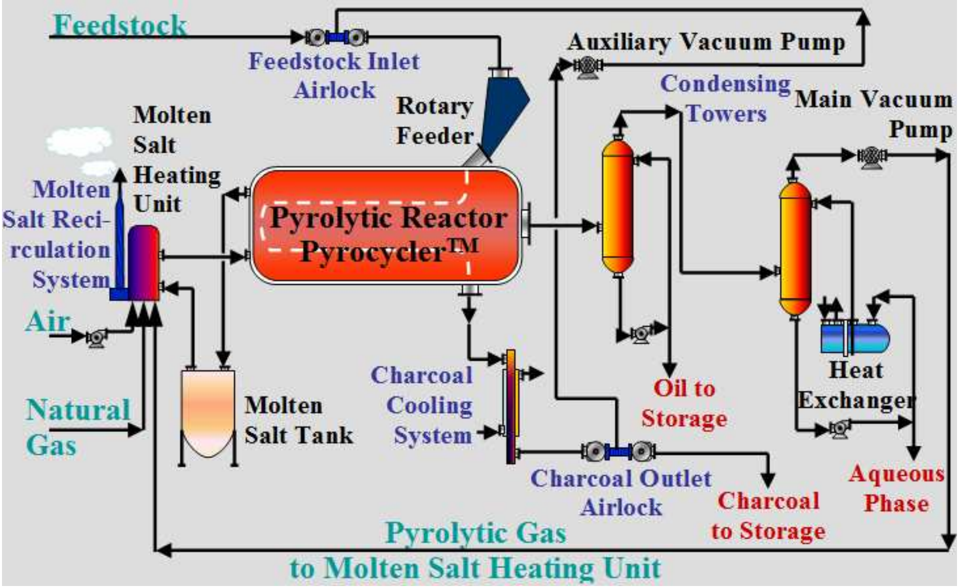

Fig. 5. Technological scheme of Pyrocycling™ Process [11]

Pyrolytic Pyrocycling™ installation

Pyrocycle™ Process was developed by a canadian-dutch firm. The raw material for the processing is bark form soft trees, obtained at a sawmill, dried outside. Composition of raw material is approximately: 31% (by volume) balsam fir (*Abies balsamea*), 55% (by volume) - white spruce (*Picea glauca*) and 14% (by volume) - black spruce (*Picea mariana*). Average humidity of raw material at inflow to the reactor is 10% (by weight). Approximated analysis of the product is: 74.8% volatile parts, 22.3% related carbon and 2.9% ash. Technological scheme of Pyrocycling™ Process is present in Figure 5.

Other examples of pyrolytical technologies

Table 2 contains majority of most popular applicable pyrolytical technologies assembling biomass into useful energy.

Table 2

Juxtaposition of most popular and newest pyrolitical technologies [12]

Technology	**Producer**	**Material**	**Efficiency**	**Temp.**
			[kg/h]	**[ºC]**
BTG Flash Pyrolyse	BTG Biomass Technology Group [13]	Biomass	250, 5000 (Starting-up Installation)	500
Pyrocycling Process [15, 16]	Pyrovac Group Inc., Ecosun b.v. [14]	Biomass	3500	475
ENTECH Pyrolytic Gasification System	ENTECH Renewable Energy Technologies PTY Ltd. [17]	Biomass & Organic Wastes	Series of Types 200 - 36000	500
Waste Gas Technology	Waste Gas Technology Ltd. [18]	Dried Sludges	500	750÷850
Ragailler Dry Destillation	RATech [19]	Municipal Wastes & Biomass	n.a.	450÷560
HD-PAWA-THERM	UC Prozesstechnik GmbH [20]	Sludges	n.a.	600÷700

Conclusions

Biocarbon, liquid biofuels and gas (water or generator gas) are the products of thermal decomposition of biomass. Transport, storage and farthest processing are economically and ecologically more profitable, due to boosted density of energy in these processed biofuels, than rigorous biomass, which is light and has small calorific value.

Methods of converting biomass into useful energy, presented in this paper, are only a small clipping of solutions available on market. However, depletion of theme was not the purpose of authors, but presenting the most important, technologically advanced processes, together in one manuscript, which helps to systematize current knowledge on this theme. Because of editorial limitations, we could not manage significant themes such as SunDiesel [21], fuel cells (FC) [22], ORC [23] and other.

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NOWOCZESNE METODY TERMOCHEMICZNEJ KONWERSJI BIOMASY W PALIWA GAZOWE, CIEKŁE I STAŁE

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Abstrakt: Wykorzystanie biomasy do produkcji ciepła w procesach bezpośredniego spalania lub współspalania z węglem, polegające na konwersji zawartej w niej energii chemicznej związków węgla, wodoru i tlenu w energię cieplną w kotłach, jest najtańszym, lecz - zdaniem wielu ekspertów - najmniej efektywnym i ekonomicznie najmniej opłacalnym rozwiązaniem. W przypadku łącznej produkcji energii cieplnej i elektrycznej w elektrociepłowniach opalanych biomasą (drewnem, słomą, surowcem z plantacji energetycznych, RDF-em itd.) nakłady inwestycyjne są trochę wyższe, ale dzięki spalaniu fluidyzacyjnemu, kogeneracyjnym układom skojarzonym, trigeneracji, układom ORC itd. sprawność konwersji rośnie, a także poprawia się efekt ekonomiczny i ekologiczny. Najkorzystniejszą jednak zarówno z punktu widzenia ekonomicznego, jak i technicznego metodą przetworzenia biomasy jest jej częściowe utlenienie, zgazowanie i piroliza, pod kątem produkcji paliw płynnych, z ewentualnym wykorzystaniem syntezy Fischer-Tropscha, uwodornienia i hydrokrakingu w odniesieniu do produktów termicznego rozkładu biomasy. Niniejszy artykuł zawiera przegląd obecnie stosowanych, nowoczesnych technologii wykorzystujących te procesy do produkcji biopaliw gazowych, ciekłych i stałych.

Słowa kluczowe: konwersja biomasy, piroliza, paliwa

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OBTAINING OF PETROLEUM RESINS USING PYROLYSIS BY-PRODUCTS
14. PETROLEUM RESINS WITH FLUORINE ATOMS

OTRZYMYWANIE ŻYWIC PETROCHEMICZNYCH Z PRODUKTÓW UBOCZNYCH PIROLIZY ROPY NAFTOWEJ
14. ŻYWICE PETROCHEMICZNE ZAWIERAJĄCE ATOMY FLUORU

Abstract: Petroleum resins with fluorine atoms (PRFs) have been synthesized *via* cooligomerization of unsaturated compounds presented in the C_9 fraction, which is the by-product of hydrocarbons pyrolysis to ethylene, using functional peroxy oligomer as an initiator. The effect of initiator amount, temperature and reaction time on the PRFs yield and molecular mass has been determined. The possibility of synthesized PRFs using as additives for bitumen-polymeric compositions based on oil bitumens has been shown.

Keywords: resin, by-product, cooligomerization, bitumen, peroxide

It has been shown earlier [1] that the C_9 fraction which is a by-product of ethylene production, may be used for the obtaining of petroleum resins with epoxy [2], carboxy [3], hydroxy [4] and other functional groups [5]. The presence of reactive functional group in the molecule of petroleum resins (PRs) allows to extend the PRs application area, for example for the formation of protective composite materials [6]. On the other hand, it is well-known [7, 8] that the presence of fluorine atoms in the polymeric molecule allows to increase the heat characteristics of goods, as well as their attrition and corrosion resistance. So in this work we have studied the possibility of PRs with fluorine atoms obtaining. For this purpose we used our previous approach: the use of the C_9 fraction as a raw material and cooligomerization proceeding with peroxy initiator. In our case as a peroxy initiator the oligomeric product by following formula was used:

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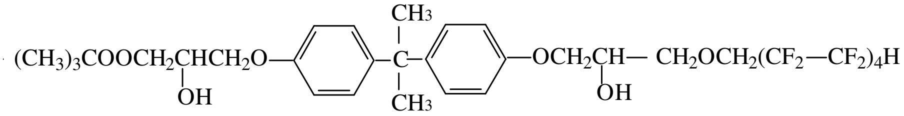

This FPO compound was synthesized by us using peroxy derivative of diglycidyl ether of dioxydiphenylolpropane and fluorine-containing alcohol-telomer $HOCH_2(CF_2–CF_2)_4H$. FPO contains reactive –O–O– bonds capable to decompose at heating to 383 K and higher temperatures. Free radicals are formed initiating the cooligomerization of unsaturated compounds (styrene, dicyclopentadiene, vinyltoluenes, indene, etc) which are present in the C_9 fraction followed by PRs forming. At the same time the formed oligoradical with fluorine fragments is responsible for the synthesis of PRs with fluorine atoms.

Experimental

Reactants and their characteristics

The initial C_9 fraction was taken from diesel oil pyrolysis plant at concern "LUKOR" (Kalush, Ivano-Frankivsk region, Ukraine) and was used as received. The characteristics of the C_9 fraction is described in [1].

FPO is a viscous product of light-yellow color with a molecular mass of 800 g/mol and active oxygen content of 3%.

Bitumen BN 70/30 was received from blown bitumen plant at JSC "NPK-Galychyna" (Drogobych, Lviv region, Ukraine). Its characteristic is given in Table 1.

Table 1

Bitumen characteristics

Index	Bitumen BN 70/30	Bitumen BNK 45/190
Needle penetration depth at 298 K, 0.1 mm	15	160
Softening temperature by "ring and ball" method [K]	345	350
Tensile strength (ductility) at 298 K [cm]	3	3
Solubility in toluene or chloroform [%]	99.0	99.6
Mass change after heating [%]	10	0.23
Flash point [K]	503	525
Mass part of water	-	-
Needle penetration depth at 298 K in the residue after heating [%]	-	80
Mass part of paraffin [%]	-	4.7
Penetration index	-	2.5

Bitumen BNK 45/190 was received from blown bitumen plant at Shebelinka gas-plant (Kharkiv region, Ukraine). Its characteristic is also given in Table 1.

Methodics of kinetic investigations of C_9 fraction cooligomerization

Initiated cooligomerization of unsaturated compounds presented in the C_9 fraction was studied in glass ampoules. 20 g of the C_9 fraction and 30% solution of FPO initiator in acetone were loaded into the ampoule. Then it was blown by inert gas, soldered, placed into the thermostat and sustained at 389÷423 K for 10÷50 hours. After the end of the reaction the mix was cooled to room temperature and poured into petroleum ether. After decantation the bottom viscous layer was dried at 363 K and residual pressure of 133÷266 Pa till the mass became constant. PRs yield and molecular mass were determined.

Synthesis of petroleum resins with fluorine atoms (PRFs)

PRFs were synthesized on the basis of the C_9 fraction using FPO as an initiator. 500 g of C_9 fraction and 25 g of FPO dissolved in 50 ml of acetone were loaded into an autoclave. The autoclave was placed into the thermostat and heated at 403 K for 40 hours. Then the autoclave was cooled to the room temperature and the obtained mix was distilled. During vacuum distillation two fractions were run off: at the boiling temperatures of 323÷353 K and atmospheric pressure and at the boiling temperatures of 353÷446 K and residual pressure of 7÷10 mm Hg. The vat residue was PRF of dark-brown colour with the yield of 23.2 mass %.

Bitumen-polymeric mixtures were prepared by components mixing at the laboratory plant consisting of electric heater, metal vessel with a mixer and thermometer [9]. The composition was mixed at 393 K till the mix became homogeneous. The temperature must be higher than PRFs softening temperature.

Ductility, penetration and softening temperature were determined using standard procedures [10]. The factor “adherence with glass” was determined using the procedure described in [11].

Results and discussion

PRFs synthesis

In order to establish the factors affecting the cooligomerization reaction of compounds presented in the C_9 fraction, we carried out kinetic investigations concerning the effect of FPO initiator amount, reaction time and temperature on the PRFs yield and molecular mass. The process was studied according to the procedure described in the Experimental part. The obtained results are given in Figures 1-3.

One can see from Figure 1 that at 403 K cooligomerization reaction takes place even without peroxy initiator. According to the literature data, in such a case PRs are formed via thermal polymerization of styrene, indene and other unsaturated compounds presented in the C_9 fraction. The obtained products have low molecular mass and do not contain fluorine atoms. The introduction of FPO (2.5 mass %) into the reaction mix considerably increases molecular mass of synthesized products due to the fluorine atoms. The further increase of initiator amount till 5.0 and 7.5 mass % does not practically change the molecular mass. 5.0 mass % of the initiator slightly increases the PRFs yield and using 7.5 mass % of the initiator the PRFs yield decreases. This fact may be explained by the following. At sufficiently great amount of the initiator the formed oligoradicals (as a result of the initiator decomposition) not only cause the cooligomerization of unsaturated compounds presented in the C_9 fraction but they are able to the recombination as well. Recombined radicals are not the part of PRFs molecule and they are separated from PRFs during purification of the end product. Obtained results (Fig. 1) allow to assume that the optimal amount of initiator in the reaction mix is 5.0 mass % to calculate for the raw material.

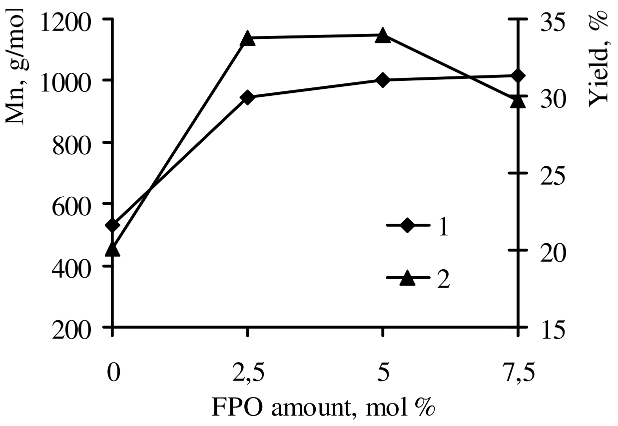

Fig. 1. Dependence of PRFs molecular mass (1) and yield (2) upon FPO amount. Process time is 50 h, process temperature is 403 K

The same situation takes place concerning the effect of process temperature (Fig. 2). At 383 K the PRFs yield is 17.2%, and at 423 K it decreases to 15.1%. If at 383 K peroxy groups in FPO slowly decompose because of their stability, then at 423 K the fast decomposition takes place resulting in recombination reaction between formed oligoradicals. Thus we may conclude that 403 K is the optimal temperature for PRFs production.

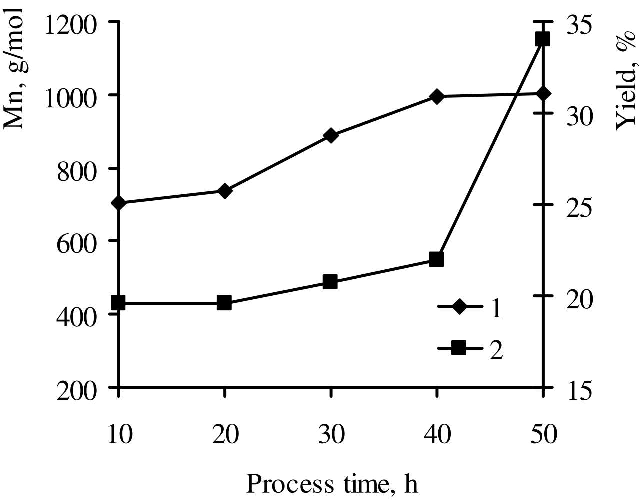

Fig. 2. Dependence of PRFs molecular mass (1) and yield (2) upon the cooligomerization time for the C_9 fraction. FPO amount is 5 mass % to calculate for the initial C_9 fraction, process temperature is 403 K

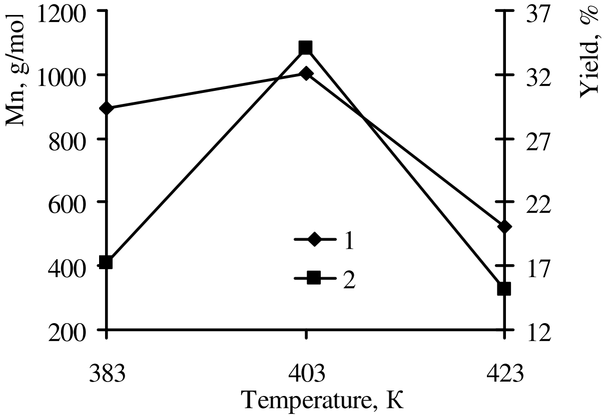

Fig. 3. Dependence of PRFs molecular mass (1) and yield (2) upon the cooligomerization temperature for the C_9 fraction. FPO amount is 5 mass % to calculate for the initial C_9 fraction, process time is 50 h

The increase of process time increases both molecular mass and products yield (Fig. 3).

Obtained kinetic regularities of PRFs synthesis were the basis for the synthesis procedure of mentioned products. It is described in the Experimental part. The synthesized PRF with molecular mass of 1000 g/mol is soluble on acetone, 1,4-dioxane, benzene, toluene and other solvents. Further PRF was studied as an additive for bitumen-polymeric compositions. Investigated mixtures were prepared in accordance with the above-mentioned procedure. The obtained results are given in Tables 2 and 3.

One can see from Table 2 that the increase of PRFs content in the bitumen-polymeric mix increases the ductility and penetration of the composition based on BN-70/30 with the simultaneous insignificant change of its softening temperature. At the same time the increase of PRFs content from 1 to 5 mass % decreases the adherence with glass. This fact indicates bas adhesive properties of modified bitumen.

Table 2

Characteristics of bitumen-polymeric compositions based on bitumen BN-70/30

Factor	**Composition characteristics at PRFs content [mass %]**			
	0	**1**	**3**	**5**
Softening temperature by “ring and ball” method [K]	345.5	345	342.2	341.5
Ductility at 298 K [cm]	2.8	2.8	3.0	4.2
Penetration at 298 K, 0.1 mm	10.0	11.0	12.1	12.7
Adherence with glass	69.0	53.1	48.9	21.8

The similar results have been obtained for the compositions based on BNK-45/190 (Table 3). The same as in a previous case, the softening temperature, ductility and penetration of obtained mixes increase. The adherence with glass remains constant. The obtained results show that PRFs in the bitumen-polymeric compositions does not react with bitumen but only plays role of plasticizer.

Table 3

Characteristics of bitumen-polymeric compositions based on bitumen BNK-45/190

Factor	Composition characteristics at PRFs content [mass %]			
	0	1	3	5
Softening temperature by "ring and ball" method [K]	351.8	356.2	356.8	357.1
Ductility at 298 K [cm]	2.0	2.5	2.7	2.8
Penetration at 298 K, 0.1 mm	150.3	154.0	160.3	164.3
Adherence with glass	94.7	100.0	94.7	80.9

Concluding remarks

New petroleum resins with fluorine atoms have been obtained using the C_9 fraction which is the by-product at ethylene production. The effect of peroxy initiator amount, temperature and process time upon the yield and molecular mass of obtained petroleum resins has been determined. New synthesized resins may be used as additives to bitumen-polymeric compositions. It has been established that the introduction of petroleum resins with fluorine atoms into the mix in amount from 1 to 5 mass % increases ductility and penetration of the composition but decreases adherence with glass indicating bad adhesion properties of modified bitumen.

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14. ŻYWICE PETROCHEMICZNE ZAWIERAJĄCE ATOMY FLUORU

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Abstrakt: Poprzez kooligomeryzację związków nienasyconych obecnych we frakcji C_9, która jest produktem ubocznym pirolizy węglowodorów PRFs do etylenu, zsyntezowano żywice zawierające fluor. Zbadano wpływ ilości oligomerycznego inicjatora otrzymywania etylenu, temperatury i czasu reakcji na wydajność i masę molekularną uzyskanego produktu. Pokazano możliwość wykorzystania żywicy PRFs jako dodatku do mieszanek złożonych z bitumu i polimerów organicznych.

Słowa kluczowe: żywice petrochemiczne, produkt uboczny, oligomeryzacja, bitum, nadtlenek

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VARIOUS FRACTIONATION PROCEDURES IN STUDY OF HEAVY METALS MOBILITY IN THE ENVIRONMENT

PROCEDURY FRAKCJONOWANIA MOBILNYCH FORM METALI CIĘŻKICH W PRÓBKACH ŚRODOWISKOWYCH

Abstract: The applicability and information content of two sequential extraction procedures for fractionation of element content of sediments, soils and gravitation dusts are compared. To this comparative study three typical samples were used: a Hungarian soil sample from the control plot of a heavy metal contamination field experiment, a contaminated lake sediment from Gödöllő, HU and an averaged airborne gravitation dust sample collected in Košice, SK. The BCR (*Community Bureau of Reference*) sequential extraction procedure was applied in its firstly issued unmodified form, which was originally developed for the fractionation of heavy metal content in aquatic sediments. The application of this batch leaching method is not free from difficulties, particularly in case of dust samples. Therefore, as an alternative for more adequate characterization of environmental mobilization a new procedure was applied based on sequential extraction with supercritical CO_2, subcritical H_2O and their 1:10 mixture in a supercritical fluid extractor (SFE).

Keywords: heavy metal contamination, sequential extraction, fractionation, soil, sediment, gravitation dust

Risk assessment of heavy metal contamination in the soil/water/atmosphere system is based on fractionation of metallic element content of environmental samples according to their environmental mobility. (The term 'fractionation' in this paper is used according to IUPAC recommendations [1].) Mobility of an element according to different solubility of different binding classes can be estimated by solvents sequentially applied which contain increasingly more and more aggressive reagents [2, 3]. The first sequential extraction procedure for characterization of mobility of heavy metals in aquatic sediments was developed by Tessier et al [4] who classified the metal content of sediments according to

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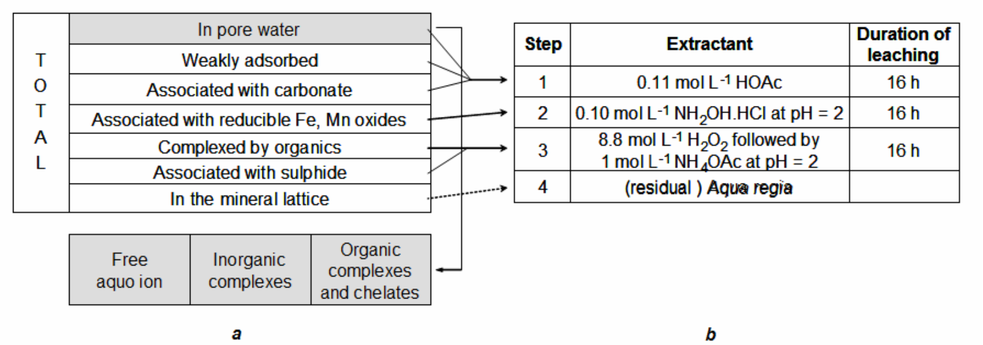
solubility and binding forms of metallic species as it is presented in Figure 1a. Based on this essential work several 5-8-step sequential extraction schemes were developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed [5]. The total time demand of these procedures is 5-6 days, while duration of the applied batch leaching steps is determined by long setting up time of partition and other heterogeneous equilibria. The BCR proposal for a 3(+1)-step sequential extraction procedure issued in 1993 is a simplified version of the above-mentioned schemes [6], but it is still time consuming and labour intensive. As it can be seen in Figure 1b, in this method the water soluble, the weakly adsorbed and the carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step, so it does not model the primary natural pathways of mobilization with water dissolution and bicarbonate formation. Due to the numerous operations and reagents applied, there is a risk of contamination during the whole procedure. Readsorption of extracted metals during the phase separation can lead to analyte losses. In the extracts the high reagent's concentrations may cause strong matrix effects during the spectrochemical element detection.



