ISSN 2300-5599

ACTA INNOVATIONS

CENTRUM
BADAŃ I INNOWACJI
PRO - AKADEMIA
RESEARCH AND INNOVATION CENTRE

no. 28

July 2018

Acta Innovations

quarterly

no. 28

Konstantynów Łódzki, Poland, July 2018

ISSN 2300-5599

Original version: online journal

Online open access: www.proakademia.eu/en/acta-innovations

Articles published in this journal are peer-reviewed

Publisher:

Research and Innovation Centre Pro-Akademia
9/11 Innowacyjna Street
95-050 Konstantynów Łódzki
Poland

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Zadania „Stworzenie anglojęzycznych wersji artykułów w Acta Innovations", „Dobór i kontraktacja uznanych zagranicznych recenzentów do oceny zgłaszanych manuskryptów", „Digitalizacja Acta Innovations w celu zapewnienia otwartego dostępu poprzez sieć Internet" i „Utrzymanie systemu antyplagiatowego" finansowane w ramach umowy 605/P-DUN/2018 ze środków Ministra Nauki i Szkolnictwa Wyższego przeznaczonych na działalność upowszechniającą naukę.

Ministerstwo Nauki
i Szkolnictwa Wyższego

ACTA INNOVATIONS

no. 28

July 2018

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REMOVAL OF 2-PHENYLBENZIMIDAZOLE-5-SULFONIC ACID USING HETEROGENEOUS PHOTOCATALYSIS

Abstract
UV filters are classified as environmental pollutants (emerging pollutants). One of the most frequently detected UV filters in real samples is 2-phenylbenzimidazole-5-sulfonic acid (PBSA). It has been shown that conventional technologies applied in sewage treatment plants are not adapted for complete removal of sunscreen agents. Therefore, there is a trend to undertake activities leading to improvement of water quality by enhancing treatment methods. This is important due to the fact that in an aqueous environment, in the presence of UV radiation or sunlight irradation, PBSA generates reactive oxygen species that can damage the DNA of living organisms.

The aim of study was to investigate an effect of pH and TiO_2 on PBSA stability in the presence of UV radiation. It was found that the rate of PBSA degradation depends on the catalyst dose and pH of solution. The photocatalysis reaction was carried out in a Heraeus laboratory exposure set equipped with a 150 W medium-pressure mercury lamp. The course of PBSA degradation process as a function of time was monitored using UV/VIS spectrophotometer and liquid chromatograph equipped with UV-Vis detector.

Key words
PBSA, UV filter, emerging pollutants, photodegradation, TiO_2

Introduction

Organic environment micro-pollutants (emerging pollutants) are a global challenge related to water quality. These substances have been identified in the environment but they are not included in routine environmental monitoring programs. Their fate in the environment and ecotoxicological impact on living organisms are unknown [1]. The micro-pollutants of the environment include, among others, pharmaceutical products and personal care products which are used every day and at the final stage they get into surface water or sewage [2]. One of the components of personal care products are UV filters. These compounds are mainly used in sun creams and other cosmetic preparations (lipsticks, make-up agents, lotions, shampoos) protecting people against the harmful effects of UV radiation [3].

It was revealed that UV filters get into environment together with sewage as a result of washing off from the skin or clothes. These compounds were detected in surface waters, recreational waters as well as in sewage and sediments even at levels of $mg \cdot L^{-1}$ or $mg \cdot kg^{-1}$ [4, 5]. The maximum levels of UV filters have been determined in summer, as most cosmetics containing sunscreens are used during this period [3, 5, 6, 7]. In water matrices, the most frequently are detected derivatives of benzophenone, cinnamic acid and benzimiadazole [8].

2-Phenylbenzimidazole-5-sulfonic acid (PBSA), as one kind of sunscreen, is widely used in sunscreen formulations and cosmetics because of its strong absorption in the UVB region [9]. PBSA is characterized by high polarity. It has been identified in surface waters at the level from 109 to 2679 $ng \cdot L^{-1}$ [10]. Studies have shown that PBSA under the influence of sunlight irradiation can cause DNA damage, because it is a source of reactive oxygen species (ROS) [11].

Some studies have shown that UV filters are stable against biotic degradation. In addition, toxicological studies suggest that some organic filters have estrogenic and antithyroid properties and can be bioaccomulated [12, 13]. Hence, UV filters are a potential danger to human health and the ecosystem. Moreover, products of UV filter conversions under the influence of environmental agents can be more toxic than the initial compounds. For this reason, they are considered as priority pollutants, which should be subject to special monitoring [14].
Another important aspect is that UV filters which penetrate wastewater are not effectively removed. Conventional wastewater treatment methods are not suitable for disposal of organic micro-pollutants. Liu et al.

https://doi.org/10.32933/ActaInnovations.28.1 • 2300-5599 •

observed on the municipal wastewater treatment plant which consisted of primary sedimentation and secondary activation of the processed sediments, the efficiency of elimination of 6 UV filters at the level of 5-82% [15]. In turn, application of adsorption on the sediment of lipophilic filters (log Kow> 4.0) such as avobenzone, homosalat, 4-methylbenzylidenecamphor (4-MBC), octyl-dimethyl-p-minobenzoic acid (ODPABA), octocrylene and 2-ethylhexyl 4-methoxycinnamate (EHMC) eliminates them from wastewater at the level of 30-70% [15-17]. Coagulation process and flocculation were also ineffective methods for elimination of 2,4-dihydroxybenzophenone (BP-1) and 2-hydroxy-4-methoxy benzophenone-5-sulfonic acid (BP-4) [17, 18]. Low effectiveness of degradation UV filters was achieved in the process with the use of natural light. The tested filters contain chromophore groups, whose photoactive states are very stable and can change energy absorbed from light into thermal energy without changing their chemical structure [19]. However, in the process of water disinfection, benzophenone-3 (BP-3), 4-MBC, EHMC and octocrylene were eliminated by 17-25%. In addition, this process produces halogenated by-products which can be toxic [20, 21]. Therefore, the attempts are undertaken to find more effective methods for inactivation or elimination of sunscreens from wastewater [22].

Advanced oxidation processes (AOP) have been successfully used to remove various organic pollutants such as pesticides and herbicides from water environment [23-25]. Due to the simplicity and effectiveness, one of the most often applied AOPs is UV/H_2O_2 system which degrades organic compounds as a result of selective attack of OH• radicals [26]. An effective solution is also homogeneous photocatalysis with Fenton reagents. SO_4^-•, which is characterized by strong oxidizing properties at various pH values of solutions and is recommended for the degradation of organic compounds of considerable durability. Another method is heterogeneous photocatalysis using nanoparticles of TiO_2 catalyst [27, 28]. TiO_2 P25 is a photoactive, highly chemically stable, cheap and non-toxic catalyst [28].

This paper presents results of studies on the heterogeneous photocatalysis of organic PBSA UV filter under various experimental conditions in the presence of UV irradiation.

Materials and methods

Materials

All chemicals were purchased from commercial suppliers and used without purification. 2 phenylbenzimidazole 5 sulfonic acid (PBSA, CAS: 5466-77-3) was obtained from Sigma-Aldrich (USA). Reference standards (pH 2- pH 14) were obtained from POCh (Poland). TiO_2 P25 (Surface Area 50 $m^2 \cdot g^{-1}$) TiO_2 PC105 (Surface Area 90 $m^2 \cdot g^{-1}$), TiO_2 PC500 (Surface Area 350 $m^2 \cdot g^{-1}$), were supplied by CristalACTiV™.

Reaction conditions: Photocatalytic experiment

The photocatalytic experiments were conducted on a laboratory scale using a Heraeus reactor equipped with a medium-pressure mercury lamp with a range of 200-600 nm. The mercury lamp was cooled with water to temperature of 20ºC. Water solutions of PBSA at a concentration of 10 $mg \cdot L^{-1}$ were introduced into laboratory reactor. Then, the specified doses of TiO_2 catalyst were added. The system prepared in this way was subjected to UV irradiation. In order to ensure uniform distribution of the reactants, the solution was mixed using a magnetic stirrer (200rpm). Composition of the tested solutions is presented in Table 1. Effect of the specific surface area of catalyst on the photocatalysis rates was investigated using three types of titanium dioxide: TiO_2 P25, TiO_2 PC 105 and TiO_2 PC 500, which were added in an amount of 20 mg. Effect of pH on the rate of photocatalysis was checked using TiO_2 P25. The pH value and proportions of catalyst in the individual systems is given in Table 1. The pH of solutions was adjusted with buffers. Photocatalyst doses were determined during preliminary tests. The time of catalyst contact with water PBSA solution before irradiation was set to 15 minutes in order to achieve a balance between adsorption and desorption.

Table 1. The reaction conditions and substrate proportions used in this study

System number	PBSA [mg·L^{-1}]	TiO_2 P25 [mg·L^{-1}]	pH	UV [W]
1	10	-	7	150
2		1	7	
3		5	7	
4		10	7	
5		20	7	
6		40	7	
7		1	3	
8		1	5	
9		1	12	

Source: Author's

Analytical methods

Sampling procedure

Samples for quantitative analysis were drawn every 5 minutes. 10 ml of solution was sampled from each system studied. Separation of water mixture from catalyst was carried out using a filtration kit, which consisted of a 45µm PTFE filter. Change in PBSA concentration as a function of time was controlled by the spectrophotometric and chromatographic methods.

Spectrophotometric analysis

UV/Vis Academy Spectra View 2100 spectrophotometer was used for spectrophotometric analysis. Spectrophotometric analysis was carried out in the range of 200-400 nm. The detection wavelength was 245 nm and 302 nm for PBSA.

High performance liquid chromatography

Chromatographic analysis was carried out using a high performance liquid chromatograph SHIMADZU, equipped with UV-Vis SPD-20AV SHIMADZU detector. Discovery® HS Supelco C18 column (15 cm × 4.6 mm, 5 µm) was used for separation. The mobile phase consisted of 1% acetic acid in water and 96% ethanol in a ratio of 80:20 (v:v). The flow rate was 1 ml/min with a 20 µl injection volume. The detection wavelength was 245 nm and 302 nm for PBSA. HPLC analysis based on peak areas.

Results

Effect of UV radiation and TiO_2 catalyst on PBSA degradation was controlled by two methods: spectrophotometric and chromatographic. In the first stage, both methods were verified in terms of linearity and repeatability. Limits of detection (LOD) and quantification (LOQ) were also determined.

Table 2. Linear range, calibration curves, relative, relative standard deviation (RSD) and LOQs and LODs

Parameters	HPLC method	Spectrophotometric method
Range [mg·L^{-1}]	0.0003- 10.0	0.3- 10.0
R^2	0.9997	0.9983
RSD [%]	3.2	2.0
a	26280	0.0867
b	- 3854.9	0.0273
LOQ	0.3 µg·L^{-1}	0.3 mg·L^{-1}
LOD	0.1 µg·L^{-1}	0.1 mg·L^{-1}

Source: Author's

y=ax+b

Both methods are characterized by linearity and repeatability (Table 1.). For the spectrophotometric method, the linearity range was in the range of 0.3-10.0 mg•$L^{-1.}$ The standard curve was determined based on solutions with concentrations of 0.3; 0.5; 1.0; 2.0; 5.0; 10.0 mg • $^{L-1}$. For the HPLC method, the linearity range was in the range of 0.0003-10.0 mg • L^{-1}. The calibration curve consisted of 8 points with concentrations of 0.0003; 0.0001; 0.001; 0.01; 0.1; 1.0; 10.0 mg • L-1. Each point of the calibration curve was performed in a four-fold repeat for two methods. The LOD and LOQ were determined as described Voigtman et al.[29]. The LOD for the HPLC and spectrophotometric method was calculated based on the signal to noise ratio. The LOD value was three times the value of the noise. The limit of quantification was three times the limit of detection (LOQ = 3LOD). The HPLC UV-Vis method allows us to determine PBSA concentration at lower level than spectrophotometric method.

In the next stage, the effect of UV irradiation on stability of PBSA was checked. It was found that PBSA was degraded by 90% within an hour. The obtained results are consistent with those described by Abdelraheem et al. [11], who showed that in the water environment PBSA is capable of the photo-generating reactive oxygen species under UV irradiation. The nascent oxygen radicals are precursors of further PBSA conversions, which can result in formation of products with significantly higher toxicity than the substrate. Change of absorbance in time is presented in Fig. 1.