Step	Extractant	Duration of leaching
1	0.11 mol L^{-1} HOAc	16 h
2	0.10 mol L^{-1} $NH_2OH.HCl$ at pH = 2	16 h
3	8.8 mol L^{-1} H_2O_2 followed by 1 mol L^{-1} NH_4OAc at pH = 2	16 h
4	(residual) *Aqua regia*	

Fig. 1. a) Element fractions in aquatic sediment as classified by Tessier et al [4], Caroli [2], and Kersten et al [3], b) Original BCR sequential extraction scheme (Ure et al [6], Quevauviller et al [7], López-Sánchez et al [8])

The CRM 601 sediment reference material issued in 1997 was certified only for five element (Cd, Cr, Ni, Pb and Zn) to this procedure [8, 9]. During the elaboration of the next (BCR 701) sediment materials, the original BCR procedure was modified to avoid the analyte losses during the second leaching step due to the pH instability [10-12]. This change, however, can cause difficulties when the consistency with former data is required. The BCR procedure in its original and modified versions was successfully applied to aquatic sediments and soils, however, soil CRM was not issued up to now [13]. Zemberyova [14] successfully utilized the modified BCR three-step sequential extraction procedure for fractionation of Cd, Cr, Cu, Ni, Pb and Zn in different soil reference materials of Slovak origin. Kubova et al [15, 16] successfully applied the BCR three-step sequential extraction and the dilute HCl single-step extraction procedure for soil-plant metal transfer predictions in contaminated lands. With extension of BCR usage to soils and aerial gravitation dust samples one has to calculate with further difficulties. For example, in the modification of the BCR procedure the high carbonate content samples were not considered, in spite of the fact that the amount of acetic acid may not be enough to dissolve the total calcium carbonate content of 1 g sample weighed in according to the BCR protocol. Gravitation dust can significantly contribute to heavy metal contamination of soils and sediments, particularly at sites affected by industrial activity or traffic. However, the application of the BCR procedure to such kind of samples is not free from further difficulties. The available sample quantity is mostly less than that is required to BCR procedure, therefore miniaturized BCR procedure by Dabek-Zlotorzynska et al [17] and realization of BCR procedure in continuous flow system by Shiowatana et al [18] was proposed, too. Another problem may arise from the high organic matter content of such samples (dusts, sediments) which can form separate phases during the leaching. To overcome the above-mentioned problems the elaboration of a quite different continuous flow sequential extraction procedure was started at our laboratory a few years ago [19]. The samples were mixed in appropriate rate with pure quartz sand (SiO_2) weighed into a column of a supercritical fluid extractor (SFE). Firstly supercritical CO_2, then under the same conditions subcritical H_2O and finally their 1:10 ratio (V/V) mixture were applied as extractants as it is described in Table 1.

Table 1

Scheme of the sequential extraction in the supercritical fluid extractor (SFE)

Step	Extractant	Chemical information	Duration
1	Supercritical CO_2 (in SFE)	CO_2-soluble mobile organic bound fraction	60 min
2	Subcritical H_2O (in SFE)	Water soluble fraction	60 min
3	H_2O/CO_2 (10:1) (in SFE)	Carbonate bound fraction	60 min
4	HNO_3/H_2O_2 (out of SFE)	Residual	

Further validation with high carbonate containing soil reference samples has proved that the complete dissolution of carbonates during the 3rd step requires longer time (90÷180 min) [20]. Firstly an apolar organic fraction which can contain organic pollutants, too can be obtained by this procedure. In the 2nd step the water-soluble, and in the 3rd step the carbonate-bound fraction can be collected. The present paper will compare the application onto Hungarian and Slovak soils, sediments and gravitation dusts of original (unmodified) BCR and the above-mentioned continuous flow $(CO_2)/(H_2O)/(H_2O+CO_2)$ sequential extraction (henceforth SFE). Readsorption of the analyte after the third step of the BCR procedure will be estimated by solid sample analysis. In a preliminary work a comparative study with CRM 601 and BCR 701 using the modified and unmodified BCR procedures was performed [21] to control data consistency with our former investigations on fractionation of contaminated lake sediment samples [22]. Simultaneously an attempt was made for the acceleration of BCR-procedure by sonication. The results of this latter are published elsewhere [23].

Experimental

Selection of samples

Sediment

A sediment sample was selected from the Gödöllő-Isaszeg lake system studies (Heltai et al [22, 24, 25]). This sample has a relatively high organic carbon and $CaCO_3$ content ($CaCO_3$ = 7.6%, TOC = 11%), and it has been analyzed many times formerly.

Soil

A soil sample was selected from a field experiment of heavy metal contamination performed by Research Institute for Soil Science and Agrochemistry (RISSAC) at Nagyhörcsök (Hungary) experiment site [26]. The selected untreated soil sample contains $CaCO_3$ = 4.8% and TOC = 3.5%.

Gravitation dust

The gravitation dust sample was collected during a year by the Department of Chemistry of the Technical University of Košice in the urban and industrial area of Košice [27-29]. During their former studies high amount of organic and inorganic carbon and heavy metals were detected in these samples ($CaCO_3$ = 2.9%, TOC = 33%).

Reference material

The BCR 701 lake sediment sample was used as described in the original BCR information [9, 30].

Sequential extraction procedures

BCR procedure

The BCR sequential extraction procedure was carried out according to the original protocol [6, 7] (Fig. 1b). In the present investigation nitric acid/H_2O_2 digestion was applied in a Milestone 1200 MEGA microwave oven according to our former studies for gaining the residual fraction [19, 22, 24, 31] instead of *aqua regia* digestion.

After the 3rd extraction step to control the readsorption of the analyte solid samples were taken from the BCR 701 residue as it shown in Figure 2. First a small part of the upper layer was taken, then the remaining bulk part was dried and homogenized.

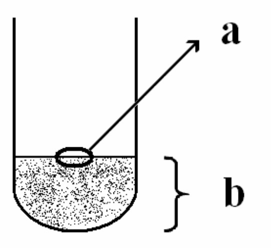


Fig. 2. Solid sampling from the solid residue of BCR 701 sample after the 3rd BCR extraction step: a) upper layer, b) homogenized bulk

Sequential extraction in a supercritical fluid extractor (SFE)

The solid samples were mixed manually with SiO_2 (Reanal) in a mass ratio of 1:20. Stainless steel extraction columns were filled as follows: first a layer of 1 g SiO_2, then 10 g of sample-SiO_2 mixture (and SiO_2 for the procedure blank measurements, respectively), and the remaining volume was filled with SiO_2 again. Extractions were performed in a supercritical fluid extractor consisting of two Jasco PU 980 HPLC pumps (the CO_2 pump was cooled to –6°C), a Jasco CO 980 column oven and Jasco 880-81 back pressure regulator (heated to 60°C) as shown in Figure 3. Solvents were applied as presented in Table 1 but the duration of the 3rd step was extended to 90 min according to our optimization study [20]. The extractions were performed under the following conditions: solvent flow rate 1 cm^3 min^{-1}, oven temperature: 80°C, pressure: 27 MPa. Extracts were collected in polyethylene bottles and analyzed by inductive coupled plasma optical emission spectrometry (ICP-OES) and inductive coupled plasma mass spectrometry (ICP-MS), respectively. The measured concentrations were corrected by subtracting the concentrations of the procedure blank.

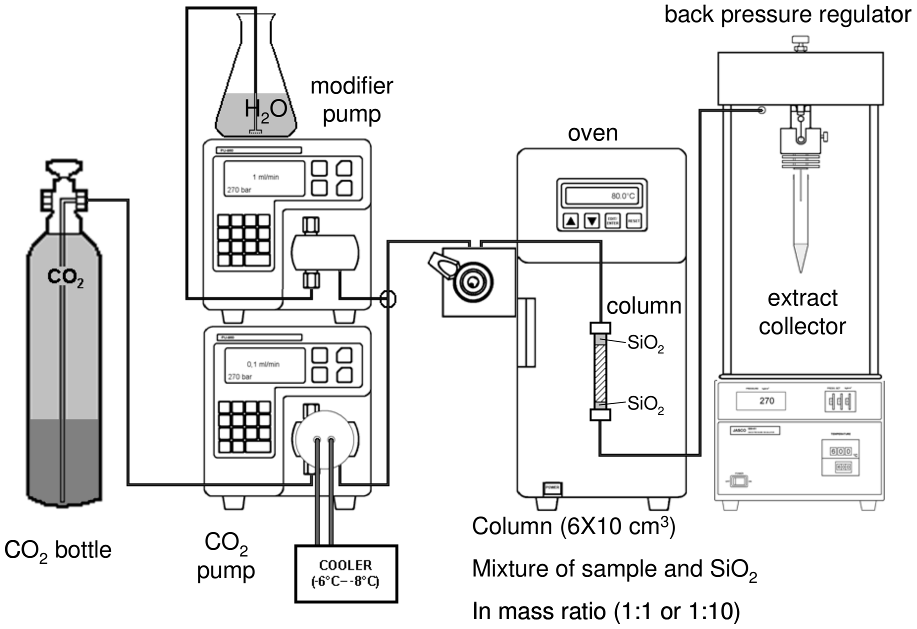


Fig. 3. Supercritical fluid extractor system used for sequential extraction

Element analytical detection

ICP-OES detection of Zn, Cd, Pb, Ni, Cr, Cu in BCR extracts

Jobin Yvon 24 sequential ICP optical emission spectrometer was used with the following operation parameters: incident power 1.1 kW, plasma argon gas flow 12 dm^3 min^{-1}, sheath argon gas flow: 0.2 dm^3 min^{-1}, nebulization argon gas flow: 0.35 dm^3 min^{-1}, nebulizer: Meinhard type, sample uptake rate: 1.5 cm^3 min^{-1}. Calibration for each type of extract was performed by Merck multielement standard with matrix-matching dilution.

ICP-OES detection of Al, Ca, Fe, K, Na, P, S in SFE extracts

Perkin Elmer Optima 3300 DV ICP optical emission spectrometer was used with the following operation parameters: incident power 1.3 kW, plasma argon gas flow 15 dm^3 min^{-1}, auxiliary argon gas flow: 1.0 dm^3 min^{-1}, nebulization argon gas flow:

0.95 dm^3 min^{-1}, nebulizer: Meinhard type A, sample uptake rate: 1.0 cm^3 min^{-1}, axial plasma observation, SCD detector.

ICP-MS detection of elements (As, B, Ba, Be, Cd, Ce, Co, Cr, Cu, Er, Gd, Ge, Hg, Ho, In, La, Li, Lu, Mg, Mn, Mo, Ni, Pb, Sc, Se, Sr, Ti, V, Y, Yb, Zn) in SFE extracts

Thermo Elemental X series ICP mass spectrometer was used with the following operation parameters: incident power 1.4 kW, plasma argon gas flow 14 dm^3 min^{-1}, auxiliary argon gas flow: 0.95 dm^3 min^{-1}, nebulization argon gas flow: 0.8 dm^3 min^{-1}, sample uptake rate: 1.0 cm^3 min^{-1}, Pole Bias –3.1 V, Hexapole Bias 4.5 V, extraction –118 V, focus 3 V, analog detector 2500 V, PC detector 3850 V, CCT gas (7% H_2 + 93% He) flow 5.9 cm^3 min^{-1}, integration time 0.1 s, stabilisation time 35 s, diameter of sample transport pump tube 1.02 mm, collision cell technology.

Solid-sampling spectrochemical analyses of BCR-residues of BCR 701 sample

The direct solid-sampling spectrometric analysis of solid residues from BCR procedure was provided using a DC Arc AtomComp 2000 AES Spectrometer (Thermo Jarrell Ash, Franklin USA). In this instrumentation an Echelle-based polychromator is used for the optical system and the spectral range reaches from λ = 175 nm to λ = 1050 nm. A two-dimensional Charge Injection Device (CID) functions as a detector, which is a single, solid state chip composed of over 250,000 small individual sensitive detector elements. The experiments with the AtomComp 2000 were performed with an exposure time of 90 seconds, an electrode distance of 4 mm (graphite electrodes, Electrokarbon, Topolcany, Slovakia), 10 mg of solid sample weighed into the carrier electrode. The following arc-current programme was applied: the arc was ignited with 3.5 A, increased in 5 seconds to 14.5 A and then to 16 A in 15 seconds. It remained constant at that current until the end of exposure time of 90 seconds. For calibration synthetic samples were produced as mixtures of spectral pure oxides of analytes, matrix elements and graphite powder. Measurements of the synthetic calibration samples as well as the analyzed samples were repeated five time.

Results and discussion

BCR procedure

The extracted concentrations related to sample dry mass obtained in soil, sediment, gravitation dust and in CRM 701 samples are summarized in Table 2. It can be observed that the measured concentrations of Zn, Cd and Pb in the BCR 701 sample are in good agreement with the certified values but extraction efficiency of Ni, Cr and Cu is less than that of modified BCR procedure as it was experienced in our preliminary study, too [21, 30].

The results of the solid residue analysis of BCR 701 sample after the 3rd BCR extraction step are summarized in Table 3. It can be observed, that at the surface of both parallel sample the analyte element concentration was significantly higher than in the bulk of the residue.

Table 2

Extracted element concentrations (mg kg^{-1} related to dry mass) obtained by the unmodified BCR sequential extraction in BCR 701, soil, sediment and gravitation dust samples (n.d.: not detected)

BCR step	Element	CRM 701		SOIL	SEDIMENT	DUST
		Certified	Measured			
1st	Zn	205 ± 6	186.80 ± 1.07	5.83 ± 0.01	348.67 ± 0.67	1033.33 ± 1.64
	Cd	7.34 ± 0.35	6.81 ± 0.04	1.27 ± 0.04	3.55 ± 0.01	2.96 ± 0.003
	Pb	3.18 ± 0.21	3.73 ± 0.01	0.29 ± 0.02	16.76 ± 0.04	63.47 ± 0.10
	Ni	15.4 ± 0.9	8.92 ± 0.12	n.d.	3.67 ± 0.01	0.09 ± 0.003
	Cr	2.26 ± 0.16	n.d.	n.d.	1.68 ± 0.01	n.d.
	Cu	49.3 ± 1.7	32.03 ± 0.25	1.16 ± 0.01	7.39 ± 0.01	1320.64 ± 1.25
2nd	Zn	114 ± 5	90.96 ± 0.17	3.75 ± 0.01	172.96 ± 0.38	336.03 ± 0.51
	Cd	3.77 ± 0.28	3.36 ± 0.01	0.35 ± 0.002	1.60 ± 0.01	1.19 ± 0.002
	Pb	126 ± 3	76.80 ± 0.06	3.03 ± 0.03	97.20 ± 0.12	210.00 ± 0.65
	Ni	26.6 ± 1.3	14.43 ± 0.01	0.75 ± 0.01	3.63 ± 0.02	n.d.
	Cr	45.7 ± 2	15.52 ± 0.01	n.d.	19.73 ± 0.11	1.07 ± 0.01
	Cu	124 ± 3	54.75 ± 0.04	1.07 ± 0.01	9.05 ± 0.08	740.61 ± 2.95
3rd	Zn	45.7 ± 4	25.00 ± 0.12	2.70 ± 0.01	71.95 ± 0.14	330.62 ± 2.65
	Cd	0.27 ± 0.06	0.80 ± 0.001	n.d.	0.67 ± 0.01	1.07 ± 0.001
	Pb	9.3 ± 2	37.73 ± 0.11	18.60 ± 0.09	143.27 ± 0.31	229.43 ± 1.14
	Ni	15.3 ± 0.9	4.38 ± 0.03	1.53 ± 0.01	0.78 ± 0.01	1.67 ± 0.03
	Cr	143 ± 7	44.38 ± 0.15	4.17 ± 0.01	71.03 ± 0.26	16.05 ± 0.13
	Cu	55.2 ± 4	28.87 ± 0.10	2.93 ± 0.01	22.03 ± 0.03	1205.78 ± 1.93
4th	Zn	95 ± 13	52.91 ± 0.12	39.17 ± 0.05	37.29 ± 0.12	280.64 ± 1.63
	Cd	0.13 ± 0.08	0.91 ± 0.002	0.60 ± 0.004	0.69 ± 0.01	1.64 ± 0.01
	Pb	11.0 ± 5.2	10.48 ± 0.08	5.44 ± 0.06	22.95 ± 0.07	46.23 ± 0.31
	Ni	41.4 ± 4	15.75 ± 0.03	11.04 ± 0.01	24.75 ± 0.13	24.87 ± 0.13
	Cr	62.5 ± 7.4	29.67 ± 0.11	27.72 ± 0.04	78.52 ± 0.41	38.27 ± 0.24
	Cu	38.5 ± 11.2	15.37 ± 0.05	10.01 ± 0.03	6.15 ± 0.01	278.09 ± 3.92
Summa	Zn	459.7 ± 7	355.67 ± 0.37	51.45 ± 0.02	630.87 ± 0.33	1980.62 ± 1.61
	Cd	11.51 ± 0.19	11.88 ± 0.01	2.21 ± 0.01	6.51 ± 0.01	6.85 ± 0.004
	Pb	149.48 ± 2.60	128.75 ± 0.06	27.36 ± 0.05	280.17 ± 0.14	549.13 ± 0.55
	Ni	98.7 ± 1.78	43.48 ± 0.05	13.32 ± 0.02	32.82 ± 0.04	26.63 ± 0.04
	Cr	253.46 ± 4.14	89.57 ± 0.07	31.89 ± 0.02	170.97 ± 0.20	55.38 ± 0.09
	Cu	267 ± 4.98	131.01 ± 0.11	15.17 ± 0.01	44.62 ± 0.03	3545.13 ± 2.51
Total	Zn	454 ± 19	339.88 ± 0.37	39.41 ± 0.02	552.25 ± 0.33	1645.25 ± 1.61
	Cd	11.7 ± 1	9.35 ± 0.01	0.37 ± 0.01	4.93 ± 0.01	4.72 ± 0.004
	Pb	143 ± 6	112.63 ± 0.06	14.81 ± 0.05	223.04 ± 0.14	443.87 ± 0.55
	Ni	103 ± 4	58.24 ± 0.05	14.01 ± 0.02	42.36 ± 0.04	30.18 ± 0.04
	Cr	272 ± 20	160.82 ± 0.07	22.61 ± 0.02	236.94 ± 0.20	40.17 ± 0.09
	Cu	275 ± 13	143.06 ± 0.11	10.38 ± 0.01	53.37 ± 0.03	3102.55 ± 2.51

Table 3

Results of the solid residue analysis of BCR 701 sample after the 3rd BCR extraction step; [(a) upper layer, (b) homogenized bulk]; [(1) and (2) samples from two repeated procedures]

Element	BCR 701			
	1 a	1 b	2 a	2 b
Ni [ppm]	87.7±2.77	63.3±2.15	61.6±1.47	48.8±0.87
Zn [ppm]	186±5,93	92.3±3.06	20.6±0.33	n.d.
Cu [%]	0.043±0.002	0.041±0.001	0.026±0.0001	0.031±0.001
Cr [ppm]	144±10.54	106±12.05	94±3.40	89±6.74
Pb [ppm]	151±8.33	140±7.37	146±6.40	111±5.12

SFE procedure

The extracted concentrations of Pb, Cu, Zn and Cd related to sample dry mass from soil, sediment and gravitation dust samples obtained by SFE sequential procedure are summarized in Figure 4. The other elements listed by the element analytical detection were also detected, but their concentration could not be evaluated reliably after the correction with the procedure blank.

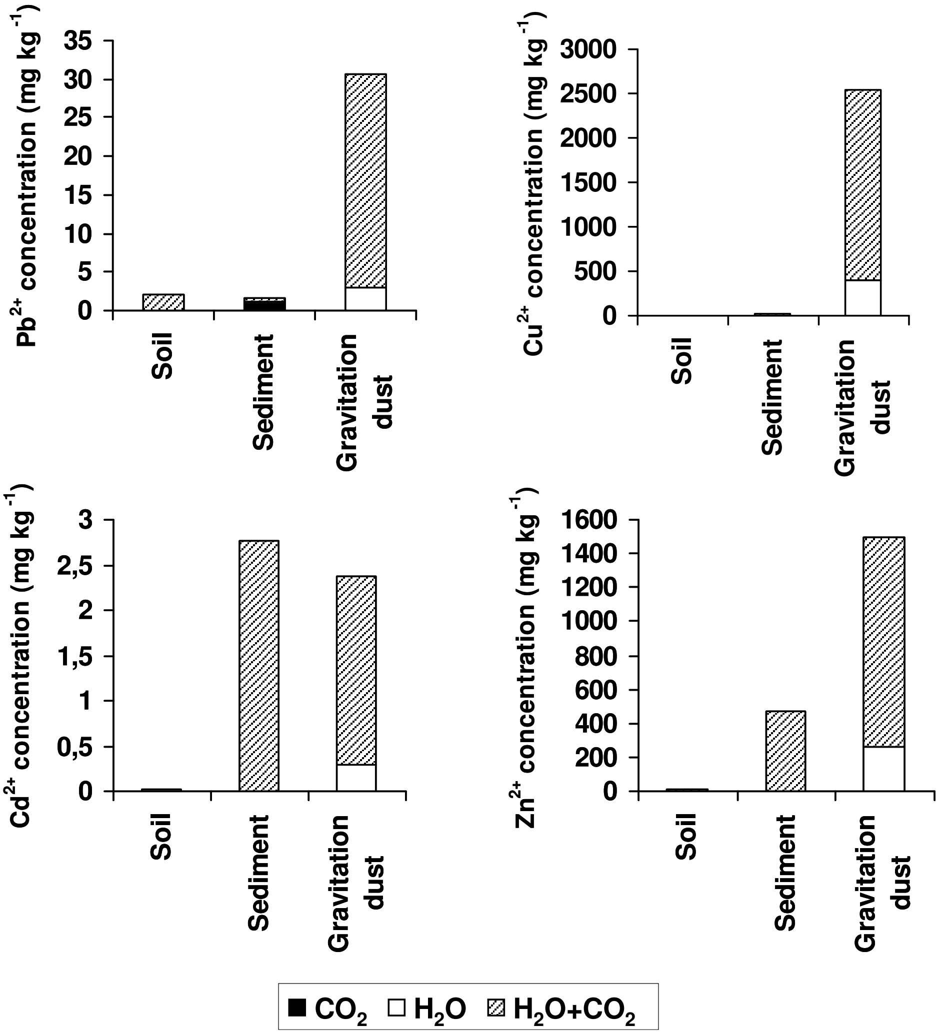


Fig. 4. Extracted Pb, Cu, Zn and Cd concentrations (mg kg^{-1} related to dry mass) in the fractions obtained by the SFE sequential extraction of the soil, sediment and gravitation dust samples

The results show that the easily mobilizable lead, copper and zinc contents in the gravitation dust sample are much higher than in the sediment and soil sample, whereas cadmium content is similar in case of the gravitation dust and the sediment. The ratio of the fraction extracted by subcritical water-carbon dioxide mixture (ie the carbonate-bound fraction) is the highest for all four elements in the gravitation dust sample. Significant zinc and cadmium content can be detected from the sediment sample, mostly in the carbonate-bound fraction, whereas lead was found mainly in the fraction extracted by supercritical carbon dioxide (ie bound to organic material). The latter results are in good agreement with our former studies on the BCR sequential extraction of the sediments from the Gödöllő-Isaszeg fishpond chain [19, 24]. Lead was detected in the soil sample in similar concentration to the sediment, but mainly in the carbonate-bound fraction.

Comparison of results gained from BCR and SFE procedures

Comparison of extracted amounts by BCR 1st step [BCR(1)] and SFE 2nd + 3rd step [SFE(2+3)] is summarized in Table 4. It can be observed that the sum of water soluble (SFE 2nd step) and carbonate bound (SFE 3rd step) fractions is mostly higher than the amount gained by BCR 1st step, however, lead was found in higher concentration in the BCR (1) fraction of the sediment and gravitation dust sample.

Table 4

Comparison of the element contents [mg kg^{-1} related to dry mass] found in the 2nd and 3rd step of the SFE procedure [SFE (2+3)] and 1st step of the BCR procedure [BCR (1)] extracts (n.d.: not detected)

Sample	**Extract**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Soil	SFE (2+3)	n.d.	n.d.	n.d.	n.d.	2.06	n.d.
	BCR (1)	1.27±0.04	n.d.	1.16±0.01	n.d.	0.29±0.02	5.83±0.01
Sediment	SFE (2+3)	2.76	n.d.	n.d.	1.76	0.54	475
	BCR (1)	3.55±0.01	1.68±0.01	7.39±0.07	3.67±0.01	16.76±0.04	349±1
Dust (PM10)	SFE (2+3)	2.37	n.d.	2532	n.d.	30.6	1495
	BCR (1)	2.960±0.003	n.d.	1321±1	0.093±0.003	63.5±0.1	1033±2

Conclusions

On the basis of our results it can be established that the total heavy metal contamination level of different kind of solid environmental samples increases in the order of soil < sediment < gravitation dust. The information about environmental mobility of element content of different kind of solid environmental samples gained by BCR procedure is limited to six elements (heavy metals) in sediments according to its validation [9, 30]. By this procedure the water soluble and carbonate bound fractions cannot be distinguished, while they are measured together, however, it characterizes more detailly the heavy metal mobilization by redox reactions in aquatic environment. The SFE procedure offers an alternative to the BCR procedure for the characterization of the above mobilization pathways for different kind of samples. During the 1st extraction step by supercritical CO_2 the apolar organic adsorptive layer is removed from the surface of particles, thus the hydratation and dissolution in water is promoted. The extracted amount by SFE (2+3) step is commensurable with BCR (1) step. SFE (2+3) extracted amount is higher than BCR (1) in most cases, while it contains a significant amount of metals complexed with water soluble humic acids [25]. The SFE extracts are more diluted than those of BCR, matrix effects are lower, and it requires a better detection power than ICP-OES eg ICP-MS. Further improvement of the SFE method should be performed, so columns of smaller size can be used for the same sample amount with less SiO_2, so that the blank values will decrease.

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PROCEDURY FRAKCJONOWANIA MOBILNYCH FORM METALI CIĘŻKICH W PRÓBKACH ŚRODOWISKOWYCH

Abstrakt: W pracy porównano dwie procedury ekstrakcji stosowane do frakcjonowania osadów, gleby i pyłów grawitacyjnych. W badaniach wykorzystano trzy rodzaje próbek środowiskowych: próbki gleby z działki kontrolnej zanieczyszczonej metalami ciężkimi - doświadczenie polowe, próbki zanieczyszczonych osadów dennych z jeziora Gödöllő (Węgry) i próbki powietrza zawierające pył grawitacyjny pobrane w Koszycach, SK. Pierwszą procedurą, jaką zastosowano, była ekstrakcja sekwencyjna BCR, która została pierwotnie opracowana dla frakcjonowanie zawartości metali ciężkich w osadach dennych. Zastosowanie tej metody ługowania nie jest wolne od trudności, szczególnie w przypadku próbek pyłu. Dlatego, jako alternatywę dla lepszej charakterystyki środowiska, zaproponowano nową procedurę, polegającą na zastosowaniu kolejnych ekstrakcji za pomocą ditlenku węgla w stanie nadkrytycznym, wodą w stanie podkrytycznym i ekstrakcyjnym roztworem nadkrytycznym (SFE) będącym ich mieszaniną 1:10.

Słowa kluczowe: zanieczyszczenie metalami ciężkimi, ekstrakcja sekwencyjna, frakcjonowanie, gleby, osady, pył grawitacyjny

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MONITORING OF THE DISTRIBUTION OF SOME HEAVY METALS DURING BREWING PROCESS

MONITOROWANIE DYSTRYBUCJI METALI CIĘŻKICH W PROCESIE PRODUKCJI PIWA

Abstract: Herbicides, fungicides and bactericides containing heavy metals used in agriculture make it possible to find these toxic metals in beer. The aim of this work was to monitor the distribution of some toxic heavy metals as Cd, Pb, Ni, Cr, As and Se during beer production. The experiments were observed in pilot plant scale conditions. Except arsenic only a very low fraction of other metals passed into beer. Grain absorbed the majority of the metals (primarily Hg and Pb, the least in the case of As). The yeasts absorbed smaller part of the heavy metals, mainly Ni, As and Se. From the above-mentioned heavy metals only the arsenic was the metal from which the substantial part passed into beer (about two-thirds of added amount). Even after such a large spiking of the brewing water by the concentrations of 0.1÷0.5 mg/dm^3 of individual heavy metals, the content of heavy metals, except for arsenic, in beer remained below the legislative limits.

Keywords: heavy metals, raw materials, brewing process, beer, AAS

The purpose of preparing hopped wort is to transfer extractive substances from the malt and bitter substances from the hops to the solution. An indispensable part of malt extract is formed by minerals, whose total content in the dry matter is about 2÷3%. However, so-called trace elements form just about 0.02% of malt extract. This also applies to toxic metals, which are distributed from the raw materials to the finished beer and brewing residuals. The concentration of metals in the intermediate stages, ie in sweet wort and hopped wort, depends not only on their content in the raw materials (malt, hops and water [1-7]), but also on their ability to transfer into solution during the brewing process [4-11]. This ability is affected by chemical properties of the specific elements and physical-chemical factors, such as temperature, extract concentration, pH and others which act during mashing, wort boiling and during wort cooling. Another decrease occurs during

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fermentation. The content of metals in beer in generally very low; thus, in these terms, beer is considered one of the cleanest foods [12-18].

The purpose of this study was to monitor the distribution of selected metals throughout the production process. In the first part of the work, Cu and Al were selected. Increased concentration was studied for these two metals due to their possible presence in some pesticides used to treat hops. The second part simulated the possibility of contamination by toxic metals added to brewing water. It was determined whether this contamination would cause an increased concentration in beer or whether the metal would be separated during the process (eg in spent grain, trub, during fermentation etc.).

Experimental

Technology used

The brews were brewed in a pilot copper four-vessel brewhouse with direct fire gas burner with cast out wort volume of 38 dm^3. The classical method for beer of the Czech type, that is, double mash brewing procedure with a mash-in at 37°C and an ascend with a boiling water addition to 52°C was used in the production. The break at 63°C was 10 min, the saccharification rest for both mashes was 15 min and the mash boil time was 20 min. Distilled water was used as the sparging water. All the brews were prepared as all malt with the wort original extract 10% (°P); they were hopped with hop pellets and were completely matured. Wort boil time was 90 min, the brew was hopped with 12 g of alpha-acids per 100 dm^3 (1 hl) of wort with Saaz hop pellets and hop extract 50 to 50% ratio.

The primary fermentation took place in a stainless fermentation cylinder in a separately cooled refrigerator. Cold wort was fermented at 8°C with first generation of yeast strain W 95 according to VUPS collection. Pitching rate was 0.6 dm^3 of thick yeast slurry per 100 dm^3 (1 hl) of wort. The course of the primary fermentation was controlled so that the temperature would not exceed 11°C. The total duration of the primary fermentation was 8 days, green beer started maturation at the apparent degree of fermentation approx. 71%.

Green beers were matured in modified 30 dm^3 KEG barrels at 1÷2°C for a period of 5 weeks. Finished beer was filtered on pilot plant plate and frame filter and bottled on a pilot plant bottling line under a CO_2 atmosphere with a bottle double pre-evacuation.

Analytical procedures used

Al, Cu, Fe, Mn and Zn were determined by flame atomic absorption spectroscopy (AAS), while Cd, Pb, Ni, Cr, As and Se by flameless AAS (ETA) on Varian 240 FS (2005) instrument [12, 13]. Hg was determined on TMA 254 instrument [8].

Sample take-off points

The samples were taken in the following stages of production: malt, hops, brewing water, mash in, first wort, kettle up, spent grain, cold (hopped) wort, yeast before and after fermentation, green beer, finished beer.

Mass balances of metals

Mass balances of metals were calculated from the following relations:

- malt + water = kettle up + spent grain
- kettle up = first wort + runnings

- wort = kettle up + hops
- cold wort = wort - trub
- cold wort + pitching yeast = green beer + collected yeast

Results and discussion

Study of the distribution of metals after the addition of hops with pesticides containing metals

Economically, the most significant disease of hops is *Pseudoperonospora humuli*. The pathogen attacks the leaves and cones; however, it can also attack the whole plant. It spreads especially during rainy weather, when it can significantly damage or destroy the crops. Copper fungicides, which work on contact and preventively, are still widely used for protection against *Pseudoperonospora humuli*. Another of the significant effective substances used against *Pseudoperonospora humuli* is fosetyl aluminum. It is characterized by a systematic and long-term effect. The metals present in these fungicides pass directly into the brewing process.

Cu and Al were added to the (hopped) wort of the experimental brew, a regular brew was the comparative. The amount to be added was based on specific concentrations of pesticide residue in hops (Tab. 1). The amount to be added was decided to be approximately three times the higher concentration (so that extreme cases would be included) of Cu and Al contents in hops. That concentration is approximately 600 mg Cu/kg and 200 mg Al/kg. A regular dose of hops is approximately 3 g/dm^3 of (hopped) wort. Therefore, the amount added is 5 ppm Cu and 2 ppm Al. Both these metals were added into the (hopped) wort in the form of a sulphate.

Table 1

Pesticides containing heavy metals used for treating hops and allowed in year 2008

Commercial name of treatment	**Effective substance**	**Effective substance content**	**Concentration applied**	**Disease**
Cuproxat SC	Basic copper sulphate	345 g/dm^3	0.5÷0.75%	*Pseudoperonospora humuli*
Champion 50 WP	Copper hydroxide	77%	0.75%	*Pseudoperonospora humuli*
Ridomil Gold Plus 42,5	Copper oxychloride	400 g/kg	0.35÷0.4%	*Pseudoperonospora humuli*
	Metalaxyl-M	25 g/kg		
Curzate K	Copper oxychloride	77.30%	0.30%	*Pseudoperonospora humuli*
	Cymoxanil	4.00%		
Kuprikol 50	Copper oxychloride	840 g/kg	0.5÷0.75%	*Pseudoperonospora humuli*
Kuprikol 250 SC	Copper oxychloride	420 g/dm^3	0.8÷1.2%	*Pseudoperonospora humuli*
Aliette Bordeaux	Copper oxychloride	250 g/kg	0.4÷0.5%	*Pseudoperonospora humuli*
	Fosetyl-Al	420 g/kg		
Aliette 80 WG	Fosetyl-Al	800 g/kg	0.3% (2.4÷4.5 kg/ha)	*Pseudoperonospora humuli*
Curenox	Copper oxychloride	877 g/kg	0.75%	*Pseudoperonospora humuli*
Funguran-OH 50 WP	Copper hydroxide	77%	0.5÷0.75%	*Pseudoperonospora humuli*
Cuprocaffaro	Copper oxychloride	869.6 g/kg	0.75%	*Pseudoperonospora humuli*
Kocide 2000	Copper hydroxide	53.8%	0.42÷0.56%	*Pseudoperonospora humuli*
Application dose per hectare is 700÷2000 dm^3				

The primary analytical characteristics of malt and hops including Cu and Al contents are listed in Table 2. The metal concentrations measured in the individual stages of the process are presented in Table 3.

Table 2

Selected analytical characteristics and content of Cu and Al in malt and hops

	Malt	Hops
Extract [%]	80.6	-
Protein [%]	10.8	-
Bitter substances [%]	-	14.2
Cu [mg/kg]	3.5	275
Al [mg/kg]	16	122

Table 3

Changes in the content of metals during the production process and after the addition of Cu and Al to (hopped) wort [mg/kg], [mg/dm^3]. The values in parentheses are converted to 10% extract

Sample/brew	Comparative	+ 5 ppm Cu	Comparative	+ 2 ppm Al
Mash in water	0	0	0	0
Mash in	0.20	0.22	0.82	0.78
First mash	0.06	0.07	0.70	0.66
Second mash	0.06	0.06	0.76	0.78
Mash-out	0.15	0.18	1.22	1.36
First wort	0.40 (0.27)	0.42 (0.28)	1.86 (1.23)	2.02 (1.3)
Last runnings	0.18 (1.14)	0.19 (1.20)	0.40 (3.2)	0.46 (3.7)
Kettle up (10% wort)	0.46 (0.47)	0.48 (0.47)	0.82 (0.80)	0.84 (0.82)
Spent grain	20	22	45	51
Filtered hot (hopped) wort	0.70	2.8	1.6	3.2
Hot (hopped) wort with trub	1.5	5.5	2.9	4.8
Trub	450	1850	680	1320
Cold (hopped) wort	0.10	1.2	0.32	0.62
Finished beer	0.06	0.18	<0.20	0.36

The results show that in the case of both Cu and Al, treating hops with a high dose of pesticides containing these metals will cause a slight, yet significant, increase of their content in beer. However, it is important to note that the dose normally used in production is about a third, so the increase of the concentration of both these metals in beer would be only a few hundredths ppm. The increase of Cu concentration is technologically slightly significant, but insignificant health-wise. That of Al is completely unimportant. A large part of both metals leaves in trub, which can put a strain on the environment.

Monitoring of the distribution of toxic metals during beer production

This part of the study focused on the distribution of metals from barley to malt and the green malt sprouts, the behaviour of heavy metals (Cd, Pb, Ni, Cr, As, Se and Hg) during the course of the brewing process and their distribution between finished beer and brewing residuals.

Heavy metals have the tendency to cumulate in the green malt sprouts (Tab. 4), which can cause problems in its agricultural or industrial use.

Table 4

Concentration of metals in malt sprouts and their ratio to the concentration to malt

Metal	Content [mg/kg]	Ratio of content in malt sprouts to malt
Cu	17÷34	~ 5
Fe	52÷110	~ 3
Zn	72÷99	~ 3
Mn	20÷27	~ 2
Cd	0.04÷0.12	~ 6
Pb	0.2÷0.9	~ 5
Ni	0.6÷1.2	~ 2
Cr	0.9÷1.4	~ 6
As	0.04÷0.10	~ 3
Se	0.06÷0.10	~ 2
Hg	0.008÷0.012	~ 4

The behaviour of toxic metals during production was studied in detail in a regular brew. The metal contents in used malt and hops are listed in first two rows of Table 5. Samples were taken from the brew described upwards and according to the mass balances in chap. “Mass balances of metals”, the distribution of the metals from the raw materials (total content 100%) into spent grain, trub, yeast and beer (Fig. 1) was calculated. It was confirmed that toxic metals mostly pass into the residuals (spent grain, trub and yeast), so only a negligible fraction of them pass into beer (except As, of which about half passes into beer). These results essentially correspond with the findings founded in the literature [4-6, 9, 10, 15].

Table 5

Metal content in raw materials, intermediate products and beer after adding toxic metals to brewing water [μg/kg], [μg/dm^3]

Raw materials, intermediate product, beer	Cd	Pb	Ni	Cr	Hg	As	Se
malt (dry matter)	15	41	640	120	2	22	30
hops (dry matter)	30	295	1110	880	11	60	50
water	200	500	300	300	100	300	300
spent grain orig. (dry matter)	40	80	910	278	5	69	78
spent grain (dry matter)	3050	8330	3030	2760	1700	950	3320
% total amount in spent grain	76	95	54	63	96	22	82
yeast orig. (dry matter)	19	55	3500	64	16	390	1400
yeast (dry matter)	680	480	15100	770	850	8170	8400
% total amount in yeast	1	0,2	11	1	2	7	6
finished beer	**> 1**	**9**	**85**	**80**	**> 1**	**210**	**25**

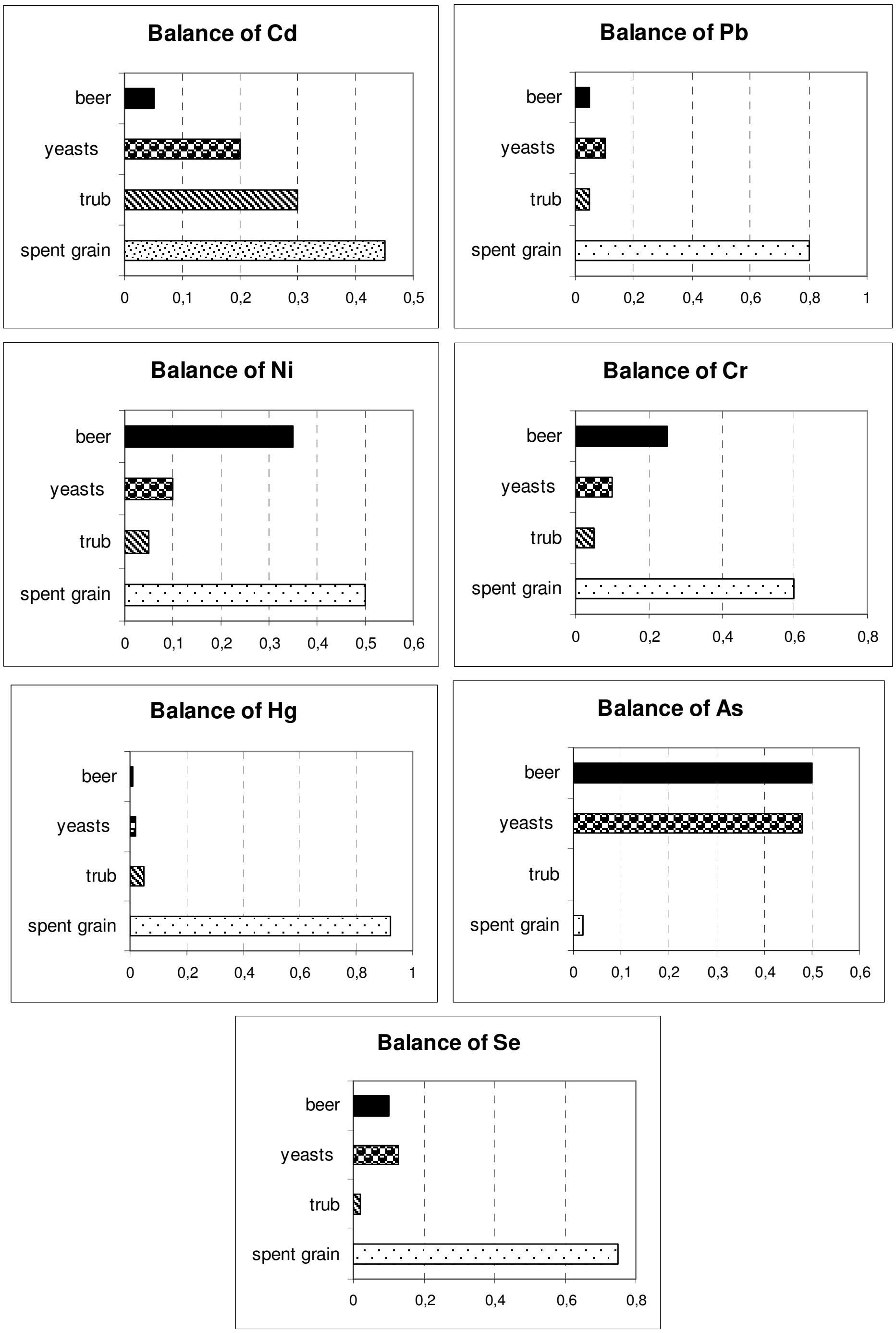

Fig. 1. Distribution of toxic metals from raw materials into brewing wastes and beer, total amount of individual metals in raw materials is 100%

Study of the distribution of toxic metals added to brewing water

A possible contamination by added toxic metals to the process (Tab. 6) was simulated and it was determined whether this contamination would cause an increased concentration in beer or whether the metal would be separated during the process (eg in spent grain, trub, during fermentation etc.).

Table 6

Addition of toxic metals to brewing water

Metal	**Addition [µg/dm^3]**
Cd	200
Pb	500
Ni	300
Cr	300
Hg	100
As	300
Se	300

The results are shown in Table 5. The amount of metal which passed into beer is graphically represented in Figure 2. As evidenced by results, relatively most of the added amount passes into beer in the case of As (about two thirds) and then for Ni and Cr (about a quarter). Absolute amounts of added metals absorbed by spent grain and yeast were estimated from the mass balances. The results suggest that Hg and Pb have the strongest affinity to spent grain; As the weakest. On the other hand, what cumulates the most in yeast is Ni and then As and Se. An important finding is that even in the case of high contamination of raw materials by toxic metals, their increased content in beer will not be observable (except As) and their level will still be below the allowed limit.

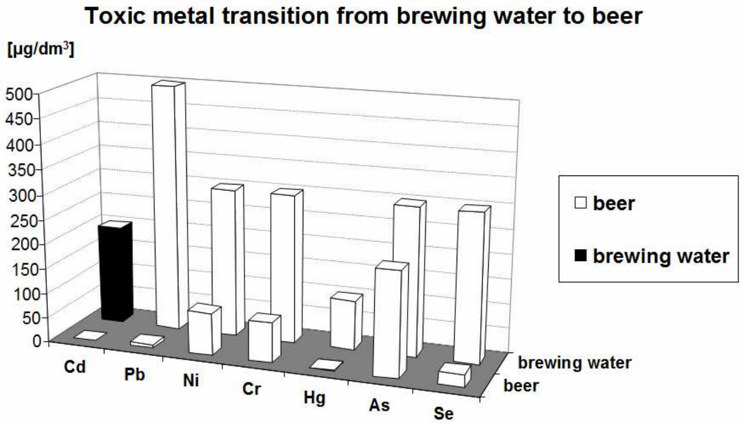

Fig. 2. Amount of metals which passed from brewing water into beer after their addition to brewing water

Conclusions

Based on pilot plant experiments, the monitoring of selected heavy metals during the whole technological process was observed. Treating hops with a high dose of pesticides containing Cu and Al caused a slight increase in their content in beer. However, the concentration increase of both these metals in beer accounts to only a few hundredths or thousandths mg/dm^3. The increase of the Cu concentration is technologically slightly significant, but insignificant health-wise. That of Al is completely unimportant.

Toxic metals, which pass into beer primarily from raw materials, distribute themselves into the waste (spent grain, trub, yeast) during the brewing process most of the time. Therefore, only a negligible fraction of them passes into beer (except As, of which more than a half passes into beer).

A possible increase of a toxic metal at the beginning of the brewing process will affect the beer only in the case of As; other toxic metals are mostly removed with spent grain and also with trub and yeast. Even after a relatively large addition of toxic metals to brewing water, their content in finished beer remained below the allowed limit (except As).