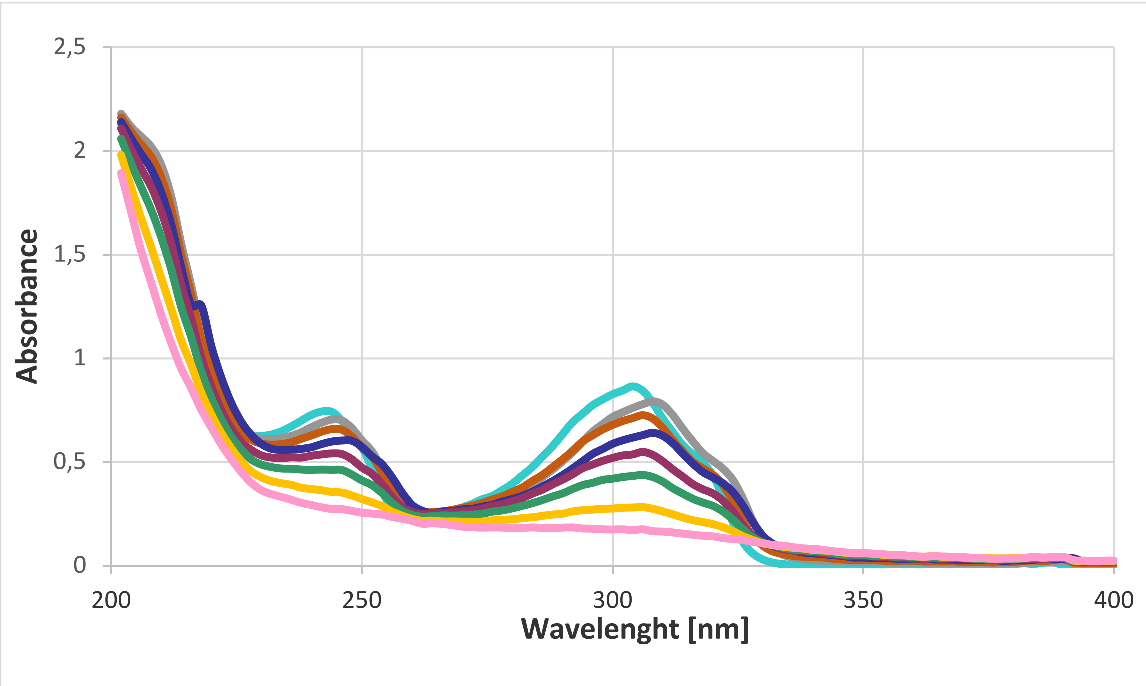

Fig. 1. Change in absorbance of PBSA under the influence of irradiation as a function of time: — 0 min; — 10 min; — 20 min; — 30 min; — 40 min; — 50 min; — 60 min; — 70 min

Source: Author's

Another method used for degradation of organic contaminants is heterogeneous photolysis. It consists in simultaneous use of TiO_2 and UV catalysts. Introduction additionally TiO_2 to PBSA/UV system affected the rate of UV filter degradation. The tests were carried out using three TiO_2 catalysts differing in surface area i.e. TiO_2 P25, TiO_2 PC 105 and TiO_2 PC 500. The satisfactory results were obtained in the presence of each of the photocatalysts used (Fig. 2.). The highest loss in PBSA concentration was observed in the presence of TiO_2 P25, characterized by the smallest specific surface area. Therefore, TiO_2 P25 was used for further investigations.

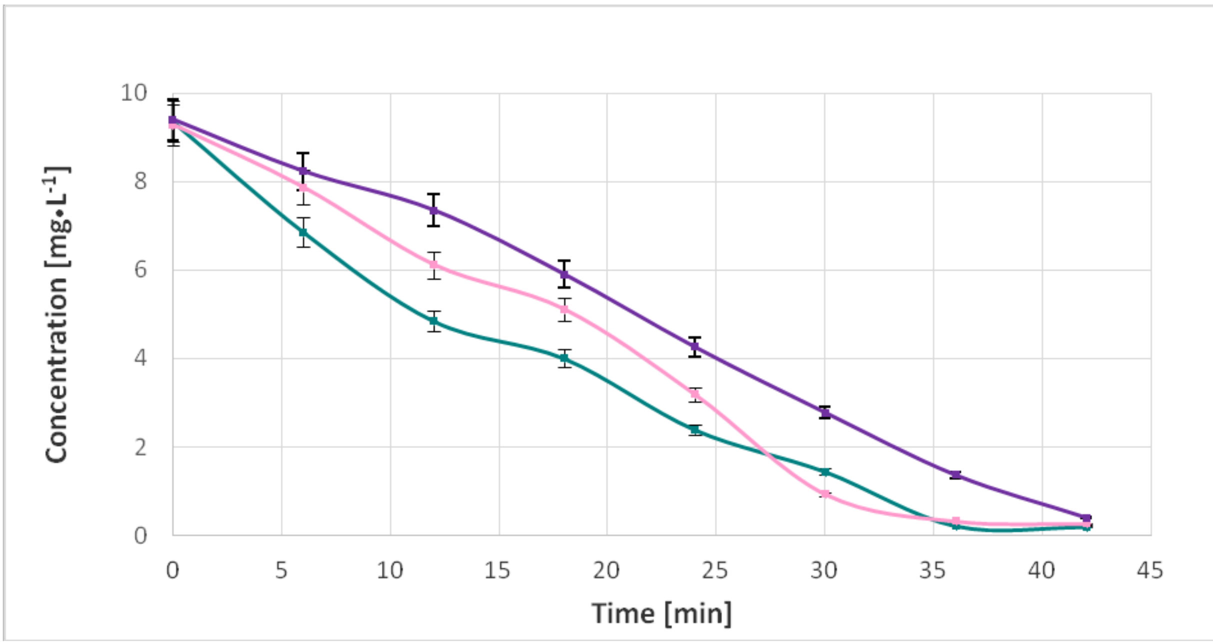

Fig. 2. Comparison of the effect of titanium oxides on PBSA degradation: —■—TiO_2 P25; —■— TiO_2 PC105; —■— TiO_2 PC500
Source: Author's

The catalyst dose is of great importance in the PBSA photodegradation process. The heterogeneous photolysis reaction was performed using 1, 5, 10, 20 and 40 mg of TiO_2 P25. It was found that with the increase of the TiO_2 dose, the rate of PBSA degradation increases (Fig. 3.). After 15 minutes of reaction, in the mixture with the highest dose of TiO_2, the filter concentration loss was found to be 85%. However, in the mixture with 1 mg of TiO_2, this result was achieved not before 50 minutes of reaction. However, it should be noted that the use of a large amount of catalyst involves the need to carry out filtration of the system prior to performing the determination of PBSA concentration, because the catalyst suspension precludes measurement and can contaminate the apparatus.

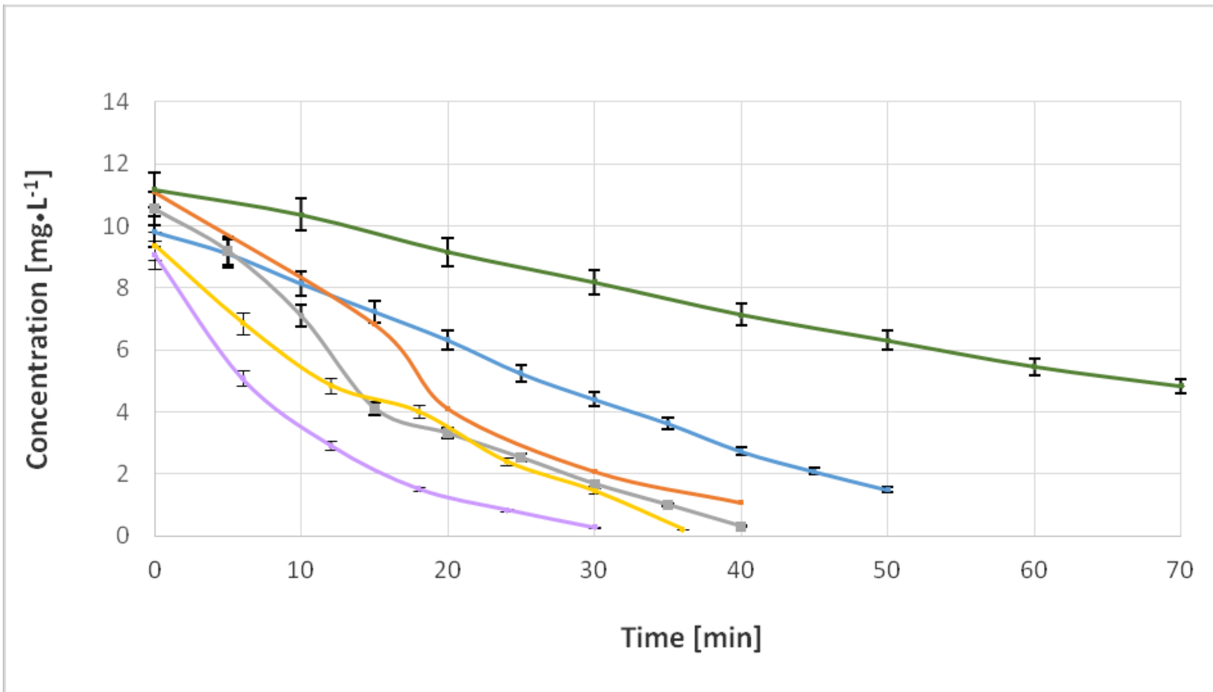

Fig. 3 Effect of TiO_2 dose on PBSA stability : —■—without TiO_2; —■— 1 mg TiO_2; —■—5 mg TiO_2; —■—10 mg TiO_2; —■—20 mg TiO_2; —■—40 mg TiO_2
Source: Author's

Another important parameter that should be taken into consideration during the heterogeneous photolysis of PBSA is pH of solution. The systems with addition of 1 mg TiO_2 adjusted to pH 3, 5 and 12, respectively, and the system without addition of buffer pH = 7 were used in the studies. The effect of solution pH on photocatalytic degradation is a complex problem related to the ionization states of organic compounds, the catalyst surface charge as well as the formation rate of HO• and other active radicals in the reaction solution [30, 31]. The pH of the solution also changes the energy level (2 energy levels) TiO_2 [32]. According to our studies, PBSA photodegradation in the presence of TiO_2 depends on pH. It was observed that degree of degradation in acidic medium is considerably higher than at neutral pH (Fig. 4). According to Ji et al. [9], it can be caused by electrostatic attraction between $TiOH_2^+$ and PBSA-H, which facilitates adsorption of PBSA on the surface of TiO_2.

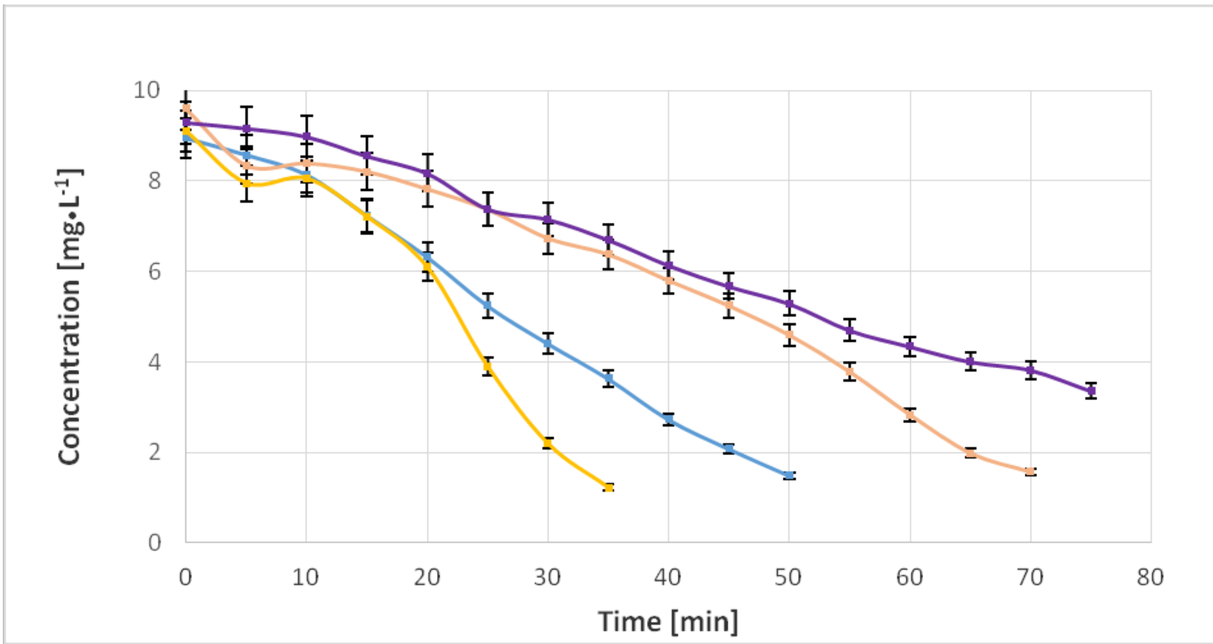

Fig. 4. Effect of pH on the rate of heterogeneous catalysis: : —■— without buffer; —■— buffer pH=3; —■— buffer pH=5; —■— buffer pH=12

Source: Author's

The photodegradation process in an alkaline medium runs differently. In an alkaline medium (pH ≥ 12), electrostatic repulsion between TiO^- and PBSA-2H is much stronger than the effect of HO• formation, which consequently slows degradation of the compound [9]. Similar results were obtained by Soto-Vazquez [33]. The results obtained indicate an important role of TiO2 in the photolysis process. Previous studies on PBSA photodegradation without TiO2 at different pH have shown that the protonated form of PBSA-2H was excited, moreover quantum efficiencies in the basic and acidic media were much higher than in neutral medium and this affects the increase in degradation rate [34]. Similar results were obtained by Tsoumachidou et al., who studied the effect of pH on the photocatalysis of another UV filter *p*-aminobenzoic acid (PABA). They found that the degradation proceeds faster in the acid medium, while in the alkaline medium the rate of photocatalysis decreases [35].

Conclusion

Photodegradation of water solution of 2-phenylbenzimidazole-5-sulfonic acid (PBSA) in the presence of a TiO_2 catalyst suspension was carried out. Presence of TiO_2 distinctly affects degradation of PBSA. The rate of degradation of the compound tested depends on catalyst dose and pH of the reaction medium. The study on the effect of pH on PBSA solution showed that the highest degradation occurred at pH=3. However, in basic medium, the process proceeds slowly. Heterogeneous photocatalysis with participation of TiO_2 is considered to be one of the methods of advanced oxidation processes (AOP). The results obtained indicate that it can be used for degradation of organic pollutants, such as sunscreens. Due to its photochemical properties, TiO_2 can directly oxidize the adsorbed chemical substance or form an adsorbed hydroxyl radical HO·. This, in turn, as a reactive oxidant, is capable of non-selective reaction with the most resistant organic substances polluting water.