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MONITOROWANIE DYSTRYBUCJI METALI CIĘŻKICH W PROCESIE PRODUKCJI PIWA

Abstrakt: Metale ciężkie zawarte w środkach chwastobójczych, grzybobójczych i bakteriobójczych stosowanych w rolnictwie są obecne także w piwie. Celem pracy było oznaczenie stężenia niektórych toksycznych metali ciężkich, jak: Cd, Pb, Ni, Cr, As i Se, powstających podczas produkcji piwa. Badania prowadzono z wykorzystaniem instalacji pilotażowej. Ogólnie stwierdzono małe wartości stężenia metali ciężkich w piwie, wyjątek stanowił arsen. Ziarno akumuluje większość metali (przede wszystkim Hg, Pb i As), natomiast drożdże akumulują mniejsze stężenia metali ciężkich, głównie Ni, As i Se. Z oznaczanych metali ciężkich tylko znaczna część arsenu przeszła do piwa. Stężenie metali ciężkich w piwie, z wyjątkiem arsenu, było mniejsze od dopuszczalnego stężenia wyznaczonego przez normy prawne.

Słowa kluczowe: metale ciężkie, surowce, produkcja piwa, piwo, AAS

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IMPACT OF MICROWAVE DISINTEGRATION ON ACTIVATED SLUDGE

WPŁYW DEZINTEGRACJI MIKROFALOWEJ NA OSAD CZYNNY

Abstract: Microwave disintegration of activated sludge causes organic matter transfer from the solid phase to the liquid phase. This process results in an increase of the COD value in liquid by ca 614 mg O_2/dm^3 and protein concentration by ca 340 mg/dm^3. Microwave radiation positively influences the sludge volume index (SVI) decrease from 195 to 54 cm^3/g. Our research confirmed that the application of an electromagnetic wave may become a new effective way of improving sewage treatment and processing sewage sludge.

Keywords: activated sludge, microwave disintegration, COD, proteins, sludge volume index (SVI)

Destroying cell walls of microorganisms and consequently releasing intracellular substances into the surrounding liquid are conducted with the use of various disintegration methods. The most common methods of cells disintegration are: enzymatic digestion, lysis with the use of detergents and organic solvents, cutting, homogenization, sonification, grinding, differential centrifugation, shaking with glass balls, osmotic shock and freezing/defrosting.

In the recent years, some of the disintegration methods used in biotechnology have been applied in the sewage sludge processing. Among the used methods were:

- the application of thermic energy [1-3],
- the application of enzymes [4, 5],
- ozonation [6, 7],
- acidification [8],
- alkalisation [9],
- the application of high pressure [10-12],
- mechanical mincing [13],
- the application of ultrasound energy [14-16],
- the application of microwave radiation [17-20].

The most important aims of applying disintegration include:

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- releasing intracellular enzymes into the environment which cause direct decomposition of pollutants,
- exposing organic substances and making them more accessible for the remaining biomass (taking into account the disintegration of a part of activated sludge or sludge in septic tanks),
- releasing an organic substrate (surplus sludge in case of disintegration), which may be the source of easily assimilable organic carbon for the denitrification process in case of its deficiency in the sewage flowing to the bioreactor,
- a possibility of applying disintegration in sewage treatment processes to remove the foam generated in bioreactors and eliminate the foaming in septic and settlement tanks.

One of the sewage sludge disintegration methods is the usage of microwaves. Microwave radiation is a type of electromagnetic radiation with a wavelength from $\lambda = 1$ m to ~ 0.1 mm the microwave spectrum ranges from the infrared to ultra short waves, of frequency $\nu = 3 \cdot 10^9 \div 3 \cdot 10^{12}$ Hz [21].

Microwaves radiate in the form of mutually diffusing electric and magnetic vibrations. Microwaves vary from other electromagnetic waves in the fact that they generate the molecular move in the alternating electric field without breaking the stability of chemical bonds. The energy carried by the microwave radiation is considerably smaller than the energy of chemical bond decay.

Electromagnetic waves undergo all physical phenomena that are characteristic for wave motion. They can be transmitted or absorbed and also undergo reflection, refraction, deflection, interference and polarisation.

Microwave radiation can be absorbed by matter through dipolar polarisation (dielectric), which is responsible for the microwave heating effect, and through ionic conductivity.

A device used in generating microwave radiation is the magnetron. The magnetron uses delayed electrons, which move on a coiling spiral and radiate microwaves. In magnetrons the microwave energy is generated from electric energy. Ca 50% of energy by the frequency 2.45 GHz and 85% by the frequency 0.915 GHz undergo energy transformation.

Microwaves have a negative influence on living organisms. The basic mechanisms of the influence that the electromagnetic field has on organisms include:

- a direct influence on cell walls (membranes) which may cause their: deformation, depolarisation (a change in the electric potential of a cell's membrane), perforation or necrocytosis;
- an influence on ions move in electrolytes (which can have negative consequences for nerve conduction);
- a direct influence on water included in tissues;
- an influence on substances included in blood (for example, hemoglobin iron).

The magnetic field has a large impact on liquids. The following elements undergo changes in solutions exposed to microwaves: molecular structure of liquid, polarisation and arrangement of molecules and electric charge. Changes also occur in the course of surface phenomena, intensification of oxidation and reduction processes, selective ionisation and in such liquid characteristics as: density, viscosity, absorption of light and absorbance of solid bodies [20]. The scatter coefficient defines the liquid ability to absorb microwaves. This coefficient is characterized by the dielectric loss index, or the potential of changing an electromagnetic wave into heat, and by the dielectric constant.

Microwave radiation as a source of thermal energy has been applied in environmental engineering processes as well. The process of sewage treatment generates great amounts of sludge, whose storing and later application are expensive and only to a little extent are they managed. The sewage sludge includes more than 70% of water in its mass and the microwaves can considerably influence its characteristics and structure. Moreover, numerous bacteria, protozoa, yeast, fungi and parasite ova appear in the sludge and undergo destruction on exposure to the magnetic field [18].

Microwave heating is used for:

- sludge sanitation [18],
- sludge drying [20],
- an improvement of the activated sludge work [17, 19].

Materials and methods

The material for research comprised of activated sludge from a sewage treatment plant, applying advanced processes of biological sewage treatment, which consist of simultaneous elimination of organic compounds and bonds of nitrogen and phosphorus. The treatment plant was designed for the flow of 120 00 m^3/d. For the time being, the amount of flowing sewage is ca 90 000 m^3/d, sewage retention time ca 14 days and concentration of activated sludge in the bioreactor 4320÷4640 mg/dm^3.

In the taken samples of activated sludge the COD value was analyzed [22], the protein concentration was determined by the Lowry method [23] and also the content of suspended solids, the change of turbidity and the *Sludge Volume Index* (SVI) [22].

Disintegration process was carrying by frequency of microwaves irradiation 2.45 GHz and nominal power 900W. Disintegration was carried out over periods of 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330 and 360 seconds. COD value, protein concentration and the change of turbidity was measured for samples before and after each period of disintegration. 10 series of research were conducted and the standard deviation was calculated.

Results and discussion

Microwave disintegration of activated sludge caused changes in turbidity in every research series which is presented in Figure 1. The increase of turbidity was connected with the duration period of the microwave disintegration, which considerably influenced the decay of flocks and microorganisms' cells and also releasing matter into the liquid under research.

During the research the impact of microwave radiation on sedimentation properties of activated sludge was also determined. Figure 2 presents the changes of the SVI value under research with prolonging the time of the microwave field influencing the samples.

Average values of volume index reached the 195.5÷54.1 cm^3/g. As presented in Figure 2, the greatest decrease of the index value was achieved up to the third minute of microwave disintegration, obtaining a change by 136.4 cm^3/g. This change showed a definite improvement on sedimentation properties of sludge because low values of the volume index, ca 100 cm^3/g., indicate a high dewatering ability of sludge. Further prolonging the operation time of microwave radiation did not influence considerably the change of the analyzed parameter.

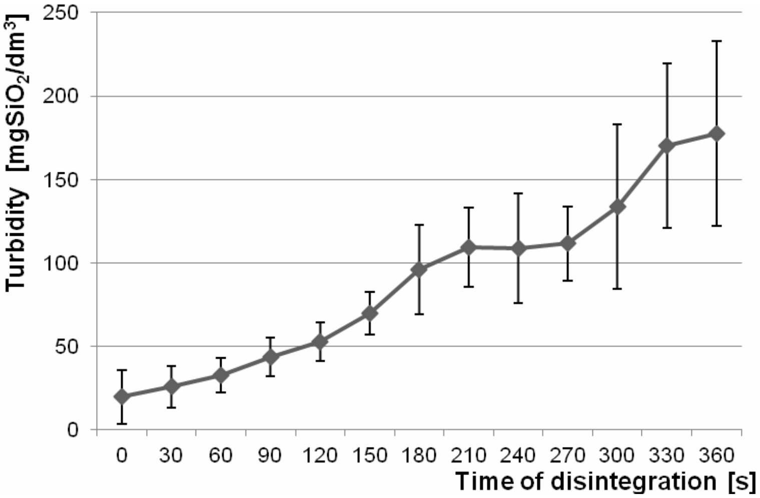

Fig. 1. Changes in turbidity in time of disintegration

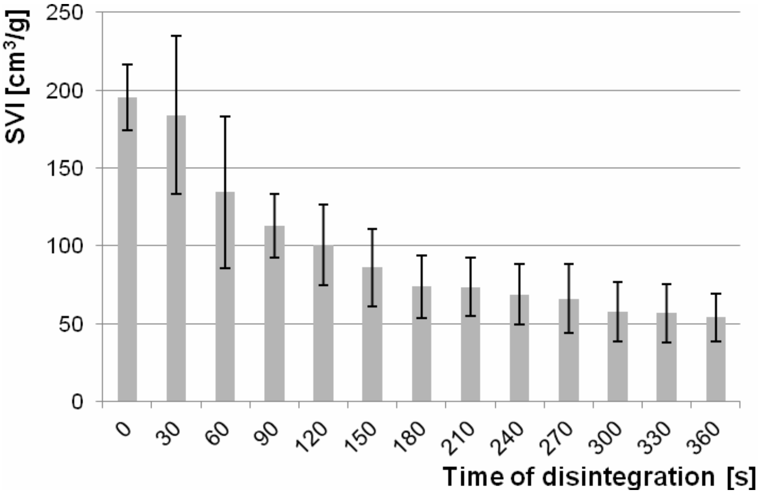

Fig. 2. Changes of SVI in time of disintegration

The microwave destruction of flocks and microorganisms in activated sludge causes a release of constitutional water by which dewatering becomes faster and concentration better. The conducted research indicated that treating the activated sludge with an electromagnetic field contributes to a change in sedimentation properties of activated sludge. It means that along with prolonging the operation time of microwave disintegration, the concentration of activated sludge gradually increased. Volume limitation of generated sludge in technical scale could have a positive impact on processing the sludge and the possibility of its management which would also give a positive reflection on economic aspects.

Microwave radiation on microorganisms in the activated sludge had a destructive influence on the release of organic substances into the over-sludge liquid, expressed in the COD and protein concentration values. As conducted research showed, the effectiveness of the applied electromagnetic field depends mainly on the amount of radiation (operation time). The most effective amount (operation time) was a 3-minute exposition of sludge to the microwave radiation (Fig. 3).

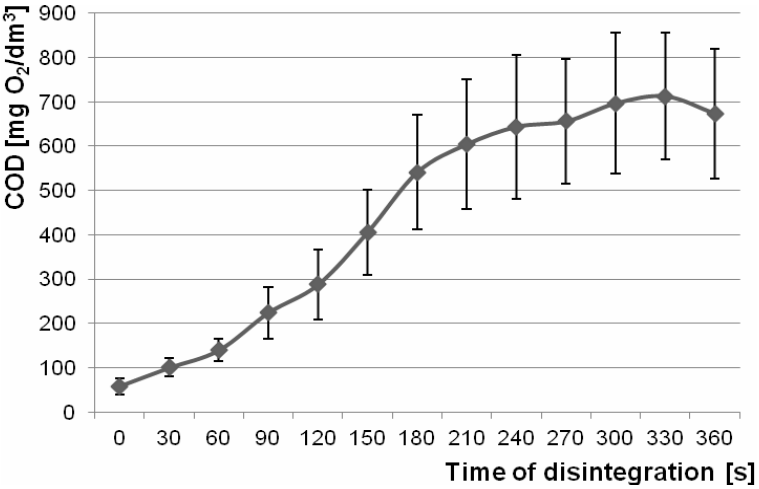

Fig. 3. Changes of COD value in time of disintegration in liquid phase

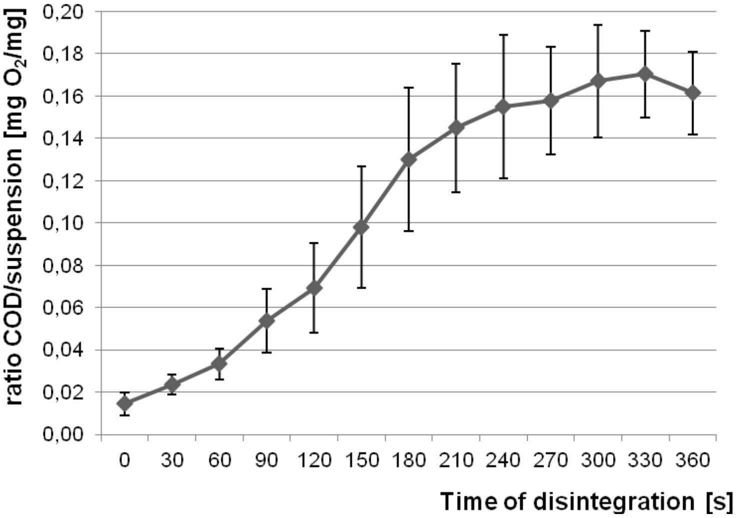

Fig. 4. Changes of ratio COD value/suspension in time of disintegration in liquid phase

The COD values changed on average from 58.5 mg O$_2$/dm^3 for the actual over-sludge liquid to 712.4 mg O$_2$/dm^3 for a sample after a 5.5-minute exposition to the microwave radiation. The greatest increase of the COD value occurred in the beginning period of exposition, eg in the period from 0 to 3 minutes, where the increase amounted 482.7 mg O$_2$/dm^3 on average. Further microwave disintegration caused an increase by another 171.2 mg O$_2$/dm^3. The largest change in the COD value was visible by the sample, which was exposed to a 3-minute microwave radiation, where the increase of the index reached 135.2 mg O$_2$/dm^3 (between 2.5 and 3 minutes). It may indicate that this period of time has the best impact on flocks in the activated sludge and the destruction of microorganisms cells, and thus on releasing organic matter into the surrounding liquid. As a result, it can be assumed that this period of time is optimal for the disintegration method under research in terms of the COD release. This fact can be observed by analyzing Figure 4, presenting the proportion of released COD and activated sludge suspension.

Using microwaves influences the increase in the proportion of soluble COD (*sCOD = soluble Chemical Oxygen Demand*) to total COD (*tCOD = total Chemical Oxygen Demand*) which has its reflection in the elevated content of organic substances released from sludge flocks. In our research the ratio of soluble COD to total COD increased by 12% under the influence of 5.5 minutes microwaves treatment. In the research conducted at the University of Malaysia, the sCOD/tCOD coefficient increased by 45% under the influence of a 7-minute microwave treatment [20].

For additional confirmation of the organic matter release from activated sludge during the microwave disintegration process, the protein concentration in the researched over-sludge liquid was determined. The protein concentration was increasing along with the time of conducting the microwave disintegration process, similarly to the COD value change (Fig. 5).

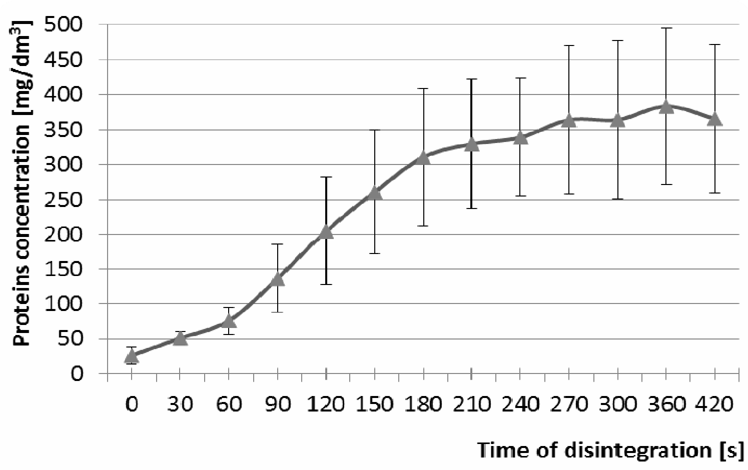

Fig. 5. Changes of proteins concentration in liquid phase during disintegration process

The protein concentration, up to the third minute of the microwave treatment, increased on average by 284.4 mg/dm^3 in the proportion to the protein concentration in the actual over-sludge liquid, reaching the level of 310.6 mg/dm^3. Further disintegration of samples, up to the 6-minute exposition, caused an increase of concentration only by 72.7 mg/dm^3 (Fig. 5).

The protein concentration changes confirmed the observation on the highest effectiveness of the microwave radiation treatment of activated sludge during the first 3 minutes.

Conclusions

The research regarding the possibilities of applying the microwave radiation for activated sludge disintegration showed that the electromagnetic field operation has a destructive influence on flocks and microorganisms in activated sludge.

Exposing the activated sludge to (electro) magnetic waves treatment causes:

- an improvement on the sludge sedimentation properties,
- a decrease of the sludge volume index from 195.5 to 54.1 cm^3/g,
- disunity of the homogenous sludge structure and releasing organic matter,
- releasing organic matter into the over-sludge liquid which was indicated by the increase of the COD value from 58.5 to 673 mg O_2/dm^3 and the protein concentration from 26 to 366 mg/dm^3.

The conducted research shows that the application of electromagnetic radiation may become a new effective method, allowing for an improvement of sewage treatment processes and processing generated sewage sludge.

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Abstrakt: Mikrofalowa dezintegracja osadu czynnego jest przyczyną uwolnienia substancji organicznej do cieczy nadosadowej. Proces ten skutkuje wzrostem wartości ChZT w cieczy o ok. 614 mg O_2/dm^3 i stężenia protein o ok. 340 mg/dm^3. Promieniowanie mikrofalowe korzystnie wpływa również na zmniejszenie *indeksu objętościowego osadu* (I.O.O.) z wartości 195 do 54 cm^3/g. Przeprowadzone badania potwierdzają, iż zastosowanie fali elektromagnetycznej może stać się nową, korzystną metodą pozwalającą na udoskonalenie procesów oczyszczania ścieków i przeróbki powstających osadów ściekowych.

Słowa kluczowe: osad czynny, dezintegracja mikrofalowa, ChZT, proteiny, indeks objętościowy osadu

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EX SITU BIOREMEDIATION OF SOIL POLLUTED WITH OILY WASTE: THE USE OF SPECIALIZED MICROBIAL CONSORTIA FOR PROCESS BIOAUGMENTATION

BIOREMEDIACJA ZAOLEJONYCH GRUNTÓW METODĄ *EX SITU*: BIOAUGMENTACJA PROCESU Z WYKORZYSTANIEM SPECJALISTYCZNYCH KONSORCJÓW DROBNOUSTROJÓW

Abstract: Spontaneous, natural self-attenuation of oil-derived pollution in a ground-water environment is relatively slow and for this reason several intensification actions are necessary to speed up the process. For the case of contaminated soil, the most favorable treatment method is *ex situ* bioremediation, in which the ground is removed from its original site and then formed into piles located in separated cleanup sites. This enables easy adjustment and control of the process parameters and allows for taking other optimization actions such as bioaugmentation with specially-prepared microorganism cultures. The experimental part of the work was done to establish optimal conditions for the development and action of soil-derived bacterial community used as *inoculum* to augment bioremediation of organic compounds. The study involved two specially-constructed test piles (A and B), each of 120 cm height and area of 10 m^2, made of soil polluted with petroleum waste (the average contaminant content was 4300 $mg \cdot kg^{-1}$). The soil was ground and fluffed by admixture of 10% bark, then supplemented with the necessary minerals and watered to provide conditions favoring microorganism growth. Next, the microbial consortium was inoculated. Free aeration was provided in pile (A) by frequent mechanical mixing, whereas pile (B) remained unmixed and was only re-inoculated with fresh microorganism cultures. The level of high-boiling organic contaminants as well as the cell density was monitored with standard methods. In pile (A) a rapid drop of oil-derived compounds content was observed and the value of 600 $mg \cdot kg^{-1}$ was achieved within 6 weeks. In pile (B) the effect was poor (3240 $mg \cdot kg^{-1}$ within 13 weeks) despite high bacterial frequency (10^8 $cells \cdot g^{-1}$). These results indicate that the lack of free gas exchange was a factor hampering microorganism metabolism and thus limiting bioremediation process. The method of intensified bioremediation was applied to biodegrade high levels of recalcitrant contaminants on a large scale at the industrial *ex-situ* soil cleanup site. Two technological piles (150 cm high) were formed using soil mixed with oily substances: (P1), total volume of 180 m^3, containing post-refinery sludges at 24000 $mg \cdot kg^{-1}$ concentration and (P2) of 90 m^3, containing oil-separator slurries at 114000 $mg \cdot kg^{-1}$. The oxygen penetration was provided with a passive aeration system made of drainage-pipes. In order to obtain maximum process kinetics, the piles were frequently surface-sprayed with fresh microbial suspensions enriched with autochthonous bacteria. After inoculation, the soil bacteria population increased by 16 to 42 times and reached the value of $3.6 \cdot 10^6$ $cells \cdot g^{-1}$. The described optimization actions, applied for the first stage of the long-term bioremediation project, enabled to achieve

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significant contaminant removal rates: over 3.5-fold at the site P1 (the resultant value of 6650 mg · kg^{-1} accomplished within 6 months) and over 5-fold at P2 (22900 mg · kg^{-1} within 4.5 months).

Keywords: *ex situ* bioremediation, petroleum-derived contaminants, sludges, biorecultivation of soil, bioaugmentation, autochthonous microorganisms, microbial consortia

Spontaneous processes of self-decontamination in the environment are too slow to make up for the devastating effect of cumulative pollution. The natural attenuation-based conversion of hydrocarbons and other organic pollutants in ground and water is associated with both abiotic and biotic processes that include volatilization, photo- and chemical oxidation, bioaccumulation and microbial transformation [1, 2]. The process may be accelerated substantially by implementing a number of available cleanup technologies which involve physical and chemical processing as well as a variety of rapidly developing biological methods [3-6]. Among the latter ones, bioremediation with environment-derived bacteria takes the advantage of the fact that these microorganisms, upon evolution and long-term selective pressure, have gained capabilities of biodegrading almost all naturally occurring substances [7]. This is especially important for the case of petroleum waste products - aliphatic or aromatic hydrocarbons and their chemical derivatives, since the environmental risk caused by these compounds is particularly high [8].