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THE IMPACT OF TiO_2 MODIFICATIONS ON THE EFFECTIVENESS OF PHOTOCATALYTIC PROCESSES [REVIEW]

Abstract
This paper outlines the recent studies on the application of photocatalysis using semiconductors, with modified titanium dioxide (TiO_2) in the process of reducing chemical contamination of surface and ground waters. During the last forty years, an increasing interest in catalysts of this type is noticeable. Hence, a wide range of methods of TiO_2 modifications have been proposed so far by using its various polymorphs, composites with metals and non-metals and polymer-coatings or impregnating it with dyes that effectively absorb sunlight.

Key words
titanium dioxide, doping, metals, non-metals, dyes, photodegradation

Titanium dioxide

Inorganic semiconductors started to be used as photocatalysts in the 70s of the twentieth century. Among substances examined so far special emphasis should be placed on titanium dioxide, TiO_2. This is an amphoteric solid, which is non-toxic and insoluble in water. It turned out that TiO_2 exhibits a high photocatalytic activity, and is also thermally resistant and relatively inexpensive. Therefore, it is considered to be one of the best examined semiconductors widely described in the literature. Titanium dioxide occurs in minerals and can be obtained from them after removal of other constituents (e.g. Fe, depending on the ore). This is an important raw material for the production of titanium metal. Due to its photochemical activity it may be used as a catalyst in photo-oxidation processes, e.g. in systems designed for removal of organic impurities from wastewater.

TiO_2 occurs in three minerals called rutile, brookite and anatase (Fig.1) [1-13].

Anatase **Rutile** **Brookite**

Fig.1. Polymorphic forms of TiO_2

Rutile (Latin "rutilus" which means red, from the color of some of its forms) is the most important and stable form of titanium dioxide. It is an accessory mineral of metamorphic and igneous rocks. Crystals of rutile exhibit birefringence. Its nanoparticles are transparent in visible light, but absorb UV light. Therefore, TiO_2 is used in the production of preparations which protect skin against harmful UV rays. Rutile may be obtained from anatase as a result of a polymorphic transformation in the temperature range 550-1000°C. Rutile is mainly used in the production of titanium white (known as pigment PW6), glass, titanium and its alloys [2,12-15].

Brookite (after H.J. Brooke, an English crystallographer and mineralogist) is the rarest form of TiO_2. It is very difficult to obtain pure brookite, without a dope of anatase or rutile. Therefore, its properties were tested to a small extent. It occurs in the form of fragile, transparent crystals. It has a poorly developed specific surface area

https://doi.org/10.32933/ActaInnovations.28.2 • 2300-5599 •

and this is the main reason why it is used on a small scale (including production of titanium metal) [1,12,13,15,16].

Anatase (Greek “anatasis” which means extension) occurs as a transparent, fragile solid with a metallic luster. Like rutile, it is an accessory mineral of metamorphic igneous rocks. Anatase is the most thermodynamically stable when its crystalline size falls below 11 nm (11-35 nm for brookite and 35 nm for rutile) [17]. Only rutile and anatase have been considered for large-scale commercial use. Generally, TiO_2 is obtained after processing of natural sources (ilmenite, rutile and anatase minerals). An alternative way is the sol-gel route, involving hydrolysis of titanium alkoxides (typically Ti-propoxide and/or Ti-butoxide). The particular polymorphs are formed during calcination of the raw TiO_2 product, anatase at 400-500°C, rutile above 600°C and their blends between 500-800°C.

From the plethora of TiO_2 polymorphs, anatase is particularly recognized for its excellent photocatalytic properties, more than rutile and brookite ones [12-14,17,18]. Catalytic activity of anatase depends, among other things, on the size of grains as well as the surface structure and its morphology. Depending on the mean grain size, microanatase (200-500 nm) and nano-anatase (10-90 nm) have been distinguished. The specific surface area of these two types of anatase corresponds to 8 – 15 m^2/g and 50 – 100 m^2/g, respectively. Generally, nano-anatase is considered more active in photooxidation processes than its microcrystalline form [12-14,17,18].

Although most literature data show that anatase is the most active TiO_2 polymorph, however, depending on the type and conditions of the realized catalytic process, the activity of anatase and rutile may be more or less similar.

Both anatase and rutile as well as their blends have been reported to prove effective photocatalysts in the degradation of a number of organic compounds, including phenols, organic acids and amines. Nevertheless, it was found that efficiency of these processes depends not only on the type of the catalyst used but also it is strongly related to the nature of the organic substrate. It has been proved, that in the case of some compounds anatase was more effective, while in others it was the rutile one. This issue clearly shows, that the photocatalytic activity of TiO_2 itself depends on a variety of physicochemical parameters which might have diversely affected its activity, including shape, size and specific surface area of TiO_2 grains as well as their pore structure and volume of pores. To understand the TiO_2 photocatalytic activity one must take into consideration the impact of such factors. It may be the case that a particular catalyst is effective in the degradation of a given chemical compound, but not necessarily for another one [2,3,19].

Mechanism of the photocatalytic reaction

Advanced processes of oxidation are determined by the formation of reactive oxygen species (ROS), including $^{\bullet}OH$, $HOO^{\bullet}$, $^{\bullet}O^{2-}$ and singlet oxygen ($^1\Delta_gO_2$). From among them, the hydroxyl radical ($^{\bullet}OH$) is considered the strongest and most reactive oxidant. For this reason, photooxidation processes may constitute an alternative to widely used methods of water treatment. Therefore, photocatalytic systems based upon the TiO_2 matrix seem to provide a very economic and prospective method of water purification. Extensive research is carried out worldwide towards the improvement of pro-ecological photocatalytic processes [5].

Photoactivity of titanium dioxide is related to the absorption of light at wavelengths less than 400 nm. Photons that correspond to this energy cause excitation of electrons in the semiconductor matrix from the valence band into the conduction band. As a result, electron-hole pairs responsible for the activity of the catalyst are generated. Oxygen and water molecules present in the system can be then converted into reactive oxygen species. Electrons on the surface of TiO_2 combine with oxygen, whereas the holes interact with the surrounding water phase to create reactive hydroxyl radicals. These are very strong oxidants, capable to degrade effectively a number of organic compounds [4,5,8,19,15,19-21]. Usually, complete mineralization of the original organic substrate and its conversion to CO_2 and H_2O is reported, along with the formation of other non-toxic inorganic compounds [2,3,19].

Modification of the TiO_2 matrix

To increase the rate and effectiveness of photodegradation processes, studies are performed on modification of the surface of TiO_2 grains by means of doping with metals and/or non-metals, dye impregnation and formation of mixtures containing specific amounts of the particular TiO_2 polymorphs.

Evonik P25

An example of the commercial mixture of TiO_2 polymorphs is Evonik P25, known as Degussa P25. It is widely used as a photocatalyst due to its high photochemical activity. Its composition varies, but normally it consists of anatase and rutile in quantity of about 70% and 20% respectively, and occasionally of the amorphous TiO_2 phase. Studies dedicated to the Evonik product revealed that particles of anatase and rutile form separate aggregates and the average size of their grains falls in the range of 25 to 85 nm. That is why this material has a relatively high specific surface area (49 m^2g^{-1}) [22-24].

The photodegradation process of naphthalene with the use of anatase, rutile and Evonik P25 as catalysts was studied. It turned out that the process was much more effective when Evonik was used, and not anatase or rutile alone. In fact, it is very difficult to find a catalyst with a titanium dioxide matrix that shows higher activity than Evonik P25 and hence it is used as a basic TiO_2 catalyst [22-24].

Metal and non-metal doping

The most common methods of TiO_2 modifications are doping and impregnation with metal nanoparticles. This may be realized by introducing the dopant at the TiO_2 synthesis stage, as well as by adding it to a finished TiO_2 product. There are many methods of doping reported in the literature, dedicated to the particular TiO_2-dopant system, which depend on its assumed application [3,25].

Metal nanoparticles used for this purpose are mainly Pt, Au, Pd, Ru, Rh and Ag. It was proved that doping with gold has a positive influence on the mobility of electrons on the TiO_2/metal surface when exposed to UV radiation, which renders the photocatalytic process more effective. With respect to platinum, the quantity of oxygen adsorbed on the Pt/TiO_2 surface (which determines the activity of the photocatalyst), decreases when exposed to UV radiation, if the quantity of Pt increases, as compared to when UV was not used [3,6,7,19,26].
The major purpose of TiO_2 metal-doping is to prevent and/or delay the process of recombination of electrons and holes, and to effectively enhance the absorption of photons from the visible range. TiO_2 matrices may also be doped with ions of metals and non-metals. To determine the whole photo-oxidation process, it is important that ions are chosen appropriately [3,6,7,19,26].

Doping the TiO_2 matrix with transition metal ions (e.g. Fe(III), Ru(III), V(IV), Mo(V), Os(III), Re(V), Rh(III)) significantly improves the activity of the catalyst in photodegradation of $CHCl_3$ under UV radiation. In contrast, the presence of Co(III) and Al(III) ions decreases its effectiveness. Transition metals were studied much more thoroughly than noble metals. However, in a number of reports the effectiveness of doping with Ru(III), Rh(III), Pt(IV) and Ir(III) ions was emphasized, as well, e.g. in the process of 4-chlorophenol photooxidation [3,6,7,19,26].

Another approach assumed to improve the photocatalytic effectiveness of the TiO_2 matrix involved doping with non-metals, mainly N, C, S, B. However, in many cases, the results reported elsewhere were inconsistent and often controversial. For example, nitrogen-doped TiO_2 appeared effective in photodegradation of methylene blue, but was quite ineffective in the case of formic acid [3, 6,9,25,27].

Doping of TiO_2 matrices with two or more different elements was also studied. It turned out that doping of TiO_2 with two different metals (e.g. Sb/Cr or Pt/Cr), two different non-metals (e.g. N/F, N/S) as well as a metal and non-metal (e.g. Pt/N) did not produce any positive impact neither on the kinetics nor efficiency of the photodegradation of phenol, as compared to the reaction in which TiO_2 was doped with one metal or one non-metal only. However, this issue appears more complex and definitely must be related to the nature of the compound to be oxidized. For instance, photodegradation of 4-chlorophenol and acetaldehyde was found to proceed much more effectively in the presence of a double-doped matrix, such as the Pt/N-TiO_2 composite, than when the TiO_2 matrix was doped with either of these dopants alone [3, 6,9,26,27].

Function of inorganic anions

Inorganic anions adsorbed on the surface of a catalyst were found to affect the photo-oxidation process. Anions, such as fluorides, phosphides and sulfides, are not directly involved in photocatalytic reactions, but significantly influence the activity of a catalyst and hence the reaction mechanism. In this respect, the fluoride ion was the best examined one. It was proved that fluoride ions interchange with hydroxide ions on the surface of TiO_2. Fluorination of the surface of TiO_2 has a major influence on its physicochemical and photocatalytic properties. It significantly changes its hydrophobic-hydrophilic character and speeds up the oxidation of organic and inorganic compounds. With the F-doped TiO_2 matrix it is possible to oxidize hydrogen cyanide, which is not possible when non-doped TiO_2 matrices have been used. However, fluorination of the TiO_2 surface is not always effective. For example, in the oxidation of platinum dichloroacetate, benzene or m-xylene, the use of TiO_2 doped with fluoride ions leads to a significant decrease in the reaction rate [3].

Dye impregnation

Catalytic properties of titanium dioxide can be improved by using a dye that strongly absorbs light in the UV-Vis range. In such a hybrid system the TiO_2 grains have been covered with a dye layer. Hence, the system modified in that way includes two cooperating photosystems: one located in the TiO_2 matrix and the other one in the chromophore system of the dye.

A dye may be incorporated into the TiO_2 matrix immediately during the synthesis (or just before calcination) of TiO_2, however in such a regime the dye may often decompose or change its photoactivity due to chemical alterations. Another method consists in surface-decorating of TiO_2 crystals due to adsorption of the dye from a solution in an organic solvent. This technique seems more safe as far as the chemical stability of the dye is concerned [29,30]. Yet another methods involve mixing of the TiO_2 and dye powders followed by homogenization of the blend using a ball mill [29,30].

It turned out that phthalocyanines, synthetic analogues of the porphyrins, are well suited for this purpose. The phthalocyanine molecule, H_2Pc ($Pc = C_{32}H_{16}N_8$ is the phthalocyanine ligand) consists of four benzopyrrole units coupled by azomethine bridges into a characteristic macrocycle. Thus its core constitutes a very stable aromatic chromophore system. Impregnation of the TiO_2 surface with phthalocyanine derivatives or other dyes enhances the lifetime of the electron-hole pairs in the semiconductor matrix (TiO_2), which improves the effectiveness of a catalyst and speeds up the photodegradation process [21,25,27-32].

The effectiveness of such hybrid systems was proved in many studies i.a. photo-oxidation of 2-propanol in gas-solid and liquid-solid systems in the presence of catalysts such as $TiO_2@LnPc_2$ (Ln = Sm, Gd, Ho) [21,25,27-32], involving a microstructural anatase matrix, with grain size over 100 nm. Another example is photooxidation of 4-nitrophenol in the water phase, with the use of microanatase impregnated with lanthanide bisphthalocyanines, $LnPc_2$ (Ln = Nd, Sm, Gd, Ho) and/or metalloporphyrins (containing divalent ions of Mn, Fe, Ni and Cu). It was found that such catalysts may significantly increase the rate and efficiency of the process [21,25,27-32].