Autochthonous microorganisms that have evolved in contaminated environments are the most active ones in terms of xenobiotic utilization [9]. Therefore, if the ground has been polluted for a period long enough to develop specialized indigenous microflora, a variety of available biostimulation techniques are sufficient to promote high-yield removal of pollutants [3, 5]. However, the stimulated spontaneous bioremediation may prove ineffective after sudden oil-spill incidents, long-term accumulation of highly toxic agents, or construction of novel soil reclamation sites, due to the lack of potent microorganisms. In such cases bioaugmentation with pre-grown, biochemically specialized and metabolically adapted bacterial consortia becomes an important step to launch biological degradation reactions [10, 11]. The best fitted and active microbial consortia can be constructed based on the robust indigenous strains isolated from other environments (soil, groundwater, industrial wastewater), heavily polluted with organic substances. These microorganisms are laboratory-cultivated and subjected to thorough selective pressure by incubating with chosen xenobiotics applied at sublethal levels [11-13]. The resultant microbial communities are then used to bioaugment remediation processes, typically, by introducing (usually by spraying) high-density suspensions directly into the soil.

If the contaminated ground can be easily removed from the original site affected by oily-waste pollution, the methods employing biostimulated and/or bioaugmented *ex situ* (off site) reclamation yield best results. This approach has several important advantages that make it the optimal biotechnology in terms of its potential to control basic process parameters and obtain fast kinetics of contaminant biodegradation. Among these are the following: (a) easy technical supervision of decontamination process; (b) profound acceleration of pollution removal due to possibility of easy implementing a variety of necessary technical actions; (c) easy monitoring, assessment and setup of conditions favorable for the development of microorganism cultures within the soil environment. On the other hand, the relatively high costs should be pointed out, which result mainly from the need to physically remove and transport large amount of soil. Also, several other technical and biological arrangements at the reclamation site are required. They comprise: site insulation, biofilter and active aeration system construction, soil grinding, mixing, and supplementation with bark and fertilizers, construction of soil piles and cultivation of active biocenoses used for bioaugmenting.

The aim of this study was (a) to evaluate the role of oxygen accessibility as a possible factor limiting the xenobiotic metabolism in biopiles; (b) to search for optimization techniques enabling to establish favorable conditions for technical-scale, bioaugmented *ex situ* bioremediation of soil heavily polluted with oily sludges and slurries.

Materials and methods

Bacterial consortium used for bioaugmentation

A specialized microbial consortium was constructed at Biochemistry Department, University of Agriculture in Krakow, to form a stable, biologically balanced and biodiverse biocenosis, capable of biodegrading environmentally recalcitrant organic xenobiotics. The community consisted of a number of bacterial strains derived from naturally occurring, autochthonous microorganisms, selected and isolated from ground and water sites heavily and long-term polluted with petroleum-derived hydrocarbons. More details on the consortium development and cultivation are given elsewhere [13].

In this study, the presence of indigenous microflora was identified in the slurries subjected to biodegradation in a field test (see below). These autochthonous bacteria were isolated and cultivated under controlled conditions in the presence of sub-lethal concentrations of organic xenobiotics, especially hydrocarbons extracted from the slurries. The new strains were then used to enrich the original microbial community. For bioaugmentation of the *ex situ* soil reclamation a dense suspension (approx. $2 \cdot 10^9$ CFU $\cdot$ cm^{-3}; CFU - *colony forming units*) of the resultant bacterial biocenosis was used as an *inoculum*.

Ex situ bioremediation in test piles

Two identical, model biopiles (A) and (B) were constructed in a separated, insulated outdoor site. The pile areas were 10 m^2 and heights - 120 cm. The piles were formed of the sandy soil collected at the polluted area of the automotive fuel station. The average contamination, expressed as the high-boiling organic content, was determined as 4300 mg $\cdot$ kg^{-1}. The soil was preliminary ground and fluffed with 10% bark, then supplemented with the necessary minerals by the use of commercially-available fertilizers to obtain the C:N:P ratio of about 100:10:1. Finally, it was watered to provide conditions favoring microorganism growth. Next, each pile was inoculated with 10 dm^3 of fresh bacterial formulation (see section above). Free aeration was provided in pile (A) by frequent mechanical mixing, and the pile was not further bioaugmented during the course of observations (6 weeks). Pile (B) remained unmixed to simulate a limited (passive) oxygen penetration; however, it was re-inoculated with fresh bacterial consortia four times every second week during the 13-week test.

The samples for bioremediation monitoring and microbial occurrence determination were collected at four independent sites, then averaged, and the resultant material was subjected to further analyses.

Technical-scale *ex situ* field cleanup project

The soil-bioremediation large-scale project was performed at the industrial *ex-situ* soil cleanup site. Two technological piles, P1 and P2, each 150 cm high and 5 m wide, were formed using soil mixed with the following oily substances: post-refinery sludges at 24000 mg · kg^{-1} concentration (P1, total volume of 180 m^3), and oil-separator slurries at 114000 mg · kg^{-1} (P2, volume of 90 m^3). The soil was fertilized with standard agricultural fertilizers in order to provide the C:N:P ratio of approximately 100:10:5, and then fluffed by admixing 5 % bark. The oxygen penetration was provided with a passive aeration system made of a dense perforated drainage-pipe network. Both piles were surface-sprayed with fresh microbial suspensions enriched with autochthonous bacteria, in the following manner: P1 was bioaugmented 7 times with 50 dm^3 of consortium suspension, every third week during the course of a 24-week bioremediation; P2 was bioaugmented 4 times with 60 dm^3 consortium, every fourth week during the course of a 18-week bioremediation.

The characteristics of the contaminated soil are given below:

P1 - a sandy-gluey soil of heterogeneous structure, dark-brownish color, strong scent of petroleum-like substances; ether extracts dark-yellow; after ether evaporation the remaining extract was dense and oily,

P2 - grey, sandy soil, little scent of oily substances; ether extract deep-brown, upon ether evaporation the remaining fraction was almost black, dense and oily, visible numerous little crystals of organic substances.

During bioremediation, the samples for process monitoring were collected and averaged as described above.

Toxicity tests of organic waste

Prior to launching the bioremediation field project, appropriate toxicity tests of both pollutant fractions, ie oily sludges and separator slurries, were made using pre-grown microbial biocenoses. In the test, the aqueous suspension of microbial consortium was applied at the cell initial density of 2.3 · 10^9 CFU · cm^{-3}. It was then cultivated in 300 cm^3 flasks at 50 cm^3 volumes under aerobic conditions for 3 days in the presence of either 2% pollutant (w/v) extracted from soil of Pile 1, or 20 % (w/v) separator slurries. Every day the samples were collected to check for the survival of bacteria. The untreated bacterial suspension served as a control experiment.

Microbiological monitoring

Determination of cell population in soil samples and in water suspensions was performed with a Koch method as described in detail by Kaszycki et al [6]. CFU on Petri dishes were counted and cell frequencies were expressed as CFU per cm^3 of aqueous samples, or CFU per g of soil.

Extraction of organic material from soil and analyses of contamination levels

The organic content of soil samples was extracted using petroleum ether, fractions boiling at 40÷60°C (POCh, Poland), and then determined with a weigh method, as described earlier [6]. All the chemicals were of analytical grade. In microbiological analyses sterile conditions were applied. Mean experimental error was calculated to be 20% and 18%

for analyses of organic content in soil and for the determination of cell frequency, respectively.

Results and discussion

In order to intensify bioremediation of the polluted soil the *ex situ* technology offers the possibility of easy implementation the most favorable process conditions. In particular, it enables the active biocenosis (both autochthonous and/or exogenously supplemented microorganisms) to develop, reveal and maintain high physiological activity. This, in turn, stimulates biological, enzyme-based removal of organics. All the actions taken, as described in detail in Materials and methods) included ground fertilization, watering, fluffing, aeration with specially-constructed systems and extensive mechanical mixing.

Another condition regarded as crucial for effective soil bioremediation is bioaugmentation with the properly prepared microbial consortia serving as inoculates. These active microorganisms are introduced into the contaminated environment and can often substantially accelerate biodegradation of different xenobiotics due to high metabolic potential, and synergic action revealed upon a variety of complementary biochemical pathways.

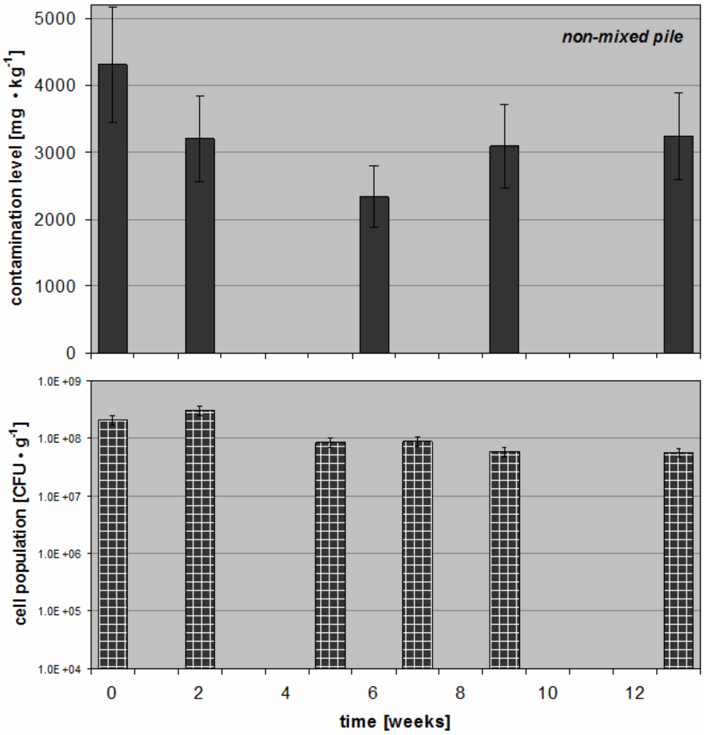

Fig. 1. Bioremediation of soil oily-waste contamination in a model *ex-situ* pile system, after inoculation with a specialized microbial consortium - a test variant with a limited oxygen penetration (pile B, non-mixed soil); upper section - biodegradation kinetics of high-boiling organics; lower section - cell population dynamics over the course of the test

In this study a specialized bacterial consortium, developed by our group, was used for bioaugmentation. Over years of long-term selection, this complex microbial community tended to reveal unique enzymatic activities thus enabling oxidation of heterogeneous organic contaminants. Previously, the elaborated biocenosis was shown to be capable of degradation of a variety petroleum-derived chemicals such as aliphatic hydrocarbons, diesel fuel, used engine oil, aromatic hydrocarbon of the BTEX (benzene, toluene, ethylbenzene and xylene) group, polyaromatic hydrocarbons (PAHs) including naphthalene, biphenyl and polychlorinated biphenyls (PCBs) [11-13].

The model experiments involving bioaugmented remediation in test piles, as shown in Figures 1 and 2, reveal the necessity to provide the microorganisms with sufficient amount of oxygen. Biodegradation kinetics obtained in a non-mixed pile (pile B, Fig. 1, upper section) was poor, despite re-inoculating the soil for several times.

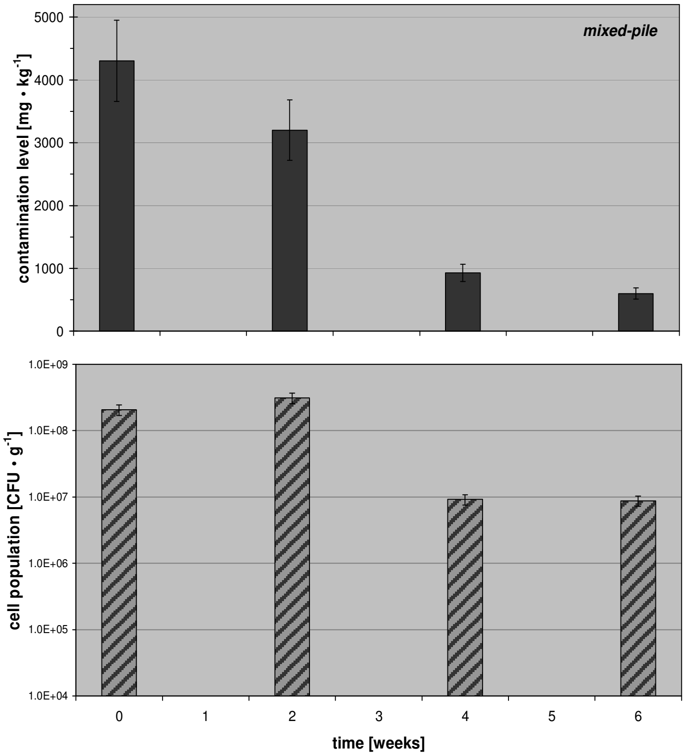

Fig. 2. Bioremediation of soil oily-waste contamination in a model *ex-situ* pile system, after inoculation with a specialized microbial consortium - a test variant with free oxygen penetration (pile A, soil systematically mixed); upper section - biodegradation kinetics of high-boiling organics; lower section - cell population dynamics over the course of the test

Note that, astonishingly, the soil cell frequency remained high throughout the test (Fig. 1, lower section). This suggests that the efficiency of the process should not be judged by mere analyses of cell population density, but rather by microorganism metabolic activity. The latter was apparently higher in the mixed pile (pile A, Fig. 2, upper section), and allowed for the fast oxidation of the bulk contaminant load. At the same time, the observed high cell population during first stages of bioremediation tended to decline, as the amount of the available carbon decreased (Fig. 2, lower section).

Prior to the field bioremediation project, appropriate toxicity tests were performed to eliminate the risk of inhibition of a biological process. As presented in Figure 3, no toxic effect was observed over a model bacterial biocenosis at contaminant concentrations comparable with that determined in technological piles. Based on these laboratory results it was reasonable to continue with the large-scale arrangements.

In the soil of piles P1 and P2, the presence of indigenous microorganisms was established and their occurrence determined as $8.6 \cdot 10^4$ CFU $\cdot$ g^{-1} and $2.2 \cdot 10^5$ CFU $\cdot$ g^{-1}, respectively. After 8 weeks of bioremediation process, the soil samples were verified again and a significant cell population increase was observed, namely $3.6 \cdot 10^6$ CFU $\cdot$ cm^{-3} and $3.5 \cdot 10^6$ CFU $\cdot$ cm^{-3}, for piles P1 and P2, respectively. At this time a marked change in the soil morphology was observed - it got granulated and the presence of oily inclusions was much less frequent.

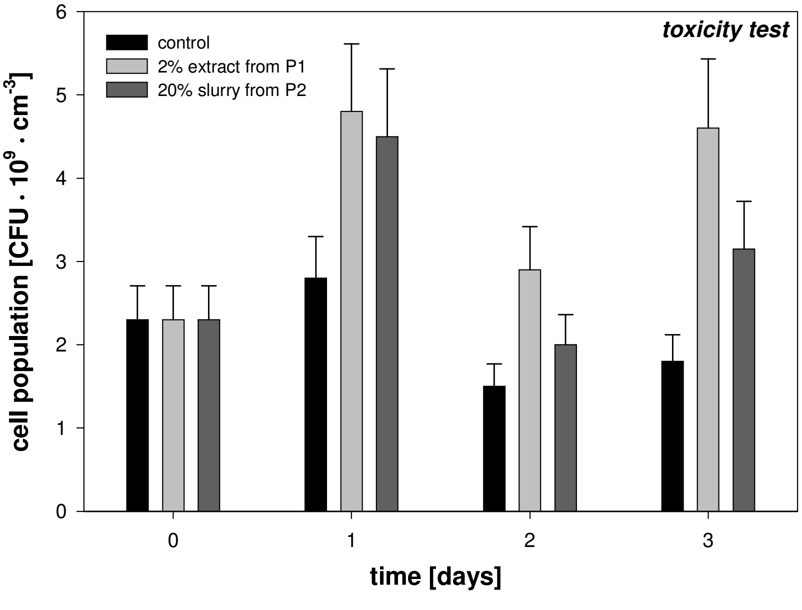

Fig. 3. Toxicity test of pollutant fractions present in piles P1 and P2; black bars - a microbial consortium suspension (cell density of $2.3 \cdot 10^9$ CFU $\cdot$ cm^{-3}) cultivated under aerobic conditions for the time course of the test (a biotic control); light grey bars - a microbial consortium, cultivated as above in the presence of 2% pollutants (w/v) extracted from soil of Pile 1; dark grey bars - a microbial consortium, cultivated as above in the presence of 20% separator slurries (w/v) treated in Pile 2

The soil cleanup project was successful and the pollutants present in both piles P1 and P2 were biodegraded efficiently, as documented in Figures 4 and 5.

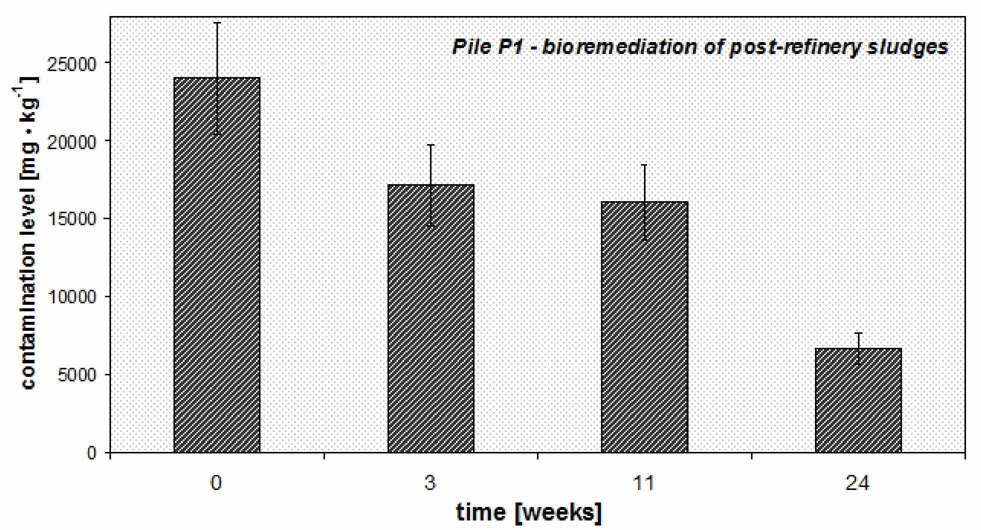

Fig. 4. Oil-derived waste removal kinetics obtained in *ex situ* bioremediation (pile P1) of soil polluted with post-refinery sludges

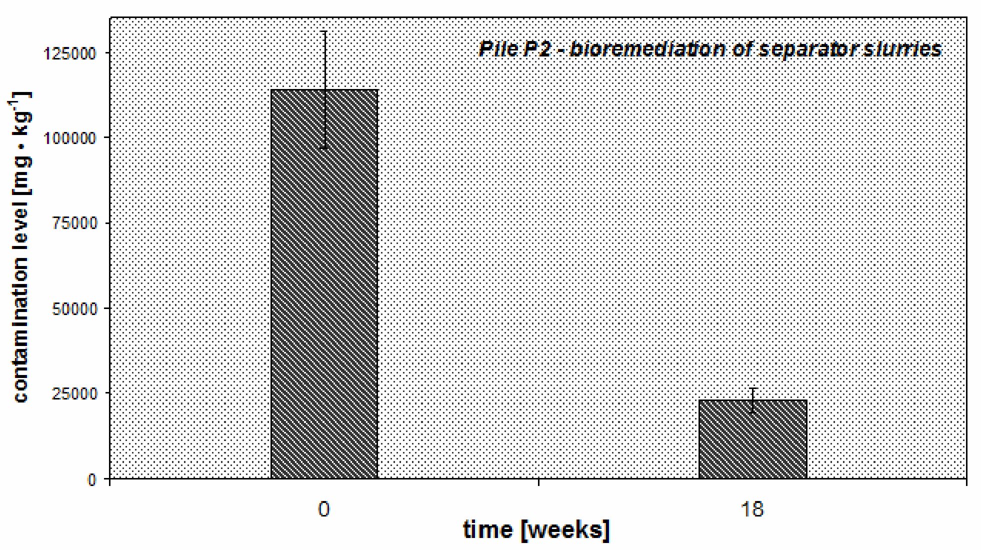

Fig. 5. Removal of separator slurries upon *ex situ* bioremediation performed in soil of pile P2

The results support the applicability of the employed method of *ex situ* bioremediation with intensified microbial augmentation. Taking into account high initial contamination levels, that is 24000 mg · kg^{-1} for P1 and 114000 mg · kg^{-1} for P2, as well as the relatively short time of the process (6 and 4.5 months, respectively), the resultant concentrations of

6650 mg · kg^{-1} and 22900 mg · kg^{-1} made it possible that the residual pollution could be eliminated within another season of bioremediation.

It should be noted that the reasonability of process bioaugmenting with exogenous bacteria has been questioned in several *in situ* and *ex situ* case studies [see 4, 5 and the references therein]. However, in the cited work it was typical to use mere commercially available bacterial formulations and not freshly grown and preadapted microorganisms, specialized at biodegrading specific set of xenobiotics.

Based on our experience [6, 11-13, and this work] as well as on other reports [1 and the references therein, 10, 14], bioaugmentation with properly-prepared bacterial cultures was crucial for initiating and stimulating soil bioremediation and made the process of pollutant biodegradation markedly shorter.

Finally, it should be stressed that microbiologically-based *ex situ* cleanup of soil is performed in an environmentally-safe manner. The site of recultivation is well insulated so that no leakage to the nearby ground and water occurs. Bacteria used for bioaugmentation are not genetically modified organisms but rather natural, environmental strains that specialize in utilization of organic xenobiotics as the sources of carbon. Their population tends to decay upon depletion of petroleum products and in the fully reclaimed ground a typical soil microflora is likely to recover.

Concluding remarks

1. Microorganisms responsible for degradation of oil-derived compounds in soil favor aerobic conditions that can be provided by mechanical mixing of ground in biopiles.
2. Microbial communities employed to bioaugment degradation of petroleum products prove strong metabolic potential against most of xenobiotics. This is achieved by biodiversity and synergic action of the multispecies consortia.
3. A bioaugmented *ex situ* soil bioremediation process performed under aerobic conditions may prove useful and efficient for cases of extremely high load of organic pollution in soil.