Summary

Hybrid systems involving the TiO_2 matrix represent a group of promising photocatalysts for application in photooxidation of organic and inorganic impurities occurring in the natural environment, including phenol derivatives, alcohols and sulfur compounds. It has been proved that doped or impregnated TiO_2 modifications demonstrate a significantly greater potential as catalysts when compared to bare TiO_2. According to literature reports, such catalysts may improve the performance of the TiO_2 matrix and thus the reaction yield by at least several percent, and in some cases reaching almost complete mineralization (80-100%) of the organic substrate [29-32]. Moreover, TiO_2 based systems operating due to absorption of solar light are also possible, which is an additional advantage when regarding the ecological aspect [31,32]. Nevertheless, one must be aware that the applied photocatalyst must be adequately and individually tailored to the compounds to be oxidized and to the reaction conditions, otherwise it would not work effectively. Incidentally, the great number of literature data provided so far may sometimes be confusing, which makes it rather difficult to unequivocally compare the photo-oxidizing power of the proposed systems based on the reported features only. This is mainly because of different methods applied by the researchers when performing the tests as well as in evaluating of their results. And although it seems clear that doping may positively affect the photoactivity of the TiO_2 matrix, one must take account of all external factors (e.g. temperature, pH, minor impurities, etc.) which may be crucial to achieve the maximum desirable catalytic effect.

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A NOVEL MICROBIAL FUEL CELL WITH EXCHANGABLE MEMBRANE – APPLICATION OF ADDITIVE MANUFACTURING TECHNOLOGY FOR DEVICE FABRICATION

Abstract
Research about exploitation the potential of waste and sludge increased drastically in the recent years. One of the most promising alternative methods of waste management is Microbial Fuel Cell (MFC), which generate clean bio-electricity using microorganisms. Organic compounds, sewage, municipal solid waste could be used as a source for microbial nutrition. The construction of MFC is one of the most important parameter in laboratory studies and during scale-up. The efficiency of MFC depends on many factors including type of membrane. To obtain optimization in terms of various operating conditions, a prototype of Microbial Fuel Cell with exchangeable membrane was projected and fabricated by additive manufacturing (AM) technology. This novel device allows to research effects of different types of separator membranes. Preliminary research showed possibility to produce 3D printed MFC systems.

Key words
Microbial fuel cell, microorganisms, exchangeable membrane, bioelectricity, additive manufacturing

Introduction

According to the increasing electrical energy demand, resource limitation and environmental pollution, there is actually common consensus to use renewable energy sources instead of fossil fuels. This has resulted in the emergence of eco-friendly, alternative power source, which are neutral to greenhouse effect. In recent years, an increasing interest in a solution enabling to gain energy and raw material from waste by bioconversion is being observed. Biotransformation is a conversion of organic materials, such as biodegradable waste, into usable products or energy sources. The transformation is possible because of biological processes or agents, such as certain microorganisms, bacteria, some detritivores or enzymes.

Fuel cells are electrochemical devices that produce energy in the form of electricity as a result of a chemical reaction (energy is stored in molecular bonds). Since 1911, when the bacteria that could produce electricity were discovered, interest in this ability and associated technologies, which exploit the electric potential of microbes, has grown [1, 2]. One of the most promising solutions, which makes use of biotransformation, is Microbial Fuel Cell (MFC) [2]. A microbial fuel cell is a man-made biological system in which electric energy is directly produced from biodegradable matter in presence of microorganisms.

In MFCs bacteria or microorganisms are being used as the catalysts to oxidize organic and inorganic matter and generate electrical current [3]. The fuel cell provides the natural environment for biological processes and leads to the necessity for ensuring adequate living conditions for microorganisms. During consumption of feedstock microorganisms produce electrons, which, after being released are thereafter transported to the electron acceptor. Hence, microbacterial energy is directly converted to electricity. Simplified working principle is shown in Fig. 1. Microorganisms grow in the surface of conductive anode in anaerobic chamber. Generated electrons are transported into cathode placed in aerobic chamber. Two chambers are physically separated by membrane, which enables protons movement.

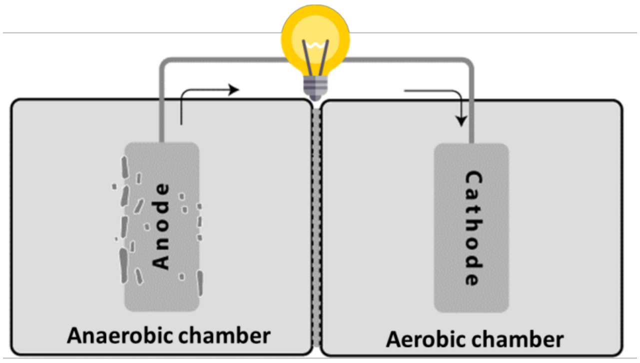

Fig. 1. Operating principle of MFC
Source: Author's

Most MFCs contain a membrane to separate the chambers. In anode compartment, oxidation takes place while in the cathode, reduction process is observed. During oxidation the electrons are produced and transferred directly to an electrode or, to a redox agent. The electron flux is transported to the cathode. By convention, a positive current flows from the positive to the negative terminal, in a direction opposite to that of electron flow [4]. Next steps of the process are presented in Fig. 2.

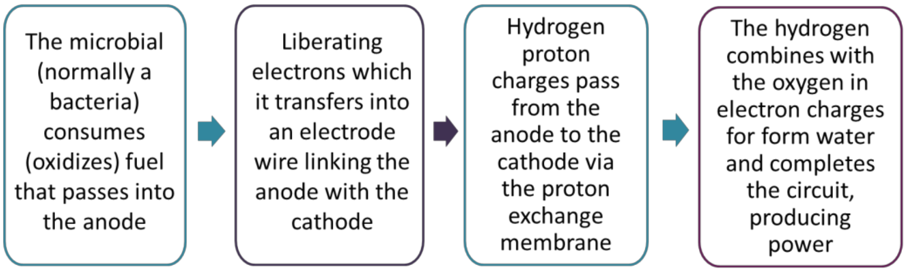

Fig. 2. Process of bioelectricity generation in MFC
Source: Author's

Electrical output is limited in MFCs and one aspect of this limitation might be directly related to the microorganisms that are established on the anode and their extracellular electron transfer efficiency [5].

Many researches about exploitation of MFC in power extraction from wastewater in the form of electricity by the bioconversion process were conducted all over the world. The results indicated that it is possible to realize the electricity generation by MFC. Sludge store nine times more energy than it is needed to their disposal using conventional method [6]. The idea of using microorganism as biocatalyst in fuel cells is not novel, it has more than 100 years old history. Researches on this field were conducted most intensively in the 60s and 70s of the last century [7, 8]. It is extensively thought that efficient production of electric energy using MFC necessitate the addition of expensive exogenous mediators. However, in 1999 a cell which energy was generated by natural existing bacteria, without using additional mediators [9]. The results of this discovery led to renewing the interest in this topic, especially in the face of the need of inventing new, alternative renewable power sources. Therefore, MFC became a promising technology, allowing to gain electric energy [10].

There are different types of microbial electrochemical technologies (MET) - microbial fuel cells (MFC) and microbial electrolysis cells (MEC). MEC is partially reversing the process to generate hydrogen or methane from organic material by applying an electric current.

Efficiency MFC and key parameters - theory

MFC construction

The principle of operating the easiest MFC depends on converted chemical energy, contained in compound, directly to electric energy. It is possible thanks to microorganism oxidizing organic matter in anodic compartment and transferring electron on closely located electrode while protons are being released to solution. This process occurs in anaerobic condition. Electrons are moving to cathode, through external electric circuit. It causes potential difference between anode and cathode and generation of electric current.

Simultaneously protons, generated on anode migrate through semipermeable membrane to oxygenated cathode. On cathode there is chemical or microbiological process of reduction, where protons combine with electrons and oxygen created water [11].

There are many different components of MFCs which are key factors in MFC constructions and operation. Electrodes, wirings, material of cell and size play an important role. Apart from that fuel cells can be classified in two types on the basis of number of compartments or chambers. Anodic chamber contain organic substances that are consumed by microbes, which simultaneously generating electron and proton. Cathode chamber is filled with electron acceptor, which not interferes with microorganisms. According to the upon requirements, the most simple MFC prototype is double or single chambered.

Dual chamber cell was first and the easiest model of MFC. Microbiological cells could function also in other configuration. In view of necessity continuous aeration solution in cathode compartments in order to furnish oxygen for reduction reaction, modification this basic model was started. The main aims of changes were implemented to reduce processes costs and to increase the efficiency of MFC. The one chamber cells have been constructed, in which resigned from membrane separate both electrode and cathode have directly contact with air [12, 13]. In a single compartment MFC System, an anodic chamber is connected to a porous air cathode. Transfer of electron to cathode, separated by gas diffusion layer to complete circuit. This type of MFC is more versatile because of limited requirement of periodic recharging with oxidative agent. Moreover, one-chamber construction ensures flexibility and lower investment costs. Also proposed another cell's configuration: flat [14], cylindrical, tubular [15] or grouped in systems enabling efficient continuous operation of these bioreactors [16]. Introduced difference concerned also way feed cells, for example substratum was doze to anode chamber continuously or in parties [17]. In open sedimentary systems used electrode combination to obtain energy, used to power telemetry device on bottom of sea or ocean [18]. Generally, in double compartment MFC systems consist of an anodic and cathodic chamber separated by proton exchange membrane, which allow proton transfer, while disallow diffusion of oxygen into anode. This type of construction is commonly used to waste treatment in lab-scale evaluation.

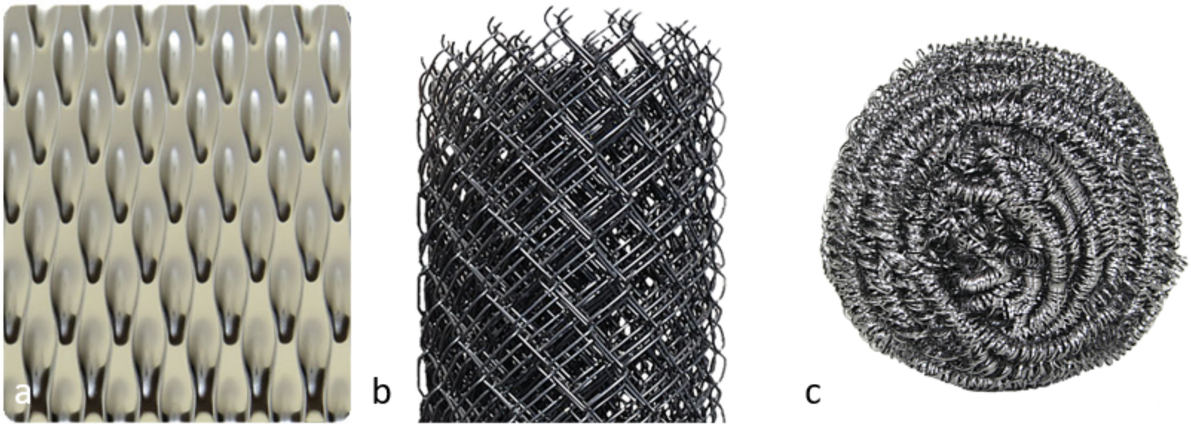

Fig.3. Different type of electrode: a) flat electrode, b) net electrode, c) steel wool electrode
Source: Author's

MFCs are being constructed using a variety of materials, and in an ever increasing diversity of configurations (see Fig. 3). The types of materials applied successfully as MFC's electrodes as well as their architecture details were previously described [19]. During laboratory studies MFC systems are tested under a range of conditions that include differences in temperature, electrode surface areas, pH, type of membrane, electron acceptor, size and operation time.

Microorganisms which produce electricity
Energy production in microbiological fuel cells is possible due to microorganisms, mainly bacteria, which after oxidizing substratum to carbon dioxide while protons and electrons are releasing, transport the latter outside cell. Part of species additionally instead transport electrons on exogenous acceptor, forward it directly an anode. Such a phenomenon is named exoelectrogenesis [20].

Main source of microorganism to MFC is usually rich in microorganism sediments, soil or waste samples. [21, 22]. In addition, attempts are often made to use previously activated sludge derived from plant-based wastewater treatment processes or from other previously operated MFCs [23, 24, 25]. Usually mixed culture of microbes is used for anaerobic digestion of substrate as complex mixed culture permits broad substrate utilization.) . Organic component like: marine sediment, soil, wastewater and activated sludge are rich source of microbes that can be used in MFCs catalytic units. Because of using various type of inoculum in the anode chamber representatives of many species of microorganisms can be found in the biofilm. In addition to the numerous unidentified organisms, are among them bacteria belonging to classes: Alfaproteobacteria, Betaproteobacteria, Gammaproteobacteria, Deltaproteobacteria, Clostridia, Bacteroidetes, Flavobacteria, Sphingobacteria, Deferribacteres, Spirochaetes, Planctomycetes, Nitrospirales [26, 27, 28]. Undoubtedly, the bacteria themselves are used properly in all current MFCs [29].

Diversity of microbial communities within MFC is determined not only by origin of sample inoculum, but also kind of fuel, presence of mediators or oxygen conditions in bioreactor [27]. To avoid compete oxygen with electron carries (mediators), in mostly MFC anode should be placed under anaerobic conditions [26]. In energy generating systems, in precisely anaerobic conditions, Geobacter, pose over 70% of all microorganisms present on anode surface and initially suspected, that this type of bacteria plays a major role in energy generation. But in another MFC, where reactor allows to oxygen leak to anode chamber, dominate organism more tolerant of oxygen [17]. In most case in community of microorganism dominant are representatives of Gram-negative species of bacteria belonging to type Proteobacteria, but species composition and quantity representatives belonging to particular classes is changing depending on inoculum type, using in cell or material from which anode was made [21, 30].