Acknowledgements

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BIOREMEDIACJA ZAOLEJONYCH GRUNTÓW METODĄ *EX SITU*: BIOAUGMENTACJA PROCESU Z WYKORZYSTANIEM SPECJALISTYCZNYCH KONSORCJÓW DROBNOUSTROJÓW

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Abstrakt: Procesy spontanicznego samooczyszczania środowiska gruntowo-wodnego, zanieczyszczonego związkami ropopochodnymi, przebiegają wolno i dlatego, w celu przyśpieszenia procesu rekultywacji skażonych obszarów, jest konieczne stosowanie zabiegów intensyfikacyjnych. W przypadku oczyszczania skażeń w gruncie uzyskuje się najkorzystniejsze efekty, stosując metodę bioremediacji *ex situ*, tzn. umieszczenia gruntu na wydzielonych stanowiskach oczyszczania. Możliwe jest wówczas efektywne i w pełni kontrolowane ustalanie parametrów procesowych. Jednym z zabiegów optymalizacyjnych jest bioaugmentacja procesu z wykorzystaniem specjalnie przygotowanych mikroorganizmów. W eksperymentalnej części pracy określono warunki optymalnego działania drobnoustrojów glebowych, wchodzących w skład konsorcjum stosowanego do wspomagania bioremediacji skażeń organicznych. Badania prowadzono w dwóch specjalnie skonstruowanych pryzmach testowych (A i B) o wysokości 120 cm i powierzchni 10 m^2, usypanych z zaolejonej ziemi (średnia zawartość zanieczyszczeń wynosiła 4300 $mg \cdot kg^{-1}$). Grunt został rozdrobniony, spulchniony ok. 10% domieszką kory, zasilony niezbędnymi substancjami mineralnymi oraz nawodniony tak, aby stworzyć optymalne warunki dla mikroorganizmów, a następnie zaszczepiony biopreparatem. W pryzmie (A) zapewniono wymianę gazową poprzez częste mechaniczne mieszanie, podczas gdy do pryzmy (B) jedynie doszczepiano świeże kultury drobnoustrojów. Zawartość skażeń monitorowano według standardowej procedury oznaczania wysokowrzących substancji organicznych w glebie. Liczebność mikroorganizmów glebowych określano standardową, płytkową metodą Kocha. W pryzmie (A) nastąpiło dynamiczne zmniejszenie koncentracji związków ropopochodnych (do 600 $mg \cdot kg^{-1}$ w ciągu 6 tygodni), natomiast w pryzmie (B) zaobserwowany spadek był niewielki (do 3240 $mg \cdot kg^{-1}$ po 13 tygodniach), pomimo dużej liczebności bakterii (ok. 10^8 $kom. \cdot g^{-1}$). Wynik ten wskazuje, że warunkiem ograniczającym bioremediację był brak swobodnej wymiany gazowej hamujący metabolizm drobnoustrojów. Metodę intensyfikowanej bioremediacji zastosowano w celu biodegradacji dużych stężeń uciążliwych zanieczyszczeń na przemysłowym stanowisku oczyszczania gruntu *ex situ*. Utworzono pryzmy technologiczne o wysokości 150 cm i objętości 180 m^3 (P1) i 90 m^3 (P2), w których ziemia została zmieszana, odpowiednio z osadami porafineryjnymi (24 000 $mg \cdot kg^{-1}$) oraz ze szlamami z separatorów olejowych (114 000 $mg \cdot kg^{-1}$). Penetrację tlenu zapewniono poprzez system biernej aeracji, utworzony z sieci rur drenarskich. Pryzmy wielokrotnie zraszano powierzchniowo zawiesiną biopreparatu wzbogaconego o drobnoustroje autochtoniczne w celu uzyskania maksymalnej szybkości procesu. Liczebność drobnoustrojów w glebie wzrosła, po zaszczepieniu, od 16 do 42 razy, osiągając wartość 3,6 $\cdot$ 10^6 $kom. \cdot g^{-1}$. Opisane zabiegi optymalizacyjne, stanowiące pierwszą fazę projektu bioremediacji, pozwoliły na uzyskanie znaczącego obniżenia poziomu zanieczyszczeń: ponad 3,5-krotnego na stanowisku P1 (do 6650 $mg \cdot kg^{-1}$ w ciągu 6 miesięcy) oraz ponad 5-krotnego na pryzmie P2 (do 22 900 $mg \cdot kg^{-1}$ w ciągu 4,5 miesiąca).

Słowa kluczowe: bioremediacja *ex situ*, zanieczyszczenia ropopochodne, szlamy, biorekultywacja ziemi, bioaugmentacja, drobnoustroje autochtoniczne, biopreparaty

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MUNICIPAL WASTE DUMPS AS THE MICROBIOLOGICAL THREAT TO THE NATURAL ENVIRONMENT

ZAGROŻENIA MIKROBIOLOGICZNE ŚRODOWISKA PRZYRODNICZEGO ZWIĄZANE Z FUNKCJONOWANIEM SKŁADOWISK ODPADÓW KOMUNALNYCH

Abstract: Municipal waste dumps are one of the biggest potential treats to the people's health. The collection of waste in the waste dump effects not only the soil, green areas, surface and groundwater degradation, but also in spreading the gas, dust and microbiological contamination in the atmosphere, which can cause serious threat to human health and life. This threat is mainly related to: microorganisms, odors, gas (biogas) emission, noise caused by the car transport, infrastructure and the waste dump's equipment, outflow of the soaking water from the municipal waste layer and its migration to the watercourses, possibility of the soil contamination by the chemicals and physical pollutants which leads to aggravation of the vegetative conditions. Microbiological analyses related to the municipal waste dumps' functionality shows the real danger from the waste dumps towards the environment and to people. Municipal waste dump can impact the nearby citizens' health by pollution of all natural environment's compartments, such as: air, water and soil not only with chemical but also with microbiological factors. Therefore it seems to be advisable to carry out the complex research on microorganisms' occurrence in different locations nearby the municipal waste dump. Health effects related to human exposure to environmental pollutants nearby the municipal waste dumps should be one of the priorities for the public health research. Knowledge of the actual state in the given area is crucial to assume if the local population is „especially exposed" to the potential harmful factors emitted by the waste dumps.

Keywords: bioaerosol, microorganisms, pollution, municipal waste landfill site

Economical and industrial development of the country as well as the improvement of the citizens' living standard has always been related with the increase of the sewage, municipal and industrial waste production. This in turn, increases the pollution and natural environment degradation, especially regarding air and soil environment [1-3].

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Municipal objects related with environment protection (compost plants, incinerators, treatment plants, waste dumps) are very often located in the direct neighborhood of agglomerations and the range of their impact towards the environment is wide - water, air, land surface, noise and the living organisms [4-7].

Municipal waste dumps are one of the biggest potential treats to the people's health and they are also esthetically inconvenient. The range of this threat depends mostly on the amount and character of the collected waste, type, shape and age of the waste dump, technology, security and land rehabilitation, topography and ground conditions as well as the current meteorological and natural conditions [4, 8].

Currently, the amount of waste in the municipal waste dumps are being limited by using modern technologies of recovery and neutralization of wastes [4, 8-11]. Even though the collection of waste in the waste dump is ecologically adverse, it will still be the main way of their disposal for many years. Unfortunately this system effects not only in the soil, green areas, surface and groundwater degradation, but also in spreading the gas, dust and microbiological contamination in the atmosphere, which can cause serious threat to human health and life [10, 12-15].

This threat is mainly related to: microorganisms, odors, gas (biogas) emission [16-20], noise caused by the car transport, infrastructure and the waste dump's equipment [16, 21, 22], outflow of the soaking water from the municipal waste layer and its migration to the watercourses [16, 17, 23, 24], possibility of the soil contamination by the chemicals (heavy metals, sulfur compounds etc.) and physical pollutants (dust) which leads to aggravation of the vegetative conditions [2, 25] and countryside deterioration [2, 22, 26].

The literature on the health effects of the environmental pollution from the waste dumps shows the probability of such problems as: congenital disorders, low birth weight, miscarriages, headaches, liver failures and neurological issues, skin changes, cancer (gastrointestinal cancer, lungs, urinary bladder cancer, leukemia), mood problems, respiratory system and sore mucous membranes symptoms [18, 19, 27].

Microbiological contamination of the atmospheric air

Atmospheric air is the natural environment's compartment of the basic importance to human, animals and plants. Its protection relies only on limitation of the pollutants' emission to the atmosphere by using „ecologically clean" technologies. Air pollution may be divided into two basic groups: natural (primary) and artificial (secondary). The artificial contamination sources are: industrial and domestic ones, which count for the high amount of the foreign matters in the atmosphere. Apart from the dusts and gases, the domestic pollution can also contain: fungi spores, bacteria and viruses in bioaerosols [28-30].

Bioaerosols are the two or three-phase structures which consist of the continuous phase (air) and the dispersed solid or liquid phase which contains microorganisms. The dispersed phase consists of small liquid parts or solid substances with pollen, fungi spores, bacteria, yeasts, viruses or dispersed microorganisms [31].

It needs to be stressed that the microbiological contamination spreads most quickly to long distances (sometimes several and even hundreds kilometers) from their sources to receptors by air [32-34]. Self-sedimentation, natural cells' death and the rainfall leaching is the most important factor which increases microorganisms' occurrence in the air [35, 36].

According to Barabasz et al [8], and Nowak et al [37] the amount of microorganisms in the air depends mostly on the quantity and quality of the dust particles in the area nearby the emission source. Therefore all factors increasing the dust pollution in the municipal waste dump, as: transport and unloading the waste, leveling with the mechanical equipment, compacting the waste layers and their covering favor the increase of the microorganisms' amount in the air [8, 32, 38, 39]. The amount of air-portable microorganisms changes significantly with environment and micro-environment changes. In general, the lowest microorganisms' concentration in the air can be found above the open sea, whereas in the urban and rural areas the concentration is much higher [40, 41].

The microbiological air pollution plays important role in occurrence of the allergic diseases, epidemics as well as in their control. It is the cause for contamination and spoilage of food, medicines, but also for the building materials' corrosion [18, 19, 23].

In normal conditions, low concentrations of bacterial and microfungal bioaerosol components do not cause any threat to human health, but the presence of the sewage treatment plants, municipal waste dumps or compost plants causes such high increase of the microorganisms' concentration in the air, that it can influence local citizens' health. Live and dead cells of the bioaerosol components (thermophilic fungi, Actinimycetales, bacteria) are the cause of very dangerous diseases like allergies or asthma [19, 22, 42, 43].

The health consequences of the air particles' inhalation depends on their size, chemical composition and microbiological properties, but also on their deposition in the respiratory system [44]. Size of bioaerosol particles can be different: generally from 0.02 to 200 μm [45]. The smallest bio-particles are viruses, which size varies from 0.02 to 0.3 μm. Bacteria and microscopic fungi cells are 0.3 to 100 μm in diameter, and pollen and other biological particles - from 10 μm up to even hundreds of micrometers [46]. Particles smaller than 5 μm in diameter, so called „breathing fractions" are capable of penetration of pulmonary alveolus and causing their allergic inflammation and other dangerous diseases. In most cases, these aerosols keep the microorganisms' cells in the air which causes deeper penetration into the respiratory system [44, 47].

Some non-pathogenic bacteria produce toxic metabolites. In this case, Gram-negative bacteria are the most dangerous ones, because of the endotoxins - parts of their cell wall. Its toxicity causes fever, shivers and respiratory system problems, headache, changes in number of leukocytes, breathing difficulties and even death [22, 26, 43].

Municipal waste dumps are the main sources of microorganisms' emission to the air [8, 35, 48-51]. Availability of the large amounts of organic matter in the waste is the source of nutrition for microorganisms. Long-term holding of the unstable waste biomass inhabited by the microorganisms and the necessity of pushing them creates the bioaerosols with high microorganisms' concentration in one air unit [34, 52]. Table 1 presents average amount of microorganisms on the municipal waste dumps „Barycz" near Krakow.

From the sanitary point of view the direct contact of people and animals with the deposited waste is the most dangerous for them, because the amount of microorganisms in the air surrounding the waste dump is decreasing with the distance up to several cells in 1 m^3. Their range of occurrence creates the border of the potential risk related to air penetration by the pathogenic microorganisms [47, 54-56].

Due to the lack of nutrients, microorganisms' presence in the bioaerosol is temporary and their type depends mostly on the specifics and characteristic of the environment [37]. Research carried out by Barabasz et al [57], Nielsen et al [38] nearby the municipal waste dumps showed that people are most exposed to the bioaerosols in summer during the collection, transport and gathering of the waste and it depends on the type of waste, way of collection and weather conditions.

Table 1

Average amount of microorganisms and the transgressions of standards on the municipal waste dumps „Barycz” [53]

Study sites	**Number of bacteria**		**Standards' transgressions**	**Number of Actino-mucetales**		**Standards' transgressions**	**Number of fungi**		**Standards' transgressions**
	min.	**max**		**min.**	**max**		**min.**	**max**	
1	78	50 000	4	0	1150	5	239	45 000	2
2	154	15 000	3	0	1117	6	44	30 000	1
3	0	558	-	0	889	3	39	26 000	1
4	39	722	-	0	78	4	39	26 500	1
5	8	12 700	2	0	239	11	50	30 000	1
6	25	14 000	3	0	28	5	33	28 000	1
7	21	267	-	0	145	3	56	31 800	2
8	6	7780	2	0	167	11	50	26 000	3
9	22	783	-	0	557	2	128	26 900	2
10	0	16 000	1	0	239	9	56	40 600	3
11	6	461	-	0	72	8	50	30 000	2
12	0	1506	1	0	78	7	28	33 000	2
13	11	308	-	0	111	2	39	29 000	2
14	4	1334	1	0	50	8	44	40 000	2
15	17	536	-	0	72	4	56	27 400	1
16	25	146	-	0	122	3	33	40 000	1
17	11	60 000	3	0	156	11	28	35 000	2
18	17	467	-	0	111	1	33	27 500	1
19	6	4000	1	0	45	3	28	775	-
20	11	11 000	4	0	54	8	39	867	-
21	0	594	-	0	29	5	67	23 872	2
Total			25			119			32

Bioaerosols, which occur in the municipal waste dumps can contain viruses, bacteria, fungi and their spores, protozoa cysts, parasites' eggs and the microorganisms' metabolites. In most cases these are saprophytic organisms, common in soil, water, on plants' surfaces and in food. Fungi spores and bacteria: *Pseudomonas, Staphylococcus, Enterobacter* and *Bacillus* are the most profuse organisms [5, 8, 34, 43, 49, 58].

Among the pathogens in the atmospheric air, the most numerous ones are: hemolytic staphylococci and coli-forms [52, 59, 60]. These microorganisms are thought to be the cause of diseases of waste dumps' employees and the nearby citizens [38, 47, 55]. The research among Dutch dustmen showed that the bioaerosol exposure was the probable cause of the severe gastrointestinal, respiratory and skin symptoms [61-63].

It needs to be considered that generally infectious bacteria are rare in the air, but they can float for a long time without losing their virulence, especially when the air is humid. Breathing such air can cause infections, dangerous diseases and sometimes epidemics [8, 61, 64]. This results from the opportunistic pathogens' presence, which are incapable of the health human infection; the infection symptoms occur in the case of immunity failures [65, 66].

Pathogenicity and virulence of the microorganisms in the air nearby the municipal waste dumps lasts for different periods of time. The time of the pathogenic microorganisms' occurrence in the air depends on the microbes, types of diseases but also on the bio-meteorological and bio-climatic state (temperature, direction and speed of wind, humidity, pressure, sun radiance and the atmospheric precipitation as well as electric phenomena) [32, 36, 40, 43, 67]. The relationship of microorganisms' emission and the atmospheric conditions causes the harmful range to be different in time and space [12, 34, 40, 68, 69].

From the epidemiological point of view the occurrence of fungal bioaerosols in the area and nearby municipal waste dumps is particularly dangerous. These bioaerosole are much more resistant to the environmental and even mechanical stress than the bacterial bioaerosols [45, 46]. Different kinds of fungi which grow on the collected waste discharge large quantities of spores into the air and produce very dangerous bioaerosols, which are often qualified to be the threat to the human natural environment [52, 56, 70].

The research by Adamiak et al [71], Barabasz et al [57] and Uflig [56] showed that the waste dumps emit the spores of many fungi, among which the most common are: *Alternaria, Aspergillus, Cladosporium, Fusarium, Penicillium, Mucor, Rhizopus, Trichoderma*. They have also confirmed that the concentration of the fungal pollution from the waste dumps in the air is mostly consistent with the fungi species which develop on the waste.

Fungal spores, which create the bioaerosols may be the cause for allergies, megrim, epidermic and organic mycoses as well as allergic pneumonias, allergic rhinitis and mycotoxicoses. High concentration of *Alternaria* spores in summer is thought to be the cause of severe asthma symptoms. Gravesen et al [72] assumed that *Cladosporium*, *Alternaria* and *Aspergillus* are the species which cause the most difficult children allergies. As the other authors showed, these are the species which dominate in the atmospheric air [8, 68, 70].

Moreover the additional threat are the species capable of mycotoxins' production - metabolites of the total harmful influence on all living organisms [73-77]. Many mycotoxins can accumulate in the animal and human organisms, showing carcinogenic, teratogenic, tremorgenic, neuro- and nefrotoxic influence [74, 76, 78]. Aflatoxins are the most harmful towards humans and animals. These are the most carcinogenic toxins produced by *Aspergillus flavus* Link, which occurs profusely in the collected municipal waste [8, 56].

Flannigan [79] showed that the fungal spores can contain mycotoxins' concentration from 1.0 to 650 μg in 1 g of the spores. This is the reason why inhaling of the high concentration of spores, hyphae fragments and other particles can have such harmful influence on human's health. Research by Creasian et al [80] on animals showed that toxins transportation by the respiratory system is much more efficient than oral or peritoneal transport. The presence of toxins-producing spores in the air causes the risk of food contamination, which can be very harmful to human's and animal's health [76, 81, 82].

According to Uflig [56] and Traczewska et al [29] fungi can be the most credible index for evaluation of municipal waste dumps' influence on the natural environment. On the basis of the carried out research they found that the number of fungi during the whole testing period was such high that it enabled evaluation of the mycological contamination. Therefore it is crucial for the modern municipal waste dump exploitation to implement the multiple protective barriers' system, which can decrease the negative influence on the natural environment.

The influence of municipal waste dumps on agrocenoses needs to be mentioned, too. The direct neighborhood of the waste dumps is inhabited by people however the plants are also being cultivated there for animals' feed and for human needs. Microbiological contamination caused by the waste dumps can spread along with the air to the adjacent areas and it can pollute the emblements and can influence the system: cultivated plant - agrophag, increasing the plants' infection. Until now, not many analyses have been carried out on this case. Ropek and Fraczek [83] tested the influence of the municipal waste dump on the bean plants. The municipal waste dump decreased the well-being of bean plants in the neighborhood. Aphid (*Aphis fabae*) and fungal diseases were the most common in the bean population in the direct neighborhood of the waste dump. Woodlots were very effective in decreasing the negative influence of the waste dump on the bean plants.

Influence of the municipal waste dumps on the soil environment

Among the natural environment, soil is the specific element, because of different types of collected pollutants, including microbiological ones, originating from the municipal waste dump. This is due to the recent building technology, which mostly relied on retrenchments of the area without any actions to prepare the ground for the waste dump and protection of the nearby areas. Therefore, in most cases the waste dumps became the potential sources of long-term, various pollutions of the ground. This depends mostly on: amount of waste dumps (legal and illegal ones), their area, construction, type and technical state of the coating, composition and way of collecting waste and the method of waste dumps' exploitation.

Huge diversity of the waste dumps' pollutants evidences the fact that they are very dangerous source of the soil contamination. These potential pollutants are: organic compounds including petrochemicals, inorganic compounds including heavy metals and large amounts of microorganisms (including pathogens) [3, 37, 84]. Incorrect waste collection is one of the factors causing the persistent chemical soil degradation [85, 86].

Soil is the natural environment for different physiological groups of microorganisms, such as: viruses, bacteria, Actinomycetales and fungi [87, 88]. Soil micro-flora is the biocenosis component which almost immediately grows and reacts for the environment changes. It depends on the diversity of microorganisms' biochemical functions and uncommonly fast physiological processes. There is also the significant relationship between the soil parameters, soil microorganisms and plants [31, 89, 90]. Number, location and soil microorganisms' activity depends among others on: soil structure, water content, temperature, pH reaction, presence of toxic chemicals and the nutrients' content [91, 92].

Therefore soil microorganisms are the factor which together with the plants' association decides on the direction and character of the biochemical processes as well as all the basic transformations related to the biological activity and with physicochemical properties of the soils.

Alcaligenes, Arthobacter, Bacillus, Enterobacter, Flavobacterium, Microccocus bacteria and viruses are the most common soil microorganisms. Also nitrogen fixing bacteria and bacteria which transform the mineral and organic nitrogen: *Azotobacter, Arthrobacter, Nitrosomonas, Nitrobacter, Pseudomonas, Serratia* and *Clostridium* are very important organisms in soil. Actinomycetales are the second most common group of microorganisms in soil. About 90% of all Actinomycetales isolated from soil are *Streptomyces* [31, 93]. Fungi are also widespread in soil environment [75, 76, 87, 88].

Apart from the naturally present microorganisms, the incoming microbes can be found, among others the ones coming from the municipal objects. Soil nearby the waste dumps can become the place of temporary or permanent occurrence of parasites' eggs, pathogenic bacteria, pathogenic fungi and their spores. Microbiological contamination of soils nearby the municipal waste dumps is mostly caused by the bioaerosols and microorganisms' spreading by the wild birds, rodents, flies and other insects [37, 94]. Soils may also become polluted during the delivery and unloading waste, incorrect waste dump exploitation and incorrect water export from the object [39, 85, 86].

The most important pathogens nearby the waste dumps are: *Salmonella* which causes typhoid fever, paratyphoid fevers and salmonelloses, *Shigella* which causes dysentery, *Campylobacter* and *Clostridium* bacteria and also bacteria which cause tuberculosis, tularemia and enteroviruses: hepatitis, poliomyelitis, meningitis, myocarditis, as well as pathogenic protozoa which cause amoebiasis, lambliosis and cryptosporidiosis. Moreover, eggs of the intestinal parasites: *Ascaris* sp., *Trichuris* sp., and *Toxocara* sp. can be found there. No doubt that *Salmonella* and *Shigella* play the special role and may be treated as the model organisms for other pathogenic bacteria [3, 85]. Very often presence of *Pseudomonas aeruginosa* Schroeter, the cause of very dangerous in-hospital purulent respiratory and urinary system infections, is the sanitary state index [95, 96].

Filtration and sorption processes as well as dying limits the vertical bacteria migration in the aeration zone. Table 2 presents main factors which influence microorganisms' retention in soil.

Table 2

Main factors influencing microorganisms' retention in the ground [3]

Factor	Characteristics
Ground type	More effective retention of microorganisms in the fine-grained than in the coarse grounds; increased sorption properties of the grounds containing loam minerals and ferric oxides
pH	Increased microorganisms' sorption together with pH decrease
Cations	Increased sorption with the cations' presence; desorption of microorganisms by the precipitation water
Dissolved organic substances	Decrease of microorganisms' sorption in the grounds with presence of humic and fulvic acids
Type of microorganisms	Significant influence of type of microorganisms on the sorption process
Speed of water flow	Decrease of microorganisms' sorption together with increase of the water infiltration speed

In the soil environment in the municipal waste dump zone, microorganisms occur temporarily due to the lack of the growth promoting conditions and because their retention time is different. The pathogenic bacteria survival time ranges between a few hours to a few months, whereas their number decreases to the amount which does not threat people's health from two to three months [97]. Literature gives extremely different data regarding the survival of intestinal microorganisms in soils, especially regarding *Salmonella* [98]. For example *Salmonella typhi* will survive for 42 days in soils which retain water eg: in peats and loams, whereas in sands it will survive only for 4 to 7 days. Stroczynska-Sikora et al

[99] showed that *Salmonella* and *Escherichia* survival rate in soils depends on the soil type and ranges between 15-81 days, and research by Olanczuk-Neyman et al [100] proved that *Salmonella* survives in soil for 28-56 days. Microorganisms' spores last for much longer in soil. One of the pathogenic bacteria which can produce spores and last for several and more years in soil are aerobic *Bacillus anthracis* Cohn and anaerobic *Clostridium tetani* Flügge and *Clostridium botulinum* van Ermengen. Obviously, the more pathogenic bacteria in soil, the higher possibility of human and animal infections [85, 101, 102].

Table 3

Dominant fungi species isolated from the soil nearby the municipal waste dump in Tarnow [103]

No	Fungi species	Frequency of occurrence
1	***Alternaria alternata***, (Fr.) Keissl	+++
2	*Alternaria chartarum,* Preuss	+++
3	*Aspergillus candidus,* Link	++
4	***Aspergillus flavus***, Link	+++
5	***Aspergillus fumigatus***, *Fresenius*	+++
6	*Aspergillus niger,* van Thieghen	++++
7	***Aspergillus ochraceus***, Wilh.	+++
8	***Cladosporium herbarium***, Link	+++
9	*Fusarium culmorum,* Saccardo	++
10	***Fusarium graminearum***, Schwabe	+++
11	*Fusarium moniliforme,* Sheldon	++
12	***Fusarium nivale***, Cesati	+++
13	*Fusarium oxysporum,* Schlecht	++
14	*Fusarium sporotrichioides,* Sherb.	+++
15	*Humicola* spp.	+++
16	*Mortierella* spp.	+++
17	*Mucor* spp.	++++
18	***Penicillium chrysogenum***, Thom	++
19	*Penicillium cyclopium*, Westling	+++
20	*Penicillium digitatum,* Saccardo	++
21	***Penicillium frequentans***, Westling	+++
22	*Penicillium fumiculosum,* Thom	++
23	*Penicillium lanosum,* Westling	+++
24	*Penicillium melagrinum,* Biourge	++
25	*Penicillium oxalicum,* Thom	+++
26	*Penicillium roseopurpureum,* Dierckx	++
27	*Rhizopus* spp.	++++
28	*Trichothecium roseum,* Link	++
29	*Verticillium candelabrum,* Bonorden	++++
30	*Zygorrhynchus heterogamus,* Vuill	+++

Key: ++++ - very numerous occurrence, +++ - quite numerous occurrence, ++ - numerous occurrence.
Species acknowledged to be the potentially toxic were bolded

Moreover, areas around the waste dumps may be the place for temporary or permanent occurrence of potentially pathogenic fungi and their spores, which become the cause of allergies and mycoses after being inhaled with the dust from the land surface [56]. Significant part of the fungi population is the potentially toxic species, capable of mycotoxins' synthesis which are harmful to human, plants and animals [37, 42, 70, 75].

Table 3 presents dominant fungi species composition in soil nearby the municipal waste dump in Tarnow.

Mycotoxins' accumulation in some cases can cause „soil fatigue", and rapid decrease of microorganisms' population. These changes occur as the result of the failure of the homeostatic ecosystem which regulates the quantity of each population [76, 87, 104].

Considering the sanitary contamination of soils caused by the municipal waste dumps, the relationship between the air pollution and the quality and quantity of the soil microorganisms is easy to notice. The pollutants' emission from the waste dump can cause the contamination of the whole arable layer in this area [37, 48]. The most polluted soils can be found in the closest neighborhood of the waste dumps, especially in the area of the limited exploitation which should overtake the most of the pollutants and separate the nearby areas from its influence [6, 105]. Usually bacteriological contamination and suspensions are transported to relatively short distances from the waste dumps. The range of their infiltration depends on their survival rates in the aquifer layer and the distance of the groundwater flow. It is assumed that they can reach from several to 100 meters from the waste dump [106].

Research by Siuta et al [107] showed that the increased microorganisms' concentration in the soil nearby the municipal waste dumps occurs only in the closest neighborhood up to several dozens of meters and only in the surface layer. Similar conclusions were drawn by Quant and Sobocinski [108] proving that the area of the tested waste dump's influence does not exceed 50 m. However according to Adamiak et al [71] regarding people's health, microbiological contamination up to 2-3 kilometers from the waste dump's borders can be harmful. Analyses carried out by Nowak et al [37] resulted in the conclusion that the differentiation can be noticed around the municipal waste dump. Different physiological groups of microorganisms are located irregularly around the object and the quantitative proportions between main groups of microorganisms are changed.

Quantity and quality of pollutants influence their durability. If the pollution is not very high, the biocenosis returns to the initial state due to its homeostasis. Microorganisms introduced to the foreign soil are incapable of reproduction and their number decreases [96].

Bacteria are the most numerous microorganisms in the area of municipal waste dumps, Actinomycetales are the second group and the number of fungi is the lowest. The surface layers of the soil contain the highest number of bacteria. With the depth the number of bacteria decreases and their content changes as well. Migration of contaminants into the soil depends on the surface layer's state. It has been proved that in the polluted but not plowed soil, high amounts of bacteria occur only in the layer from 0 to 25 cm. In the arable soil due to the diffusion to the deeper layers, high amounts of bacteria occur even 2 meters into the ground [37, 96].

Insecticidal fungi are very important group, common in the soil environment of natural biocenoses as well as in agrocenoses transformed by human [109]. These microorganisms can significantly decrease populations of many insects and decrease losses caused by these pests. The research carried out nearby the municipal waste dump in Tarnow [110] showed that this group of microorganisms is very common in the soil. The most often isolated insecticidous fungi was *Metarhizium anisopliae*. The presence of municipal waste dump did not influence on the occurrence of the insecticidous fungi in the direct neighborhood of the active section.

Microbiological threats towards the water environment

The waste collected in the waste dumps can be the source of different soil, groundwater and surface water pollutants. Water quality depends mostly on the waste content, technology of their collection and the isolation of the object. Water environments nearby the waste dumps are liable to the pollutants transported by the soaking water. Incorrect undercoat of the waste dumps which enables the contamination to infiltrate even to long distances and depths is the most dangerous to the environment [111, 112].

Influence of the municipal waste dumps on the groundwater and surface water may be various: from the spot pollutions, eg soaking water, surface flows which carry the pollutants to short distances, stream and aquifer layers drainage and waste drainage during the surface waters spates. These factors can occur individually or in complexes [102, 113].

Until now, water nearby the municipal waste dumps was tested only chemically without microbiological aspects [114, 115].

It needs to be stressed that the microbiological contamination is the constant threat to the groundwater quality. Pollution of these waters depends on the waste content and the load of the pollutants, technical aspects of soaking water capture, isolation of the ground (resulting from the natural ground structure and the technical infrastructure) and the environments' ability to self-purification. According to Marchwinska and Budka [116] constant threat to the environment is related to the fact that plastics used as the isolating membranes are being damaged in time and the infiltration of the pollutants is inevitable.

Pollutants' migration in the groundwater is very complex and not exactly known due to the large diversity of its processes. The evaluation is difficult due to various properties of the pollutants [117].

As far as ground water purification is concerned, the basic factors are: mechanical filtration, decomposition and biological assimilation, sorption, ions' exchange and dilution. However, water needs at least several years to return to its previous state [117, 118]. In microbiologists' opinion, groundwater is the part which can be used by microorganisms in the under-surface environments, which is the whole water below the land surface [119].

In consequence, groundwater is the suitable environment for population of microorganisms with the wide metabolic spectrum. Ecologically, homeostasis disturbance caused by pollutants' introduction, leads to the activation of biological regulation mechanism. Qualitative and quantitative domination is being taken over different microorganisms' species, which by different biological cycles transform the pollutants into the stable products. The homeostasis in the groundwater environment depends on the pollutants' concentration below the threshold biocenosis regulation ability. Destruction of the biotic components of the system totally inhibits the self-regulation processes [119].

The groundwater in case of the direct contact with the municipal waste can be polluted by the microorganisms. The sanitary contamination is influenced by the microorganisms' resistance and their ability to stay active in various physico-chemical environment conditions. Microbiological pollution can influence the quality of the surface water, eg: by the eutrophication and can be dangerous to people's health by spreading pathogenic microorganisms. The possibility of direct contact of the surface water and the soaking water is particularly harmful to human's and animals' health.

Pathogens and euthophicators in the pollutants are capable of changing and transformation in rivers and water reservoirs. The increasing of this phenomenon can cause deep transformation of flora and fauna and the chemical properties of water, causing the total degradation from the sanitary, esthetic and economic point of view. Polluted water can migrate outside the waste dump, causing groundwater contamination. This is the most serious problem related to the municipal waste dump collection [120-122].

Municipal waste dumps are very often called the solid, biochemical reactors. Water-soluble components of the waste and products of the physical and biochemical processes are emitted outside the waste dumps as the soaking water. They are being produced during the whole exploitation period and often many years after closing them. During the exploitation of the waste dumps the production of the soaking water is unavoidable. Their production can only be limited by thickening the waste or using the appropriate covering layers. Their quality is mainly influenced by: content of the collected waste, age and size of the waste dumps and the waste collection technique [84, 85, 123, 124].

Last years' events in Poland (heavy rainfalls, floods, heavy snows) increase the threat of the soaking water to the environment. The lack of the sewage treatment plants in the area of the municipal objects and high transport prices into the communal sewage treatment plants is the still unsolved problem [125]. The soaking water occurs when the water capacity of the waste dump is weakened. It is the result of water infiltration through the wastes and washing away of the biochemical decomposition of the organic substances and dissolved mineral compounds products.

The waste dump's soaking water which occurs in the primary period of the waste collection (about 5 years) are mainly acidic (pH 3.7÷6.4). It is due to the presence of the carboxylic acids and hydrocarbonic ions from the microbiological decomposition of the organic matter. The soaking water apart from different chemical compounds contains large amounts of microorganisms, including pathogens. Microbiological contamination can last for a few and even several years and the toxic substances can last for several dozens of years [118].

Water environment (surface and groundwater) nearby the municipal waste dumps are exposed to the pollutants transported mainly by the soaking water [112].

Conclusions

Atmospheric air is especially exposed to the microbiological pollution. Pollutants transported with the air are in turn dangerous to the soil and water environment. It is important to remember about the waste dumps' soaking water which can be the source of the soil, water and the air pollution. Microbiological analyses related to the municipal waste dumps' functionality shows the real danger from the waste dumps towards the environment and to people. Therefore it is very important to monitor the waste dumps, to control the pollutants' emission and to implement the modern technologies of the waste management, such as: incinerations, recycling, dangerous waste collection etc.

The environment protection should start from the waste production prevention, reduction of their amount and transformation of the dangerous waste into less harmful ones. The basic waste management rule is to prevent the waste production, because even the most modern and the most technologically advanced waste dumps are still described as the potential time bombs dangerous to human health and the environment [116].

There are many regulations on the waste dumps influence on the environment. These regulations, especially recently are often drastically changed, resulting from the adjusting Polish procedures to European Union regulations. Part of the problems, especially these related to the odours and microbiological contamination emission still is not legally regulated [126, 127].

Most research on the waste dumps concentrates on the chemical changes in the soil, groundwater and surface water. There is not much information on the microbiological contamination of these environments. The reason for this is the lack of common and uniform methods of evaluation of municipal waste dumps' influence on the environment's microbiological parameters.

According to Starzewska-Sikorska and Jarosz [128] it is necessary to improve the evaluation system of the environmental health dangers. It is assumed that about 25÷33% of the general number of diseases is caused by the environment pollution factors.

The assessment of the municipal waste dumps on health is very complex which needs the thorough analysis of many environmental and heath conditions as well as consideration of the relationship between the health state and the environment's quality. Municipal waste dump can impact the nearby citizens' health by pollution of all natural environment's components, such as: air, water and soil not only with chemical but also with microbiological factors. Therefore it seems to be advisable to carry out the complex research of microorganisms' occurrence in different locations nearby the municipal waste dump.

Health effects related to human exposure to environmental pollutants nearby the municipal waste dumps should be one of the priorities for the public health research. Knowledge of the actual state in the given area is crucial to assume if the local population is „especially exposed" to the potential harmful factors emitted by the waste dumps. Moreover the concerns related to the belief that the collected wastes influence human health need to be noticed.

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ZAGROŻENIA MIKROBIOLOGICZNE ŚRODOWISKA PRZYRODNICZEGO ZWIĄZANE Z FUNKCJONOWANIEM SKŁADOWISK ODPADÓW KOMUNALNYCH

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Abstrakt: Składowiska odpadów komunalnych są jednym z ważniejszych potencjalnych źródeł zagrożeń dla zdrowia człowieka. Efektem gromadzenia odpadów na składowiskach jest degradacja otaczających gleb, wód powierzchniowych i podziemnych, zieleni w pobliżu składowisk odpadów, a także rozprzestrzenianie się zanieczyszczeń gazowych, pyłowych i mikrobiologicznych w atmosferze, które mogą stanowić poważne zagrożenie dla zdrowia i życia człowieka. Związane jest to przede wszystkim z: emisją mikroorganizmów, odorów, gazów - biogaz, emisją hałasu powodowanego przez transport samochodowy i sprzęt obsługujący składowisko; ponadto wypływem odcieków ze złóż odpadów komunalnych i ich migracją do cieków wodnych. Łączy się to z możliwością skażenia okolicznych gleb zanieczyszczeniami chemicznymi, fizycznymi prowadzącymi m.in. do pogorszenia warunków wegetacyjnych roślin uprawnych, degradacji krajobrazu oraz emisją egzotoksyn. Analiza badań mikrobiologicznych związanych z funkcjonowaniem składowisk odpadów komunalnych wskazuje na istnienie realnego zagrożenia ze strony składowisk odpadów komunalnych dla środowiska przyrodniczego oraz dla samego człowieka. Oddziaływanie składowiska odpadów na zdrowie ludzi zamieszkujących przyległe tereny może następować poprzez zanieczyszczenia wszystkich komponentów środowiska naturalnego, tj. powietrza, wody i gleby nie tylko czynnikami chemicznymi, ale także mikrobiologicznymi. Dlatego wydaje się celowe prowadzenie kompleksowych badań dotyczących występowania drobnoustrojów w różnych środowiskach w rejonie składowisk odpadów komunalnych. Skutki zdrowotne związane z narażeniem ludzi na zanieczyszczenia środowiskowe w pobliżu składowisk odpadów komunalnych powinny być jednym z priorytetów w zakresie zdrowia publicznego. Znajomość stanu faktycznego na danym terenie jest bardzo istotna, aby stwierdzić, czy populacja lokalna jest „szczególnie narażona” na potencjalne czynniki szkodliwe emitowane przez składowiska.

Słowa kluczowe: bioaerozol, mikroorganizmy, zanieczyszczenia, składowisko odpadów komunalnych

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INFLUENCE OF MOISTURE ON HEAT CONDUCTIVITY COEFFICIENT OF AERATED CONCRETE

WPŁYW WILGOTNOŚCI NA WSPÓŁCZYNNIK PRZEWODNICTWA CIEPLNEGO BETONU KOMÓRKOWEGO

Abstract: The article presents the experiment which determines moisture influence on aerated concrete heat conductivity parameter. Applied experimental setup consisted of two climatic chambers generating cold and hot temperatures on two sides of the sample which was equipped with necessary sensors to measure temperature, heat-flux and moisture. For moisture determinations the Time Domain Reflectometry technique was applied, which is currently developed method for moisture determinations of building materials and barriers. The result of the experiment was determination of heat conductivity coefficient of aerated concrete as a parameter which may be used in heat and moisture transport modeling in building barriers.

Keywords: aerated concrete, heat conductivity coefficient, heat-flux, moisture, Time Domain Reflectometry

In moistened buildings fast destruction of building materials and the equipment occurs. It is mainly caused by biological and chemical corrosion and finally it runs in the increased exploitation costs. Moisture negatively influences state of mind and health of the inhabitants and is currently treated as an important problem from the environmental engineering point of view.

High water content in building envelopes causes construction degradation - metal corrosion, wooden and organic materials decay and also material structure destruction due to multiple processes of thawing and freezing during the winter season.

From the point of view of indoor air protection, water migrating in building barriers is an especially disadvantageous factor. It decreases the quality of indoor air, leading to allergic microorganisms development [1].

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Time of drying of wet elements mostly depends on barrier construction and the ambient air conditions. Generally it does not exceed 2 or 3 years and during this period moisture is a reason of higher heating energy loses due to increased heat conductivity of external building barriers.

In the walls made of red brick water can rise for about 2.5 m or even more from the ground level. Aerated concrete walls are even more susceptible to water movement.

Water contained in building barriers essentially influences heat conduction process. It changes heat parameters of the particular construction materials - heat conductivity parameter λ and thus heat properties of the whole construction and the consequence of the described phenomenon is the decrease of indoor air temperature.

Too low indoor temperatures significantly reduce thermal comfort and are the reason of too intense organisms cooling. Consequently it runs to worse work and psychophysical efficiency.

There are still a lot of unsolved problems which may lead to improve indoor environment quality. Many of them are the problems connected with monitoring and valuation of moisture transport processes in the external building envelopes and their influence on heat parameters. Some of them we touch in this paper.

Materials and methods

Aerated concrete is one of the most popular and attractive building materials. It is especially caused by its high heat insulation together with good strength parameters. That is why it is often used as a building material for both external and the internal walls.

To improve heat characteristics of the buildings, λ coefficient [W/(m·K)] value of each material should be minimized, what should limit heat flow between both boundaries of the external envelopes, λ parameter describes heat conductivity through the material. Water, being a good heat carrier, essentially increases heat conductivity of the aerated concrete decreasing its thermal properties [2, 3].

Capillary-porous structure of building materials makes them prone to water influence and thus a detailed analysis of λ value depending on moisture is reasonable.

The aim of the research was to measure heat conductivity coefficient of the aerated concrete of the following apparent densities - 400 and 600 kg/m^3 in dry state but also in various moisture states.

For the examinations the following equipment and materials were used:

- Climatic chambers system for simulation of environmental conditions at the opposite sides of the sample (Fig. 1) [4],
- TDR equipment for both reflectometric moisture determination in building materials and the temperature - with analog temperature sensors placed in the TDR LP/mts probes and digital temperature sensors - Dallas type,
- Peltier plates - used as heat flux probes,
- Multimeter for voltage readouts from the Peltier plates,
- Aerated concrete samples of the following apparent densities - 400 and 600 kg/m^3 (Figures 2 and 3).

To estimate heat conductivity coefficient depending on moisture two samples of aerated concrete were prepared (one with the density of 400 and the second one - 600 kg/m^3) with the following dimensions: 12×24×30 cm. Before the measurement, the samples were dried out in the temperature of 105°C for the first, dry stage of the experiment.

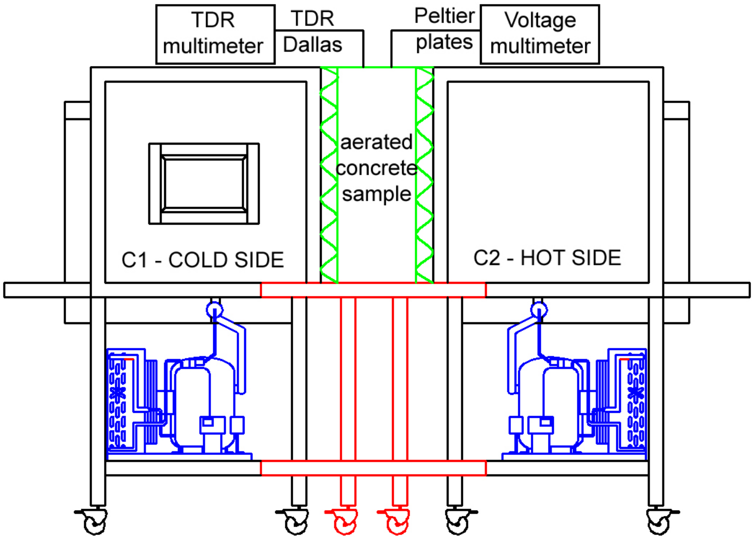

Fig. 1. Measuring set for λ coefficient determination depending on water content [4]

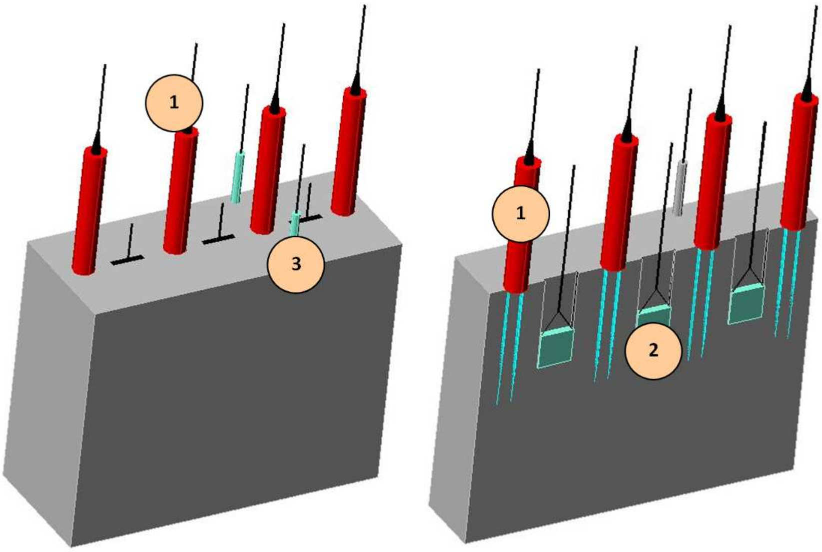

Fig. 2. Aerated concrete sample used for heat conductivity coefficient determination (left) and its cross-section (right). 1 - TDR probe, 2 - Peltier plate (heat-flux sensors), 3 - Dallas - digital temperature sensor

Fig. 3. Samples of aerated concrete used for heat conductivity determination

The samples were equipped with the suitable sensors - TDR probes (for moisture determination), Dallas temperature sensors and the Peltier plates as heat-flux sensors (Figs 2 and 3). The TDR probes and the Peltier plates were placed in a common plane forming isotherm and a constant water content line. All above described assumptions and attempts were applied to provide the comparable conditions for heat-flux and moisture determinations and eliminate other factors influencing measurement errors.

External faces of samples prepared, were thermally insulated using polystyrene (Fig. 3) to isolate them from the outside environment influence. They were put on a special table between climatic chambers and equipped with measuring probes (TDR, temperature and heat flux sensors). Open holes were filled with polyurethane foam to eliminate any heat leaks out of the system.

Then the experimental setup (multimeters and heat-cooling system) was run - left chamber (C1 in Fig. 1) generated low temperatures and right (C2) high temperatures. Temperatures in the chambers were sequentially changed to compare the temperature gradient influence on the heat flux density readouts. Described analysis allowed to estimate heat conductivity coefficient of aerated concrete.

In case of the heat conductivity λ coefficient measurements in dry aerated concrete, application of the TDR device was not necessary (moisture was equal zero). In presented experiment it was only used to check if everything runs correctly and no unpredictable moisture rises are observed. Also, the TDR probes are equipped with temperature sensors which were used to monitor temperature distribution inside the samples.

After dry stage, the samples were moistened with water and equipped again with necessary devices and sensors. Using the TDR probes and heat flux sensors we managed to determine the influence of moisture on heat fluxes read by Peltier plates and thus its influence on heat conductivity (λ) coefficient.

Results and discussion

With the described experiment heat conductivity coefficient was determined for blocks of aerated concrete of two different densities (400 and 600 kg/m^3).

Calculations were made using Fourier formula:

$$q = -\lambda \mathrm{grad} T \tag{1}$$

where: q - heat flux determined using Peltier sensor $[W/m^2]$; λ - heat conductivity coefficient (determined parameter) [W/mK]; gradT - temperature gradient between measuring points [K/m].