The most effective MFCs utilize multi- species bioanode where microbes have grown as a biofilm [31]. Mixed culture or microbial consortia seem to be more durable and efficient than single strains, which require sterile conditions. What is more isolation of mixture of species from natural sources is much easier and the total cost of the process is lower. There are some regular MFCs designs which explore metabolic tendency of single microbial species to generate electricity, for example: Shewanella species, Pseudomonas species, Geobacter species [32]. The use of pure cultures has also some technical limitations [23].

Substrates

MFCs offer the possibility of extracting electric current from a wide range of soluble or dissolved complex organic wastes and renewable biomass. A large number of substrates have been explored as feed, the pure substances as: glucose, cysteine, ethanol, acetate or mixture of biodegradable organic waste: municipal solid waste, industrial and agriculture wastewaters. The major substrates that have been tried include various kinds of artificial and real wastewaters and lignocellulosic biomass [2]. Substrate is a key factor for efficient production of electricity from MFCs. Dry wastewater and landfill leachates could be also used as an unconventional substrate form bioelectricity generation in MFC.

Membranes

Membrane is one of most important part of a MFC. It allows proton exchange but also separate the aerobic and anaerobic chamber. The main purposes of the membrane: reduce the substrate flow from the anode to cathode chamber, avoid the back-diffusion of the electron acceptor, and increase the efficiency. The membrane should also not allow either gas to pass to the other chamber – this problem is named gas crossover [33]. Splitting of the hydrogen molecule is easier by using a platinum catalyst. However, it is to split the oxygen molecule, and this causes electric losses. Today the platinum is the best option because more appropriate catalyst material for this process has not been discovered.

Many different types of membranes are used in microbial fuel cells. The most commonly used membrane is Nafion – one of proton exchange membrane (PEM), because of its excellent thermal and mechanical stability. Power generation in microbial fuel cells (MFCs) is a function of the surface areas of the proton exchange membrane (PEM) and the cathode relative to that of the anode. Pores in Nafion structure allow movement of cations but the anions or electrons are not conducted. Nafion could be manufactured with much different cationic conductivity [34]. The nanoporous membrane that uses a non-PEM to generate passive diffusion within the cell was recently developed. The membrane is a nonporous polymer filter (polycarbonate cellulose, nylon) which offers comparable power densities to Nafion (a traditional PEM) with greater durability. Porous membranes simplify passive diffusion by that means reducing the power supplied to the MFC in order to keep the PEM active and increasing the energy output.

Membraneless MFCs can deploy anaerobic bacteria in aerobic environments. However, membraneless microbial fuel cells make that cathode contamination contain the indigenous bacteria and the power-supplying microbe. The novel passive diffusion of nonporous membranes allows achieving the advantages of a membrane-less MFC without problems with cathode contamination. What is more, nanoporous membranes are cheaper than Nafion (Nafion-117, $0.22/cm2 vs. polycarbonate, <$0.02/cm2) [35].

PEM membranes could be also replaced with ceramic materials, which costs can be as low as $5.66 /m2. Good transport of ionic species is possible because of the macroporous structure of ceramic membranes allows. The materials used in ceramic MFCs are earthenware, alumina, terracotta, mullite and pyrophyllite [36].

According to the presence of membrane, there have occurred problems such as biofouling, limited proton transfer and high costs of the traditional PEM membranes. To avoid that situation, research by removing the membrane from the MFC is still conducted. There are some experimental data which show that membraneless MFC has high proton transfer rate and lower cell internal resistance. Unfortunately, it is connected with oxygen diffusion in the vicinity of anode, what makes that CE of the MFCs is dropped off by about 20% [32]. What is more, membraneless MFC leads to assemble biofilms on cathode surfaces which cause that the diffusion of oxygen is limited and by that, reduces MFC efficiency.

There are many advantages of membraneless technology like no membrane internal resistance membrane, no biofouling issues, and lower MFC operational costs. Membraneless technology is not advisable for long term MFC performance because of high oxygen and substrate crossover rate which can result in lower MFC efficiency.

Applications

MFCs have been studied as a renewable energy source. Unfortunately, application of MFCs is actually limited. With further improvements in cost effectiveness, design, and efficiency based on these near-term applications, there is a possibility to scale-up and use MFCs as a renewable energy resource.

Microorganisms could perform the double duty of generating power and degrading effluents in wastewater treatment. Actually MFCs are under serious consideration as equipment to produce electrical power in the course of treatment of agricultural, industrial and municipal wastewater. When microbes oxidize organic compounds in wastewater, electrons are released yielding a steady source of electrical current. If power generation in these systems could be increased, MFCs can provide a new method to makes operating costs of waste water treatment plants lower. Advanced waste water treatment could be more affordable in both industrialized and developing nations. What is more, MFCs are also known to generate less excess sludge if they compared to the aerobic treatment process [21, 22].

To understand and model ecosystem responses, data on the natural environment are required. Sensors distributed in the natural environment could not work without power for operation. It is a possibility to use MFCs to power such devices, in water environments where it is difficult to routinely access the system to replace source of electric. Power densities are lower in sediment fuel cells because of the lower organic matter concentrations and their higher intrinsic internal resistance. The low power density could be offset by energy storage systems which release data in bursts to central sensors [37].

The power requirement for electronic devices has been reduced due to development of micro-electronics and related disciplines. Traditionally, batteries are used to power chemical sensors and telemetry devices, but in some applications replacing batteries on a regular basis is impractical, time-consuming, and costly. MFCs could be a possible solution to this problem. Using self-renewable power supplies, which can operate for a long time using local resources could be promising application of MFCs. Researchers should focused on selecting suitable organic and inorganic substances that could be used as sources of energy [38].

Another potential application of the MFCs is to use it as a sensor for pollutant analysis and in situ process monitoring and control. Biological Oxygen Demand (BOD) is the amount of dissolved oxygen required to meet the metabolic needs of aerobic microorganisms in water rich in organic matter, for example: sewage. The correlation between the concentration of assimilable organic contaminants in wastewater and the coulombic yield of MFCs makes MFCs possible to use it as BOD sensors. An MFC-type BOD sensor could be kept operational for over five years without extra maintenance, longer in service life span than different types of BOD sensors [39].

MFCs operating on organic waste could be an interesting alternative for hydrogen production. In such devices, anaerobic conditions are maintained in the cathode chamber and additional voltage is applied to the cathode. According to this, protons are reduced to hydrogen on the cathode [40].

Project of microbial fuel cell with exchangeable membrane – experimental studies

Up to now much attention has been paid to the improvement of both MFC architecture and component materials to obtain better overall performance. However, there is still lack of knowledge about selection of potentially attractive materials with high surface area for MFC fabrication, as well as novel techniques for rapid and stable prototyping and manufacturing. Many studies published to date concern bioelectrochemical systems (BES) made out of mainly Plexiglas or glass. On the other hand, only a small part of available data was obtained in systems built from other casings like nanocure, polypropylene or polycarbonate, which seem to be very promising due to their structural properties. Thus, there is still a research gap for experimental work with thermoplastics that could lead to developing novel and much more beneficial solutions in the field of BES constructing. As it was mentioned above the performance of MFC depends not only on both electrodes materials and characteristics (e.g. surface area, conductivity, chemical stability and biocompatibility), but also on the geometry of the system, and on the internal surface of the bioreactor. Thus, in the last decades engineers made the effort to improve and simplify the fabrication procedures. The usage of popular glass or Plexiglas materials for building the MFC devices limits significantly the range of possible shapes and incorporating more detailed, small-scale elements into the outer packaging. Moreover, the process of manufacture is much more laborious, time-consuming, expensive and requires very precise work. Therefore, a completely new approach based on the Additive Manufacturing (AM), also named 3D-printing, has been proposed and tested within this work. It has already been examined for medical applications (implants, tissue engineering), building industry, wind turbines designing and fabrication etc., where it ensured lots of improvements, also from economic point of view. AM techniques can be applied for fabrication of a MFC that can promote biofilm formation. Such casing does not contain any other additional elements like clamps, screws or clips. It also does not require gaskets or sealants preventing from leakage that are common in BES made out of e.g. Plexiglas. The need for assembly can be reduced or even eliminated and the unit can be rich in micro-details and thus very complex and intricate. High degree of design freedom, utilizing flexible, thermo-plastic materials (filaments) allow to precise manufacturing of bioreactor surface with a high surface area and with a variety of shapes and sizes.

Objectives

The usefulness of 3D-printing technology and wide range of its capabilities for monolithic MFC fabrication will be demonstrated. Only a few papers [41, 42, 43, 44] propose utilization of 3D-printed bioreactors or their components instead of the classic, Plexiglas or glass devices. AM offers the ability to produce complex geometries at relatively high speeds. Taking into account the multitude of benefits offered by AM in terms of fast and precise designing and production process, such technique should be considered as a most perspective in the near future. The process of system designing and optimisation can be facilitated and improved by the use of 3D-printing, through elimination of the need for costly assembly and multi-part, time-consuming production. Moreover, it offers also a significant degree of design freedom and eliminates human errors. By changing the design parameters of each component such as surface area, shape, printing resolution, thickness and extent of filling, the structure of printed device can be easily manipulated and, in consequence its performance can be quickly improved. This is a great and general advantage of applying 3D-printing technology for MFC fabrication.

The aim of this work was to:

- Design Double compartment MFC consist of anode and cathode parts, physically separated by a membrane with movable module for exchangeable membrane.
- Apply the AM technology for MFC fabrication.
- Conduct an experiment and confirm the potential of 3D-printed MFC for the lab-scale experiments.

Design of MFC and printing procedure

Simple model of double compartment MFC was designed using Solidworks software. Size of the designed bioreactor: 120 mm x 92 mm, size of membrane: 90 mm x 80 mm.

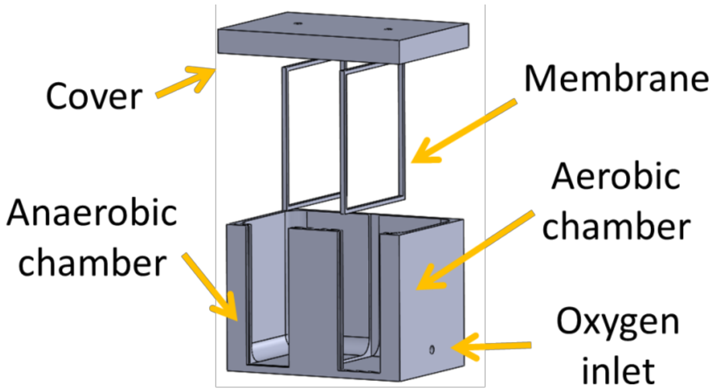

Fig. 4. Design of MFC with exchangeable membrane
Source: Author's

The model was printed with 3 D printer Zortrax M200®. Due to its unique characteristic (i.e. easy to mould, light and strong) High Impact Polystyrene (HIPS) dissolve-able filament was chosen as a coating material for MFC fabrication. HIPS is a low cost, tough plastic that is easy to thermoform and fabricate, often used for countertop point of purchase displays and indoor signs where ease of fabrication is essential. It is a thermoplastic suitable for making high quality, lightweight parts. It is soluble in D-Limonene which makes it the ideal support material. The 3D printed MFC was prepared in organic solvent before the experiment. The method of attachment membrane is shown in Fig. 5. Membrane is inserted between two frames and this module is put in special, thick channel. Good fit ensure tightness system.

Experimental methodology and first test results

Anaerobic chamber contained steel wool as an anode and sewage sludge (500 mL) from wastewater treatment plant was used as source of microorganisms. Aerobic compartment was filled with tap water (500 mL). To obtain aerobic condition the air pump was used. The chambers are physically separated with self-made agar membrane. The microorganisms were fed with 10% solution of acetic acid (2 mL).

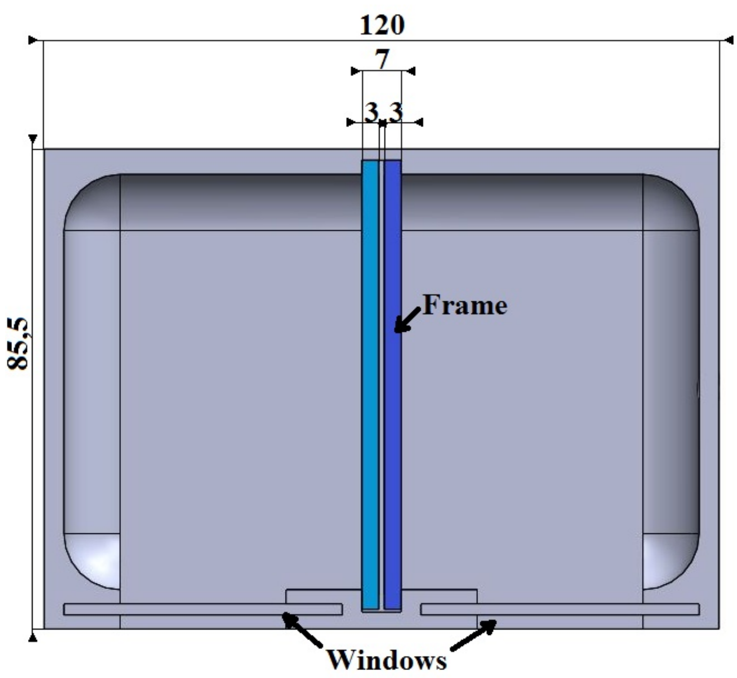

Fig. 5. MFC's view from above
Source: Author's

Experimental system consisted of: 1 - multimeter (VOM), 2 - 3D printed MFC, 3 - air pump is shown in Fig. 6. Voltage generated by microorganisms was measured and saved at the same intervals of time.

As it can be seen from the Fig. 7 the performance of MFC system was quite stable during the experiment. The highest voltage was observed at the beginning of the test (20^{th} measurement). No leakage from the device was noticed and the structure of the HIPS casing seemed to be unaffected by the introduced media. Such positive results may let to the conclusion that AM technique could successfully be applied for easy and quick fabrication of MFC for the lab-scale experiments. The next step of the study should be focused on improving the performance of MFC by its structural modifications (e.g. changing the internal porosity).

In AM technique a degree of surface modification depends on the resolution of the printer (dozens of micrometers) and the thickness of the print layer (as standard 0.4 micrometers), what allows for obtaining rough and porous structures. This can promote the formation of biofilm and the high retention of biomass in the bioreactor will be achieved. Also, the development of biofilm can eliminate the biomass wash out. Another very important issue for investigation will be to find the best thermoplastic materials for such application, which should be resistant to the aggressive media, safe for the microorganisms and durable for long-term operation.

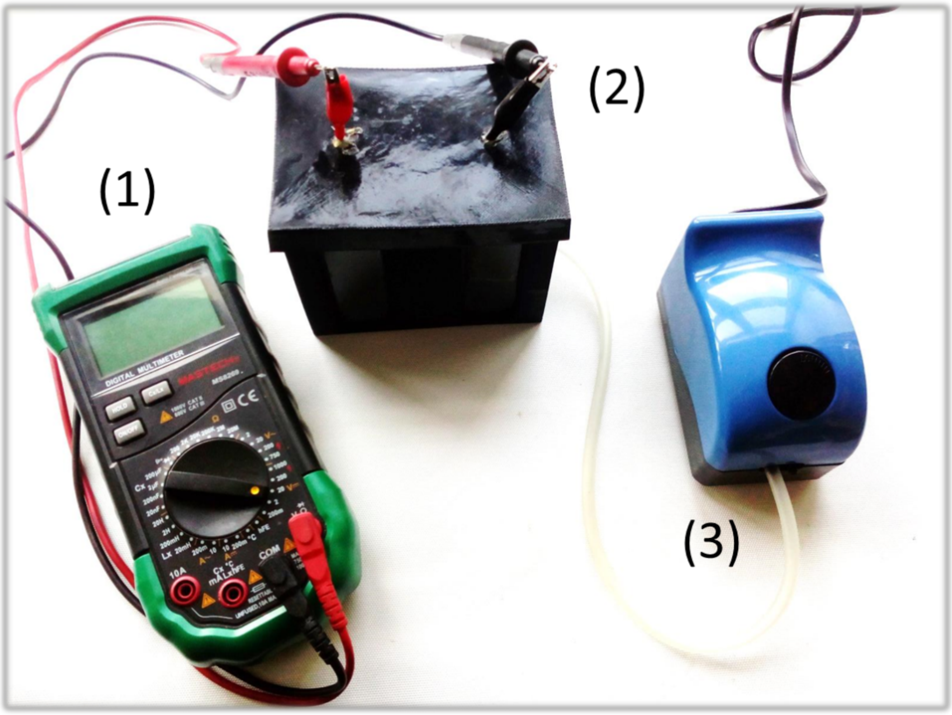

Fig. 6. Exemplary experimental system: (1) Multimeter, (2) 3D printed MFC, (3) Air pump
Source: Author's

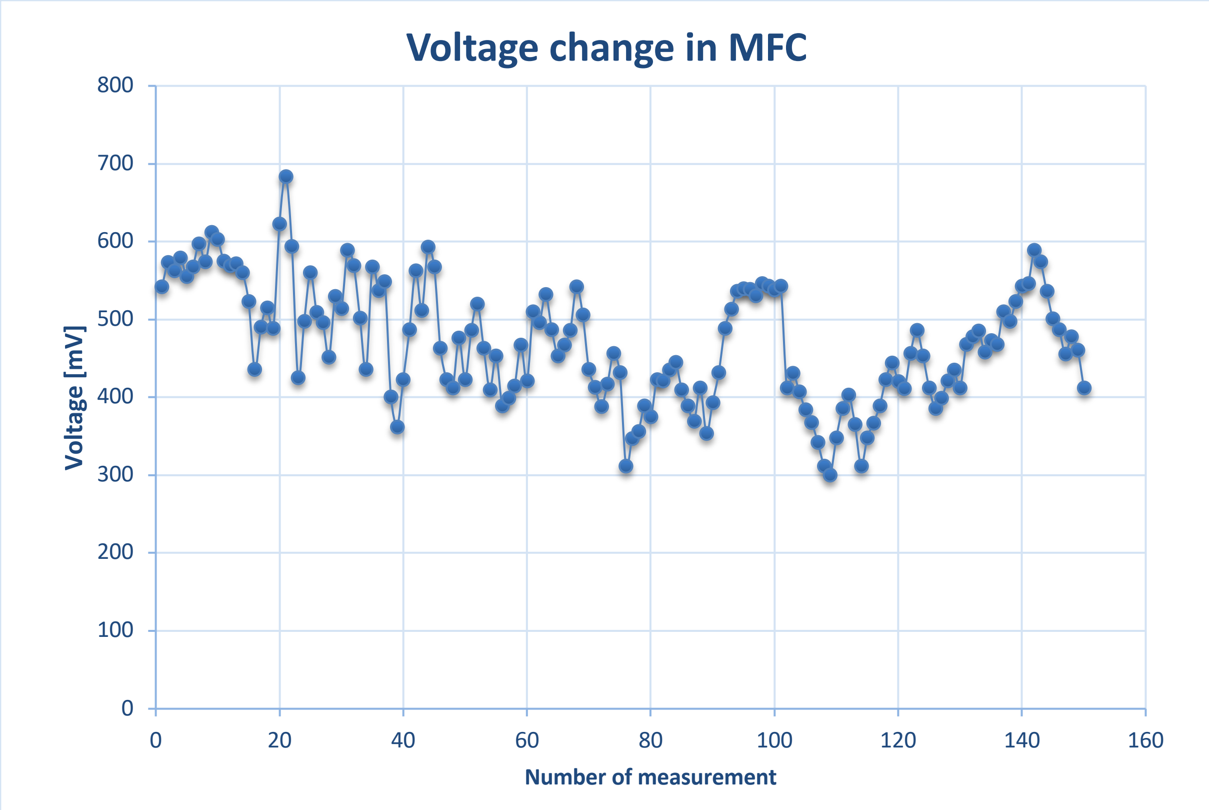

Fig. 7. Changing voltage in time
Source: Author's

Summary
There are still many challenges in bioelectricity generation. Because of the promise of sustainable energy generation from different substrates such as organic wastes, research has been intensified in this field in the last few years. The power from MFC is unstable and depends on pH, temperature, types of microbes, composition of feedstock, toxic substances and type of construction. MFC could be also used as biosensors and to produce secondary fuels (like hydrogen). The high potential hidden in waste could be used as a limitless source of energy. The proposed MFC 3D printed system with exchangeable membrane allows increasing the opportunities to research about different types, material and size of membranes. The size of 3D model could be changed and adjust to every lab test with MFC. Fast and low cost 3D printed technology provides flexibility in shape and size of device. To maximize effective specific surface area of anode, steel wool was used as a support for growing biofilm. The module where the membranes are placed enable to research the same conditions in MFC with different membrane, what reduce variable parameters. Properly selected dissolve-able filament causes stable and easy to operated working conditions. There are still many technical and economic challenges in MFC construction but if microbial fuel cells deliver on their promise wastewater will be waste not longer. In the next three years CBI Pro-Akademia, will have the great opportunity to support this kind of research activities. Within the International M-Era.net Project "BioElectroCathode", 3D printing technology (Additive Manufacturing) will be optimized and intensively developed to fabricate BES for industrial CO2 sequestration. Polish Partners (CBI and Omni3D Sp. z o.o.) together with their scientific partners from Cyprus will design and test in both lab- and semi-industrial scale, novel, memberaneless 3D printed bioreactors to determine their capability for real scale implementation.

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TRENDS IN ANIMAL PRODUCTION FROM ORGANIC FARMING [REVIEW]

Abstract
Organic farming is an alternative method for dynamic agricultural system. Products that are obtained from organic farming are referred to as ecological or organic food [1]. These include products of animal origin that come from organic farming [2]. In the case of animal production in organic farming there are particular requirements for breed, animal welfare and feeding. Additionally, the origins of animals is also of crucial importance since, basically, such animals should be purchased from organic farms. However, there can be exceptions to this requirement, for instance, if the number of animals of a particular species or of a specific breed is not sufficient [3]. The main idea behind organic production is obtaining plant or animal products maintaining good soil structure, clean water and adjusting to the natural rhythm of nature. Enhancement of the social status has led to the situation where consumers pay more attention to the quality and origins of the products they choose. Numerous scientific papers from recent years, based on consumer's opinion, show substantial impact of welfare system on the quality of animal products. Since '90s there has been a systematic surge of interest in products from ecological systems and demand for these, which in turn affect the development of this agricultural sector.

The aim of the work is to compare the changes in organic production over the last 26 years in Poland with reference to the situation in Europe and whole globe. The research has been done on the basis of statistics since 1990 up till now as well as on scientific studies. Nowadays, there are increasing numbers of farms and redirections of production, as well as changes in the sizes of farms producing organic food.

Key words
ecological production, organic, Poland, agriculture, farms

Introduction

Farming has always been one of the most important branches of economy. Yet, apart from its crucial function, which is providing agricultural crops, attention has been shifted to the influence of agriculture on shaping the natural environment. Agricultural work is a significant part of the landscape which consists of soil, water, arrangement of agricultural area or grassland as well as crops which are grown there and animals that are grazed in such landscapes[4]. Principal agricultural system based on dynamic production of agricultural crops, through excessive use of chemical fertilisers and plant protection products, leads to soil erosion, groundwater contamination or decreasing of biological diversity [4,5]. Heavy use of agrochemicals can lead to the decrease in quality of food products and contaminating these with harmful substances. Such contamination may have negative impact on the health of people as consumers. Negative effects of contaminated food are manifested through allergies, weakened immune system or civilisation diseases [1]. This has resulted in the introduction of the principle of sustainable development by many countries, main assumption of which is combining political, social and economic actions with preservation of environmental balance and permanence of environmental processes so that future generations can enjoy the use of uncontaminated environment and natural resources. In consequence of such assumptions an alternative agricultural system was formed, organic farming [4]. In Poland, organic farming is dependent to both the EU legislation and other regulations: e.g. the Polish act on organic farming of 25 June 2009. Important standards are also: the act of December 21, 2000 on the commercial quality of agri-food products and numerous regulations of the Minister of Agriculture and Rural Development. One of the many EU regulations is Council Regulation No. 2092/91/ EEC of June 24, 1991 on organic farming and labeling of organic products [6]. Organic farming is a specific form of management and production. Food is produced based on natural methods, in clean and safe environment, practically without chemical fertilisers, synthetic plant protection products and antibiotics, maintaining complete ban on growing genetically modified crops and feeding animals with feeds that are derived from such crops [7]. Moreover, such management system allows permanent soil fertility, animal health and obtaining products of good biological quality, which, in most cases, are technologically unprocessed [5]. Such products are referred to as organic food [1]. Organic food can be characterised by intensive aroma and taste, extensive freshness and abundance in vitamins and biologically active substances [8]. Negative side that contradicts the demand for organic products is their price which is 30-50% higher when compared with conventional food, yet, consumers are willing to pay more if products are of better quality [9,10].

Since 2000 there has been a growing interest in organic food among consumers worldwide, particularly in Europe and United States. Such situation is an outcome of enhancement of the social status worldwide, rise in consumer awareness of eating healthy and increased care for natural environment and animal welfare. Organic food is becoming more appreciated by consumers and organic farming is currently dynamically developing agricultural sector worldwide[11].One of the most significant institutions responsible for proper development of organic farming is International Foundation of Organic Agriculture Movements, IFOAM, institution, which provides the principles for organic farming: health, ecology, fairness and care. These exact principles are the basis for the Act of 25 June, 2009 on organic farming that is binding in Poland [11].

The present article tries to answer the question: what is the organic farming potential in Poland? That's why, the aim of the study is to compare the changes in organic production over the last 26 years in Poland with reference to the situation in Europe and whole globe.

Resources and methods

Agricultural and Food Quality Inspection (AFQI) is supreme administrative authority that is responsible for creation and execution of domestic system of control overt organic agriculture [12]. AFQI started its activity on 1 January 2003 under the national Act of December 21, 2000 on Marketing Quality of Agricultural and Food Products. International Federation of Organic Agriculture Movements (IFOAM - Organics International) is the worldwide umbrella organization for the organic agriculture movement, which represents close to 800 affiliates in 117 countries. The study has been carried out on the basis of reports on the condition of organic farming in Poland published by AFQI, IJHARS, data from Federation of Organic Agriculture Movements, IFOAM, and other scientific papers. The work presents situations of organic farms in Poland with reference to Europe and the whole world. Changes that have been occurring since 1990 till the present day are compared. The comparison includes data such as: number of organic farms, the size of organic farms, percentage of arable lands of organic farms in total number of agricultural lands in Poland and sale of organic products in Europe and worldwide.