Table 1
Dependence of heat flux measured using Peltier sensor on temperature gradient on both sides of the sample of aerated concrete sample with density of 400 kg/m^3

ΔT	**q1**	**q2**	**q3**	**λ1**	**λ2**	**λ3**
[K]	**$[W/m^2]$**			**[W/mK]**		
9.8	21.00	18.71	16.55	0.107	0.095	0.084
9.9	20.96	18.43	16.45	0.106	0.093	0.083
9.8	20.53	18.08	16.16	0.105	0.092	0.082
9.9	20.99	18.45	16.56	0.106	0.093	0.084
15.5	32.85	32.83	24.96	0.106	0.106	0.081
15.8	34.02	33.91	25.93	0.108	0.107	0.082
15.8	34.75	34.54	26.35	0.110	0.109	0.083
15	34.88	34.54	24.74	0.116	0.115	0.082
9.7	20.64	20.63	16.70	0.106	0.106	0.086
7.1	14.59	14.54	12.38	0.103	0.102	0.087
6.1	13.40	12.98	11.44	0.110	0.106	0.094
4.6	10.03	10.02	8.92	0.109	0.109	0.097
Corr. coef. (r)	0.996	0.985	0.998			
λ [W/m·K], series averages				0.108	0.103	0.085
λ [W/m·K], average value				0.099		
standard deviation s [%]				0.012		
variability coefficient ν [%]				12.26		

Table 2
Dependance of heat flux determined with Peltier sensor depending on temperature gradient on the opposite sides of aerated concrete sample with the density of 600 kg/m^3

ΔT	**q1**	**q2**	**q3**	**λ1**	**λ2**	**λ3**
[K]	**$[W/m^2]$**			**[W/mK]**		
20.4	38.55	40.20	38.71	20.400	0.151	0.158
20.45	39.58	41.27	39.42	20.450	0.155	0.161
20.2	38.69	40.42	38.90	20.200	0.153	0.160
18.5	34.77	36.42	34.80	18.525	0.150	0.157
17.8	34.03	35.57	33.89	17.8	0.153	0.160
17.1	33.58	35.04	33.29	17.125	0.157	0.164
16.7	32.93	34.39	32.68	16.65	0.158	0.165
Corr. coef. (r)	0.981	0.983	0.987			
λ [W/m·K], series average				0.154	0.161	0.154
λ [W/m·K], average value				0.156		
Standard deviation s [%]				0.004		
Variability coefficient ν [%]				2.59		

For the aerated concrete with apparent density 400 kg/m^3, λ coefficient value for the three independent sensors readouts were 0.108, 0.103 and 0.085 W/m·K (Table 1). Average value of that parameter from all sensors is 0.099 W/m·K. Correlation coefficients are the following for the suitable series: 0.996, 0.985 and 0.998 which proves good homogeneity of examined aerated concrete (standard deviation s = 0.012%, variability coefficient = = 12.26%). Literature data [3, 5] indicate that λ coefficient for this material can reach values in dry states about 0.1 W/m·K. According to the material producer website [6] λ parameter for aerated concrete 400 kg/m^3 should be 0.11 W/m·K. Results obtained show that the applied measurement method is suitable and gives satisfactory results.

Aerated concrete with the density of 600 kg/m^3 showed average value of λ coefficient equal to 0.156 W/m·K for each series (s = 0.004%, ν = 2.59%). According to the producer data - 0.16 W/m·K. Data presented in Table 1 for aerated concrete 400 indicate the value of λ coefficient about 0.10 W/m·K and for 600 kg/m^3 - about 0.17 W/m·K. Low values of standard deviation and variability coefficient confirms small measurement error, visible especially for aerated concrete with apparent density 600 kg/m^3.

In case of moist samples under a constant process of monitored desorption the aim of the experiment was to estimate the value of conductivity coefficient in the relation to volumetric water content θ. It was important for the whole experiment to use the TDR (*Time Domain Reflectometry*) probes to determine the aerated concrete moisture [7, 8]. With the measurement setup, the following values were obtained in the single series of experiment: water content, temperature gradient and heat flux.

Table 3

Heat conductivity value of aerated concrete 400 in relation to moisture with calculated standard density and variability coefficient

Water content	**λ1**	**λ2**	**λ3**	$\bar{\lambda}$	**Standard deviation s [%]**	**Variab. coef.**
[cm^3/cm^3]	**[W/mK]**					**ν [%]**
0.41	0.637	0.590	0.578	0.602	0.031	5.180
0.4	0.641	0.595	0.584	0.606	0.03	4.990
0.39	0.628	0.578	0.569	0.592	0.032	5.369
0.38	0.606	0.559	0.540	0.569	0.034	5.971
0.37	0.615	0.571	0.550	0.579	0.033	5.729
0.34	0.569	0.537	0.534	0.546	0.019	3.553
0.33	0.565	0.533	0.523	0.540	0.022	4.063
0.33	0.569	0.544	0.538	0.550	0.016	2.989
0.32	0.582	0.554	0.542	0.559	0.021	3.672
0.31	0.546	0.522	0.523	0.530	0.014	2.562
0.28	0.506	0.481	0.478	0.488	0.015	3.150
0.27	0.494	0.470	0.470	0.478	0.014	2.899
0.265	0.522	0.499	0.491	0.504	0.016	3.193
0.26	0.467	0.441	0.445	0.451	0.014	3.104
0.22	0.455	0.419	0.446	0.440	0.019	4.258
0.22	0.440	0.405	0.430	0.425	0.018	4.242
0.21	0.433	0.396	0.414	0.414	0.019	4.469
0.205	0.436	0.398	0.405	0.413	0.02	4.897
0.195	0.376	0.350	0.358	0.361	0.013	3.689
0.19	0.374	0.348	0.357	0.360	0.013	3.668
0.185	0.374	0.346	0.354	0.358	0.014	4.029
0.185	0.375	0.348	0.351	0.358	0.015	4.134
0.175	0.368	0.347	0.343	0.353	0.013	3.804
0.175	0.367	0.346	0.348	0.354	0.012	3.274
0.17	0.350	0.331	0.337	0.340	0.01	2.857
0.165	0.334	0.318	0.324	0.325	0.008	2.487
0.16	0.327	0.319	0.319	0.322	0.005	1.434
0	0.099	0.099	0.099	0.099	0.000	0.000
Correlation coef. (r)	0.988	0.985	0.976	0.984		

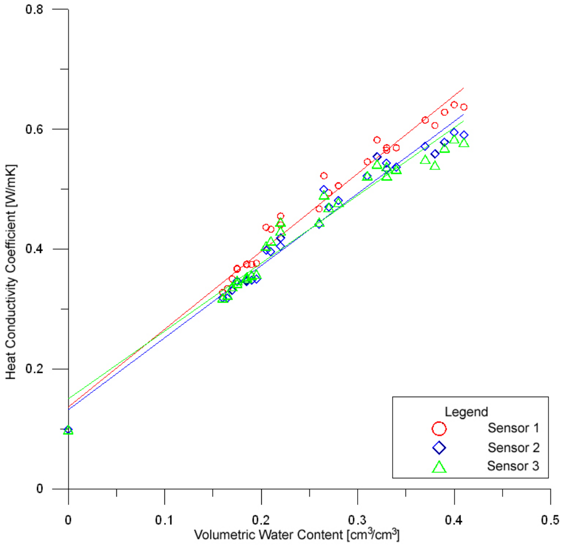

Fig. 4. Heat conductivity coefficient of aerated concrete 400 in relation to moisture

Table 4

Heat conductivity value of aerated concrete 600 in relation to moisture with calculated standard density and variability coefficient

Water content	**λ1**	**λ2**	**λ3**	$\bar{\lambda}$	**Standard deviation**	**Variab. coef.**
[cm^3/cm^3]	**[W/mK]**				**s [%]**	**v [%]**
0.46	0.673	0.570	0.596	0.613	0.054	8.738
0.44	0.660	0.558	0.592	0.603	0.052	8.613
0.43	0.629	0.530	0.565	0.574	0.05	8.746
0.43	0.604	0.517	0.545	0.555	0.044	8.002
0.42	0.599	0.507	0.532	0.546	0.048	8.713
0.41	0.605	0.518	0.524	0.549	0.049	8.851
0.40	0.585	0.505	0.508	0.533	0.045	8.508
0.39	0.588	0.512	0.522	0.541	0.041	7.633
0.39	0.598	0.525	0.549	0.558	0.037	6.668
0.38	0.579	0.515	0.547	0.547	0.032	5.850
0.00	0.156	0.156	0.156	0.156	0	0.000
Correlation coef. (r)	0.996	0.992	0.988	0.994		

With the obtained results a characteristic of aerated concrete heat conductivity depending on water content was described. All important data are presented in Table 5.

The characteristics assume the linear dependence between heat conductivity and moisture which is often used in models [2, 9, 10] of water and heat flow across building barriers according to the following formula:

$$\lambda(\theta) = \lambda_{dry} + \lambda_{mst}\cdot\theta \tag{2}$$

where: λ_{dry} - heat conductivity of dry material [W/m·K]; λ_{mst} - unit increase of heat conductivity value due to moisture increase heat conductivity of dry material [W/m·K]; θ - volumetric water content of aerated concrete [cm^3/cm^3].

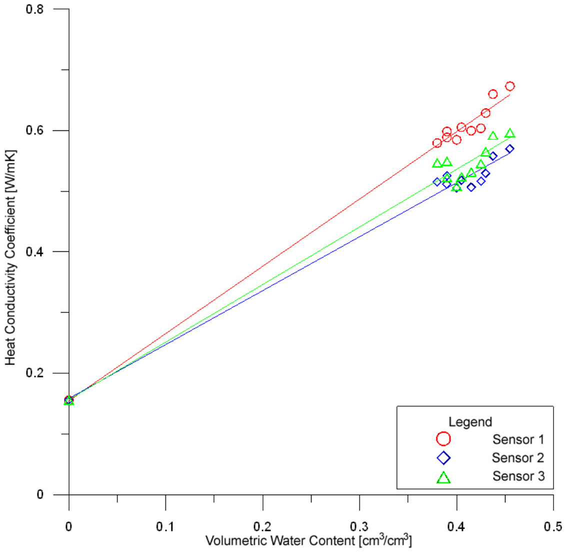

Fig. 5. Heat conductivity coefficient of aerated concrete 600 in relation to moisture

Table 5

Heat properties of aerated concrete obtained experimentally

Examined material	λ_{dry}	λ_{mst}
	[W/mK]	**[W/mK]·[cm³/cm³]**
Aerated concrete 400	0.105	1.311
Aerated concrete 600	0.157	0.982

The results obtained in this experiment can be compared with the material data contained in heat and moisture transfer simulation program Delphin [11]. These characteristics were estimated in the laboratory of Technical University in Dresden, Germany. Data contained for aerated concrete with the apparent density of 600 kg/m^3 show the λ_{dry} coefficient (in dry state) value about 0.17 W/m·K, and λ_{mst} parameter is 0.9 W/m·K per unit of volumetric moisture. In [3] value of λ_{dry} for aerated concrete 400 in dry is about 0.1 W/m·K and for the concrete 600 - about 0.16 W/m·K. In [2] the values are the following: 0.11 and 0.16 W/m·K.

Conclusions

Aerated concrete 400 is characterized by smaller value of the heat conductivity coefficient than aerated concrete 600. It could be explained by smaller apparent density with the similar compound of solid phase. But the λ_{mst} coefficient (unit rise per % vol.) is greater. Heat conductivity coefficient in dry state for aerated concrete 400 is about 6 times smaller than in saturation and for concrete 600 only 3.9 times.

It should be also underlined that the aerated concrete is strongly prone to water influence, but comparing with red brick for example, time of water desorption is longer. This fact, together with the increase of heat conductivity coefficient due to moisture rise leads to the increased heat loses during winter season and the decrease of heat-moisture comfort and indoor air microclimate.

That's why the importance of technology designs and building process organization should be improved. Especially in case of buildings made of aerated concrete [12] but also other porous materials with the special attention paid on building works, especially heat and water insulation but also rooms ventilation.

Acknowledgement

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WPŁYW WILGOTNOŚCI NA WSPÓŁCZYNNIK PRZEWODNICTWA CIEPLNEGO BETONU KOMÓRKOWEGO

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[2] Wydział Budownictwa i Architektury, Politechnika Lubelska

Abstrakt: Przedstawiono eksperymentalne badanie wpływu wzrostu wilgotności na współczynnik przewodnictwa cieplnego betonu komórkowego. Zastosowany zestaw pomiarowy składał się z dwóch komór klimatycznych generujących niskie i wysokie temperatury po przeciwnych stronach próbki wyposażonej w niezbędne czujniki do pomiaru temperatury, strumienia ciepła oraz wilgotności. Do pomiarów wilgotności zastosowano technikę TDR (*Time Domain Reflectometry*) - obecnie wdrażaną do pomiaru zawartości wody w materiałach i przegrodach budowlanych. Rezultatem opisanego eksperymentu jest wyznaczenie współczynnika przewodzenia ciepła betonu komórkowego w stanie suchym oraz w warunkach różnej wilgotności.

Słowa kluczowe: beton komórkowy, współczynnik przewodzenia ciepła, strumień ciepła, wilgotność, Time Domain Reflectometry

VARIA

CENTRAL EUROPEAN CONFERENCE ECOpole'10
Short Conference Report

The Conference ECOpole'10 was held in hotel Uroczysko (near Szklarska Poreba, Poland), from Oct. 14th, 2010 to Oct. 16th, 2010. It was the nineteenth ecological conference of the series of meetings organised by the Society of Ecological Chemistry and Engineering, Opole, PL.

129 participants, including delegates representing 7 countries (from Austria, Czech Republic, Great Britain, Norway, Poland, Slovakia and Ukraine) took part in the event and presented 20 oral contributions and 143 posters.

The Abstracts of the Conference contributions were available on the Conference website before and during the conference.

The Conference issue of the quarterly *Ecological Chemistry and Engineering S* containing among others keynote speakers papers, was distributed at the Conference Reception desk together with a CD-ROM (containing short info on Keynote Speakers, Abstracts of the Conference presentations as well as ECOpole'10 Conference Programme).

On Wednesday (13th October 2010) at 21.00 the participants were invited for Get-Together Party.

The Conference Agenda was divided into 5 sections:

* SI Ecological Chemistry and Engineering
* SII Environment Friendly Production and Use of Energy
* SIII Risk, Crisis and Security Management
* SIV Forum of Young Scientists and Environmental Education
* SV Health, Ecology and Agriculture.

The Conference was opened by prof. Maria Wacławek, Chairperson of the Organising Committee and prof. Witold Wacławek, Chairman of the Scientific Board and President of the Society of Ecological Chemistry and Engineering.

Prof. **Jacek NAMIEŚNIK** (*Gdansk University of Technology, Gdansk*, *PL*) initiated the Plenary Session with the invited lecture: "Green analytical chemistry". During the conference the plenary lectures were delivered also by other invited lecturers: prof. **Eiliv STEINNES** (*Norwegian University of Science and Technology, Trondheim, NO*): "Monitoring of air pollutants on the local and regional scale using mosses: strong and weak points", prof. **Andrzej G. CHMIELEWSKI** (*Institute of Nuclear Chemistry and Technology, Warsaw University of Technology, Warsaw, PL*): "Dreams or reality - fossil fuels, renewables or nuclear power?", prof. **Artur PAWŁOWSKI** (*Lublin University of Technology, Lublin, PL*): "Role of environmental engineering in introducing sustainable development" and prof. **Manfred SAGER** (*Austrian Agency for Health and Food Safety, Vienna, AT*): "Screening for biologically active elements: Sc, Y, La, Ce, Ti, Rb, Cs - by ICP-OES and ICP-MS methods".

Very interesting lectures were also presented by prof. **A.T. Solecki** (*University of Wroclaw, Wrocław, PL*): "Building stones as NORM (Naturally Occurring Radioactive Materials)", prof. **W. Kamiński** (*Lodz University of Technology, Łódź, PL*): "Biobutanol - methods of productions and purifications", dr **Ch. Jungnickel** (*Gdansk University of Technology, Gdańsk, PL*): "Ionic liquids - green solvents?", dr **I. Koliabina** (*Institute of Environmental Geochemistry, Kiev, UA*): "Features of absorbed uranium and strontium distribution in the sandy-clay rocks of the lower protective layer within near-surface solid radioactive waste repositories", dr **Z.A. Szydło** (*Highgate School, London, UK*): "Experimental chemistry in English schools", **B. Barańska** (*Provincial Inspectorate of Environmental Protection in Opole, PL*): "Monitoring of air quality in the Opole province" and **H. Ferster** (*Department of Safety and Crisis Management, Opole Provincial Office, Opole, PL*): "Environmental risks in the Opole province".

Thursday, a day of hard work, was finished with the Poster Session of the Section Chemical Pollution of Natural Environment and its Monitoring. Many of the discussions begun at the posters, lasted until the evening hours.

The next point of Thursday Conference Programme was the one-hour-long Musical Soirée. Students of the Public Musical School in Jelenia Gora (Band Cyjas Milongas and soloists playing the guitar, oboe and saxophone) played classical and contemporary compositions. The audience applauded the players and claimed for bis.

As usually during the ECOpole Conference, the second day included the Session of the Young Scientists (a forum of young scientists that present and discuss local ecological problems of their countries). During the Young Scientists', Environmental Education and Renewable Energy Poster Session 49 posters were presented.

At 19.00 the Conference participants were invited for a Conference Dinner.

On Thursday and Friday an exhibition of books related to the conference subject was organized by Polish Publishing House Wydawnictwa Naukowo-Techniczne (WNT), Warsaw and Society of Ecological Chemistry and Engineering, Opole.

On Saturday morning an ecological excursion was organised to the Center of Ecological Education in Karkonosze located in Karkonosze National Park in Szklarska Poreba. During this excursion conference participants could see the exposition "Virtual Karkonosze".

Closing the conference, prof., prof. Maria and Witold Wacławek made short recapitulation. In general, ECOpole'10 was focused on monitoring of the quality of natural environment, its effects on human life, environmental education as well as application of renewable sources of energy.

They expressed gratitude to all participants for coming and taking active part in the Conference and thanked all Chairpersons of Sessions.

They announced, that full text of the presented papers will be published (after obtaining reviewers' positive opinions) in the successive issues of the journals *Ecological Chemistry and Engineering A* and *S* and they will be distributed to all participants.

The Extended Abstracts of the presentations will be published in two subsequent issues of semi-annual *Proceedings of the ECOpole*.

Thanks to the financial support of the Polish Ministry of Scientific Research and Higher Education, it was possible, among others to publish Extended Abstracts and full Conference contributions as well as to help to pay the fees for the young scientists taking part in the Conference.

At the end they invited all Colleagues to attend the ECOpole'11 conference, which will be held at the Conference Center „Rzemieślnik" in Zakopane, PL in next October.

Maria Wacławek

INVITATION FOR ECOpole'11 CONFERENCE

CHEMICAL SUBSTANCES IN ENVIRONMENT

We have the honour to invite you to take part in the 20th annual Central European Conference ECOpole'11, which will be held in **13-15 X 2011** (Thursday-Saturday) at the Conference Center „Rzemieslnik" in Zakopane, PL.

The Conference Programme includes oral presentations and posters and will be divided into five sections:

- **SI Chemical Pollution of Natural Environment and its Monitoring**
- **SII Environment Friendly Production and Use of Energy**
- **SIII Risk, Crisis and Security Management**
- **SIV Forum of Young Scientists and Environmental Education in Chemistry**
- **SV Impact of Environment Pollution on Food and Human Health**

The Conference language is English.

Contributions to the Conference will be published as:

- abstracts on the CD-ROM (0.5 page of A4 paper sheet format)
- extended Abstracts (4-6 pages) in the semi-annual journal *Proceedings of ECOpole*
- full papers will be published in successive issues of the *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna* (Ecol. Chem. Eng.) ser. A or S.

Additional information one could find on Conference website

ecopole.uni.opole.pl

The deadline for sending the Abstracts is **15.07.2011** and for the Extended Abstracts: **1.10.2011**. The actualised list (and the Abstracts) of the Conference contributions accepted for presentation by the Scientific Board, one can find (starting from 15.07.2011) on the Conference website.

The papers must be prepared according to the Guide for Authors on Submission of Manuscripts to the Journals.

At the Reception Desk each participant will obtain a CD-ROM with abstracts of the Conference contributions as well as Conference Programme (the Programme will be also published on the Conference website).

Further information is available from:
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ZAPRASZAMY
DO UDZIAŁU W ŚRODKOWOEUROPEJSKIEJ KONFERENCJI
ECOpole'11
W DNIACH 13-15 X 2011

SUBSTANCJE CHEMICZNE W ŚRODOWISKU PRZYRODNICZYM

Będzie to **dwudziesta z rzędu** konferencja poświęcona badaniom podstawowym oraz działaniom praktycznym dotycząca różnych aspektów ochrony środowiska przyrodniczego. Odbędzie się ona w Ośrodku Konferencyjno-Wypoczynkowym „Rzemieślnik" w Zakopanem. Doroczne konferencje ECOpole mają charakter międzynarodowy i za takie są uznane przez Ministerstwo Nauki i Szkolnictwa Wyższego. Obrady Konferencji ECOpole'11 będą zgrupowane w pięciu Sekcjach:

- **SI Chemiczne substancje w środowisku przyrodniczym oraz ich monitoring**
- **SII Odnawialne źródła energii i jej oszczędne pozyskiwanie oraz użytkowanie**
- **SIII Zarządzanie środowiskiem w warunkach kryzysowych**
- **SIV Forum Młodych (FM) i Edukacja prośrodowiskowa**
- **SV Wpływ zanieczyszczeń środowiska oraz żywności na zdrowie ludzi**

Materiały konferencyjne będą opublikowane w postaci:

- abstraktów (0,5 strony formatu A4) na CD-ROM-ie;
- rozszerzonych streszczeń o objętości 4-6 stron w półroczniku *Proceedings of ECOpole*;
- artykułów: w abstraktowanych czasopismach: *Ecological Chemistry and Engineering/Chemia i Inżynieria Ekologiczna (Ecol. Chem. Eng.)* ser. A i S oraz niektórych w półroczniku *Chemia-Dydaktyka-Ekologia-Metrologia*.

Termin nadsyłania angielskiego i polskiego streszczenia o objętości 0,5-1,0 strony (wersja cyfrowa + wydruk) planowanych wystąpień upływa w dniu 15 lipca 2011 r. Lista prac zakwalifikowanych przez Radę Naukową Konferencji do prezentacji będzie sukcesywnie publikowana od 15 lipca 2011 r. na stronie webowej

ecopole.uni.opole.pl

Aby praca (dotyczy to także rozszerzonego streszczenia, które powinno mieć tytuł w językach polskim i angielskim, słowa kluczowe w obydwu językach) przedstawiona w czasie konferencji mogła być opublikowana, jej tekst winien być przygotowany zgodnie z wymaganiami stawianymi artykułom drukowanym w czasopismach *Ecological Chemistry and Engineering* ser. A oraz S, które są dostępne w wielu bibliotekach naukowych w Polsce i zagranicą. Są one takie same dla prac drukowanych w półroczniku *Chemia-Dydaktyka-Ekologia-Metrologia*. Zalecenia te są również umieszczone na stronie webowej konferencji.

Po Konferencji zostaną wydane 4-6-stronicowe rozszerzone streszczenia wystąpień w półroczniku *Proceedings of ECOpole*. Artykuły te powinny być przesłane do **1 października 2011 r**. Wszystkie nadsyłane prace podlegają zwykłej procedurze recenzyjnej. Wszystkie streszczenia oraz program Konferencji zostaną wydane na CD-ROM-ie, który otrzyma każdy z uczestników podczas rejestracji. Program będzie także umieszczony na stronie webowej Konferencji.

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