History of organic farming

The beginnings of the development of organic farming in the world date back to 1930s. Pioneers of alternative management on a global scale include Sir Albert Howard, considered as organic farming pioneer, J.I. Rodale (United States), Rudolf Steiner (Germany), Lady Eve Balfour (United Kingdom), Hans Mueler (Switzerland) and many others. It was in these countries as well as in Denmark and the Netherlands that first biodynamic farms were formed [13,14,15]. First organic farm in Poland was formed in 1930 by S. Karłakowski in Szelejewo. War and the period of the post-war hindered the development of other farms in Poland, the emphasis was put on agricultural intensification [8,10]. Return to the idea of organic farming took place at the turn of 1970s and 1980s [8].

Fig. 1. Organic farming logo
Source: [3]

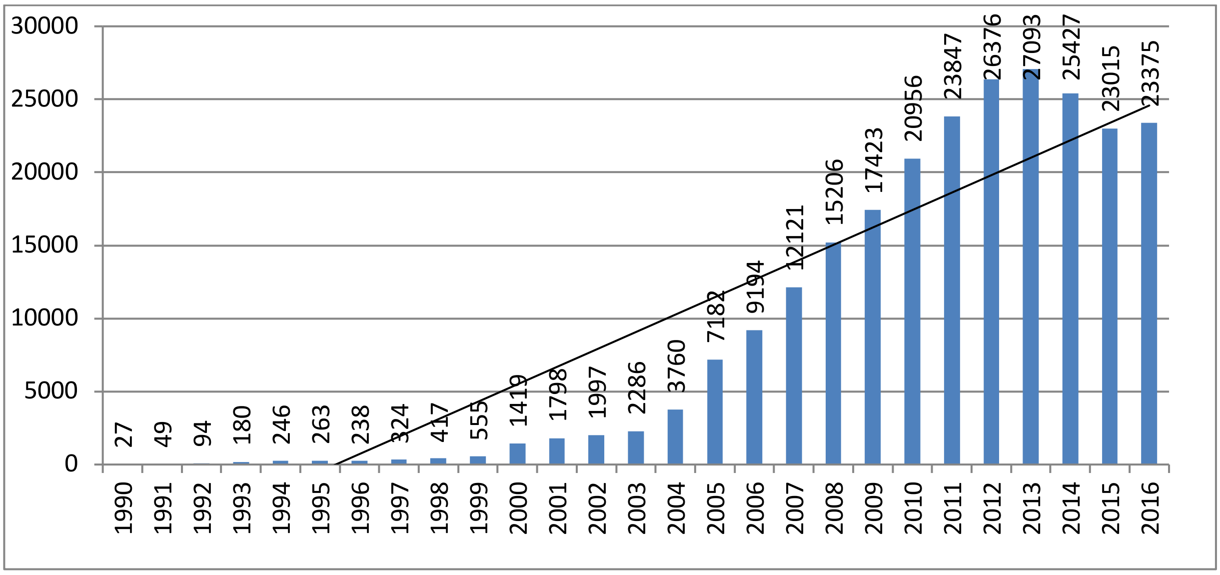

Fig. 2. Number of organic farms in Poland in years 1990-2016.
Source: [19], [21]

The first country to support organic farming politically was Denmark. It was there that first regulations of law, basic production criteria, principles of supervision and certification were introduced. In 1988 in Germany there were first subsidies for organic farmers, subsidies were obtained from agriculture projects within the European Union. It was the introduction of agri-environmental programmes that triggered the development of organic farming in Scandinavia, Italy and Austria [16]. Currently, all norms regarding production, distribution, control and labelling of organic products are determined by Council Regulation (EC) No 834/2007. Legal basis in Poland are regulated under the Act of 5 December, 2014 on amendment of the Act of 25 June, 2009 [17]. March, 2009 was the year of introduction of new logo for labelling organic products. The logo is the official symbol of the EU. It presents twelve stars that form a leaf on a green background (Figure 1.). One colour version is also allowed [18].

Organic farming in Poland in comparison with the situation in Europe and worldwide

In comparison with other European countries, natural environment in Poland is characterised as the one that has favourable wealth of nature, low level of soil degradation and traditional rural landscape [19].The growth of organic farming in Poland traces back to 1990 when a group of farmers started transforming their farms between 1986-87 as well as to the formation of Association of Ecologically Produced Food, EKOLAND, in 1989, association, which in 1990 granted 27 farm certifications [8]. Till 1999 number of farms had been increasing very slowly and reached the maximum with 555 farms which was the effect of low demand for such products. In 2001, in comparison with 1999, the number of farms increased by 224%. Forthcoming Act on organic farming and introduction of subsidies were the factors that encouraged farmers to transform the production, mostly from extensive to organic [19]. Polish and EU integration allowed sales market for products labelled with the "leaf" and granting the financial support for the production which caused proliferation of organic farms in Poland from 2004 till 2013. There were 3800 farms with the area of 82 730 ha when the integration of Poland and EU took place (Figure 1). Introduction of funding regarding organic farming caused dynamic growth in number of farms, yet, it did not affect the production. Part of the farms fulfilled only the basic requirements, usually these were extremely extensive farms, sometimes with any production [20]. In 2013 number of organic farms accounted for 27 093 farms with the total area of 669 969 ha [21].

In 2014 the number of farms dropped by 6.1 percentage points in comparison with the previous year. In 2015 the decrease accounted for 10.48%. However, in 2016, number of organic farms rose by 1.54% and reached 23 375 organic farms with the total area of 536 579 ha in Poland. For comparison, in Czech Republic in 2016, there have been over 4 250 organic farms registered with a total area of over 505 000 ha [22]. In the case of Slovakia there have been over 416 organic farms registered with a total area of over 187 000 ha [23]. Figure 2. depicts a clear uptrend of biodynamic farms in Poland. Based on individual calculations it should be noticed that following the accession of Poland to the EU the number of organic farms rose by more than 6 times whereas the size of organic farms by 6.5 times. In 1990 Poland was the last one to be on the list of largest producing countries of the EU, yet, in 2015 it was sixth. Among the countries that were larger producing countries than Poland were: Italy (52 609), Spain (34 673), France (28 884), Germany (25 078) and Austria (23 070) [19]. Upon data presented by Eurostat, more than 271.5 thousand of agricultural producers were engaged in organic farming in the EU in 2015. In 2010 there were 234.3 thousand of organic farmers in EU. This number rose by 13.7% in EU within the period of 5 years.

Table 1. The changes in the area under faming on the continents and in Poland in 2005, 2009, 2012 and 2015 (A), the numbers are given in millions of hectares and the percentage of the area under organic farming in the total area of agricultural lands in 2005 and 2012 (B).

	A					B	
Continent	1999	2005	2009	2012	2015	2005	2012
Australia	5.3	11.81	12.1	12.6	22.8	2.57	2.88
Europe	3.7	6.76	8.2	11.08	12.7	1.34	2.28
Poland	0.069	0.16	0.42	0.66	0.58	-	-
North America	0.7	2.22	2.5	3.01	3.0	0.57	0.74
South America	1.2	5.06	8.1	6.84	6.7	0.81	1.11
Asia	0.2	2.68	3.3	3.22	4.0	0.2	0.23
Africa	0.2	0.49	0.9	1.15	1.7	0.05	0.11
In total	11.3	29.02	35.1	37.9	50.9		

Source: [20,21,24,25,26,27,28]

In 2010 the highest number of organic farmers fell on Africa (512.67 thousand), then it was Asia (503.86 thousand), South America (272.23 thousand), Europe (234.26 thousand), North America (16.87 thousand) whereas the lowest one on Australia (3.13 thousand) [24]. Though Australia belongs to countries with the lowest number of organic farmers, farmers in Australia have big farms, on average, it's 5611 ha per one farm. The smallest area of farms falls to Africa (2 ha) and Asia (6 ha). Farms in North America are quite substantial in size with the average of 157 ha, whereas the average farm in Europe reaches 36 ha and in South America 30 ha [24].

The area under organic farming in respect of the whole world increased almost four times within the last years. The most dynamic growth, and the most visible one, took place in Asia as the area under organic farming there rose 19 times, as a comparison, in Poland it was more than 7 times (7.4).

The growth of organic farming in Poland was more dynamic than the one in Europe (2.4) or North America (3.3). In Africa, over the period of 7 years (2005-2012), the percentage of the area under organic farming in the total area of agricultural lands rose almost by 55%, which was the greatest change of all, while in Europe by 41%. The least substantial change was noted in Asia.

Changes of the concentration of organic farms in Poland

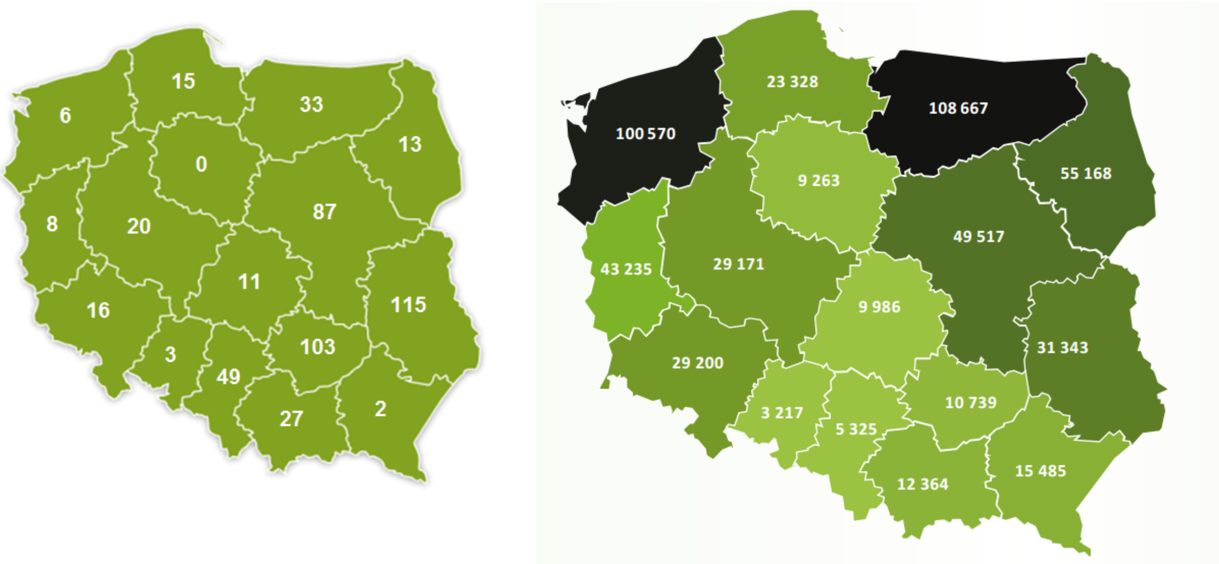

Fig. 3. Changes of the concentration of organic farms in Poland in 1999 and 2016.
Source: [21], [27]

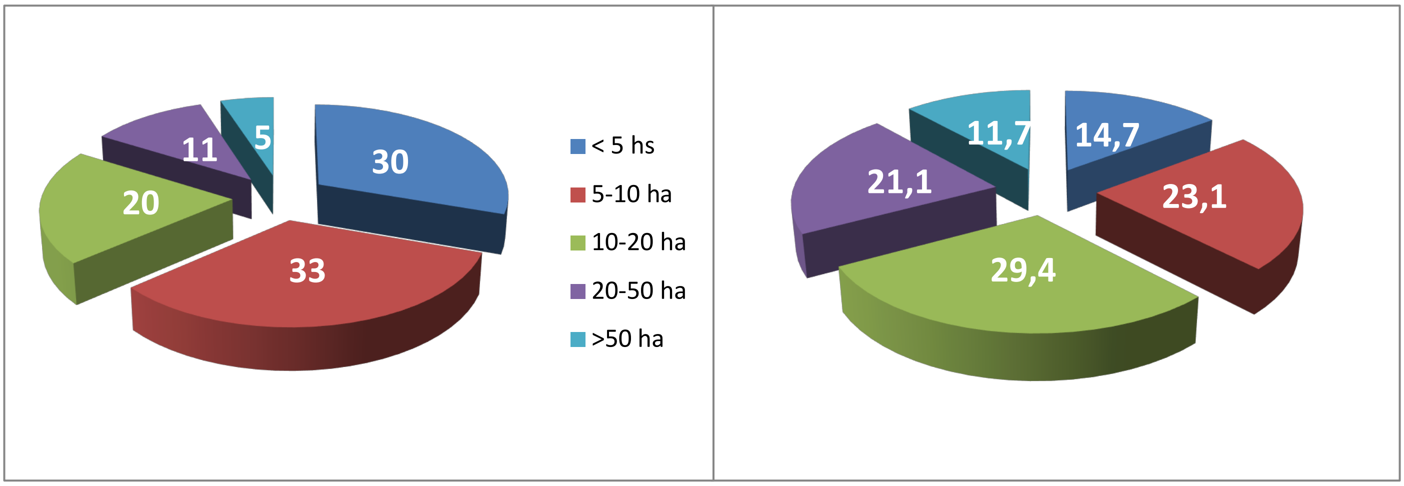

Fig. 4. Changes of the size structure of organic farms in 1999 (left) and 2016 (right) in Poland [%].
Source: [21], [27]

Over the course of the last 17 years the number of organic farms in particular voivodships in Poland has risen. In 1999 there were 555 organic farms, yet, in 2016 their number reached 23 375 farms. In 1999 the highest concentration of organic farms fell to Świętokrzyskie and Lubelskie voivodships (more than 100 farms in each of these). Through these 17 years the rise of consumer awareness, growth of the demand for organic products, providing subsidies for organic farming and the opening of the European market have led to the growth of the number of organic farms. In 2016 the highest concentration of these was found in Zachodniopomorskie and Warmińsko-Mazurskie voivodships and the lowest one in Opolskie and Śląskie voivodships. It turns out that along with the change in number of organic farms there was also the change in arrangement of the size of the area of organic farms. As stated by a lot of authors the factor that resulted in modifications of small unbacked farms in organic farming were the subsidies[20]. Farming in Poland can be characterised by quite a big dispersion of farms; there are mostly farms managed by families, farms which concentrate large number of farmers in general [29]. The size of organic farms is presented on Graph 2.. The right graph depicts the situation of 1999 whereas the left one of 2016. During the period of 17 years, the percentage of small farms decreased by 10 ha, from 63% to 43.1%. Percentage of small farms decreased by 31,5%, while the area of medium size farms (10-50 ha) rose by 63% in relation to 1999. Additionally, percentage of large farms (more than 50 ha) rose from 5% to 11.7%. This constitutes a growth of 134%. What also changed was the average size of organic farms in Poland. On the grounds of individual calculations based on the reports of IJHARS it can be deducted that in 1999 a statistical farm in Poland had the area of 12.6 ha, while in 2016 the area of a statistical farm reached 22.96 ha.

Characteristics of the Polish, European and global market

The growth of number of producers and the area under organic farming are the result of the growth of the demand for organic products. The demand exceeds the supply substantially which stimulates the development of this production method. Possibility to gain higher incomes through redirection of production makes farmers more interested in organic production. Still, this factor is the negative one since by investing in the market an institution very often causes market's misrepresentation [19]. In some cases this provokes starting farms that have no relation to the real production [20]. Organic food market in Poland is developing dynamically though there happens to be inappropriate adaptation of supply to the areas of real demand [17]. Farmers find it problematic to sell the goods that are produced on a small scale and to meet the market demand for the batch size of particular products. Insufficient number of factories that process organic products hinders the sale of such products. It forces farmers to sell their goods at regular prices to factories that are not specialised at organic farming [29]. Despite the obstacles Polish market can be characterised by dynamic growth up to 30% annually. In 2014 it constituted 3% of the global food market. The percentage of Polish organic food in Europe accounts for 5.7% in 2013 [17]. Germany is the leading country of organic products on the European market. In 2012 the sale of organic products there reached 7 040 million euros which constitutes 30% of the total value of turnover in Europe that was estimated for 22 795 million euros. Additionally, in 2017, organic food products generated revenues of about 10.04 billion euros, an increase compared to the previous year at 9.48 billion euros generated [30]. The second place on the EU's list belongs to France (4 004 million euros), then there is the Great Britain (1 950million euros), Italy (1 885 million euros) and Switzerland (1520 million euros). Polish market was estimated for 120 million euros [31]. In 2015 the sale in Europe reached 29.8 billion euros, amounting to the sale of 8.6 billion euros in Germany and 167 million euros in Poland [25]. Growth tendency is also visible on the global market. Following 2000 the value of sales rose by 63 billion US dollars. In 2015 the USA generated 43.3 billion dollars which constituted 53% of the global turnover that was estimated for 81.6 billion US dollars (75,7 billion euros). Figure 3 presents changes in the global sale of organic products. The most dynamic changes and the rise in the turnover of organic products was noted in the first decade of the XXI century. Between 2000-2005 it was 79.8%, between 2005-2010 83.5%, which was the highest one, but taking into consideration recent times the growth of sale was at the level of only 38%.

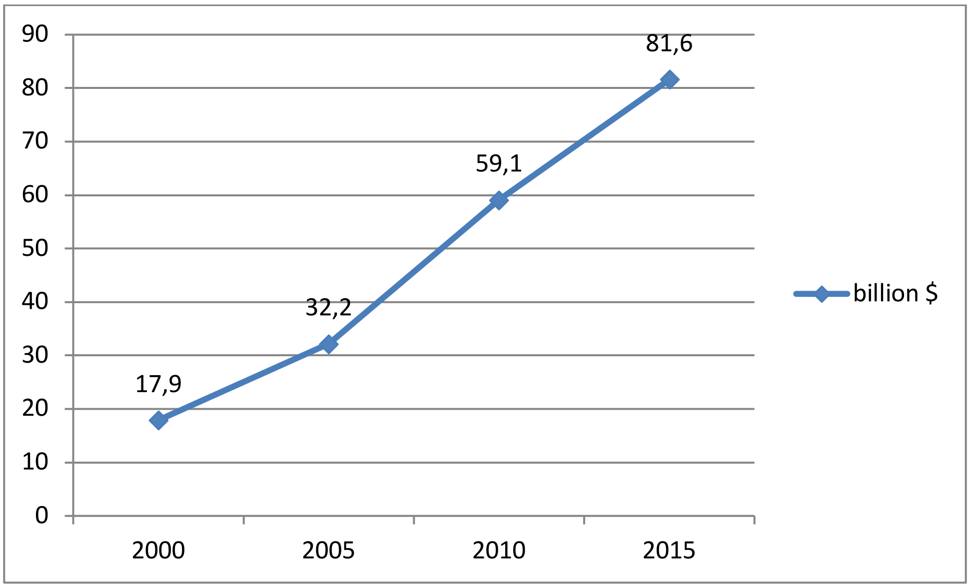

Fig. 5. Growth in organic food and drink sales on the world 2000-2015.
Source: [25]

Summary and conclusions

Organic farming can be characterised as one that has been developing dynamically in Poland, Europe and globally. Organic food market is becoming more and more significant, in 2015 the value of the European market amounted to 29 billion euros which makes 39% of the global turnover. As financial situation gets better, the interest of consumers in organic farming also rises. The factor that proves people's interest in organic products is the ever increasing percentage of sales of organic food. This constitutes great prospect for further development of organic farms in the world. Since 1990 there has been a tendency of growth of the number of organic farms in Poland as well as in the world. Along with the growth of the number of organic farms there is also the growth of the areas of land used biodynamically and their contribution to the total number of agricultural land. Over the course of the last 17 years there has been a change of structure of organic farms in Poland as small farms have been outnumbered by medium size and large farms. IFOAM- Organics International reported [6], that 57.8 million hectares were organically managed at the end of 2016, representing a growth of 7.5 million hectares over 2015; it was the largest growth that have been ever recorded. Which means, that organic farmland increases by 15%. In the case of countries, the largest organic share of agricultural are the Liechtenstein (37.7%) and French Polynesia (31.3%). While, the top 3 countries market in billion euro's: USA 38.9, Germany 9.5 and France 6.7. The highest increase in organic market growth was demonstrated in Ireland - 21.8%. This indicates that the market is still developing, and no a limit to demand has yet been identified.

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ENERGY ANALYSIS OF MUNICIPAL WASTE IN DUBROVNIK

Abstract
In each touristic city waste management system has to overcome the impact of visitors. Dubrovnik, famous as popular touristic destination, particularly notices tourists visiting city. Therefore potential impact of waste management in touristic cities, such as Dubrovnik, is presented. The paper includes estimation of yearly waste production by inhabitants and tourists visiting those city. Waste digestion is a method for biogas production. On the basis of the preceding estimation combined-cycle installation generating heat and electricity is proposed. The model combines Brayton cycle with low temperature Kalina model based on Rankine cycle. Literature analysis presents state of the art in this field. The simulation is prepared in Cycle-Tempo. Numerical analyses lead to technical issues, which have to be taken into consideration during waste utilization with such installation. Thus benefits and threats are discussed. The presented analysis assesses the maximal electric gain, which subsequently should consider waste preparation and purification.

Key words
Waste Management, Kalina Cycle, Brayton cycle, Anaerobic Digestion, Biogas, Asimptote Cycle-Tempo.

Introduction
City of Dubrovnik with ambient surrounding villages is separated from mainland Croatia by Bosna and Hercegovina to which belongs 12 miles of coastline. Thus such area surrounded within international boundaries is independent region. It impacts both politics and economy. The miscellaneous history and Mediterranean localization are appreciated by tourists, thus tourism in Dubrovnik is core of the economy in the city. Dubrovnik with 43 731 residents is a relatively small city. Nevertheless, total number of tourists visited Dubrovnik in 2015 is estimated around 889 700 [1] and around 1 million visitors visits with cruise ships, which berth in port for few hours [2].

Naturally municipal management in the region is also separated from mainland. Influence of waste management in the city is studied. The two waste producers – tourists and inhabitants are taken into consideration. The concentration of touristic demand is noticeable and impact of mass tourism to the environmental infrastructure in this city is burdensome. The paper focuses on the utilization of municipal waste produced in Dubrovnik by anaerobic digestion and biogas combustion in low temperature installation. Simulation prepared in Cycle-Tempo allows to assess the applicability of such bio-gas combustion in cities like Dubrovnik.

Energy industry in Croatia and Dubrovnik
Croatia has considerable green energy production – due to noticeable potential for new renewables country reached balanced electricity production. According to data prepared by Eurostat [3] total Croatian electricity production in 2014 exceeds 4353 ktoe (kilo tons of oil equivalent). The Fig. 1 juxtaposes the changes in electricity production in Croatia. Taking into consideration year 2014 the proportions of primary production are following: crude oil 14%, natural gas 33%, renewables 52%. The share of electricity produced of non-renewable waste is negligible in the country’s electricity mix.

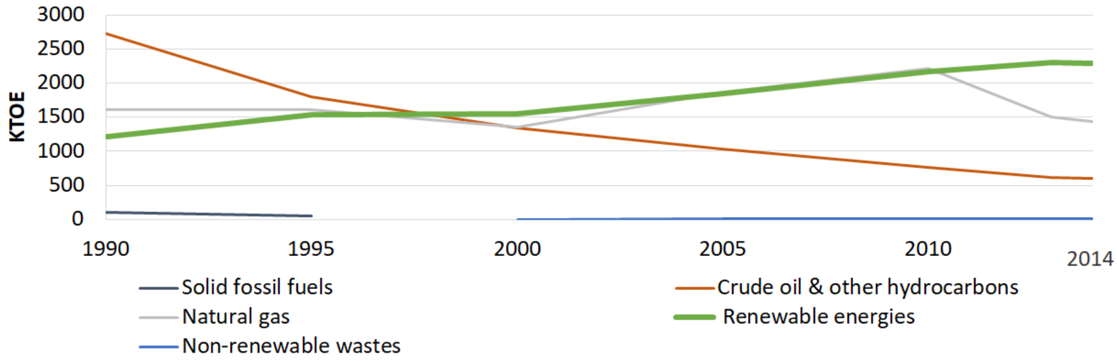

Fig. 1. Primary production of energy resources in Croatia within last 3 decades
Source: [3]

Dubrovnik, similarly to whole Croatia, has high potential for renewables – hydro, wind and solar. Therefore the most significant electricity producers in Dubrovnik area are green installations. Hydroelectric power plant is located on the coast in Plat, 15 km southeast of Dubrovnik and crosses two countries – Croatia and Bosnia and Herzegovina. Power plant is supplied by Bileća lake. Water flows through two 282 m long underground pipelines. Two aggregates with 126 MW of installed capacity each are in the underground engine chamber [4]. There is also small hydro power plant Zavrelje 5 km from Dubrovnik with installed capacity of 2 MW. Hydropower is flexible, but also predictable and reliable. That makes it possible for hydropower to be the regulator that fills the gaps when other renewables can't produce. On the opposite side is wind power, the unstable and unpredictable power source. Sea coast of Dubrovnik has suitable weather conditions for wind turbines. One wind farm is located close to city Slano northwest from city of Dubrovnik. Plant consists of twelve turbines, each 85 m high. Diameter of blades is 103 m. Each turbine has power of 2.85 MW, total 34.2 MW power wind turbines [5]. Krajacic et al. [6] observed that in region of Dubrovnik positive correlation between green production and electricity demand. When production of wind and solar electricity is lower the missing energy is supplied with conventional generation. Municipal waste is potential source of biogas, which is another way of green energy production. In this paper authors propose biofuel production that combustion will give potentially more green electricity in Dubrovnik region.

Waste in Croatia and Dubrovnik

Potentially different waste products could be treated as energy source in waste management system. Two waste sources are considered – solid waste and wastewater. Solid waste management is important issue in the Croatian environment. According to Schneider et al. [7] 3.7 Mt of waste was produced in 2007 in Croatia. Waste is produced in 52% by municipal utilities and in 48% by industry. Omitting segregated waste, production of mixed municipal waste is 393 kg per capita. Unfortunately, the majority of waste is landfilled. Wastewater treatment, during which waste sludge is obtained, is second potential waste source. According to Serdar et al. [8] it is estimated that only about 43% of Croatian population is connected to sewage installation. During standard waste-water treatment process natural sludge is deposited in disposal sites. This solution causes major risks, thus partial industrial utilization is proposed. The capacity of sludge is estimated to 250 000 tons per year [8].

According to David Styles [9] tourists may generate up to twice as much solid waste per capita as local resident. In report presented by Kožić [10] it is estimated that Croatian tourism participates with share of 3.8% in total quantity of waste (tourists produced 63 371 tons of solid waste in 2012) and the share of tourism in water consumption of Croatia ranges from 4% to 5% of total water supply.

The intensive tourism strongly influences the waste management sector in the Dubrovnik region too. Gruber et al. [11] described the waste management in touristic cities on the basis of survey among waste workers. According to the research, the impact of tourism in the city is especially noticeable. Fig. 2 compares the city with other remarkable touristic regions. The result is justified – tourism in such a small city is significantly visible in waste sector.

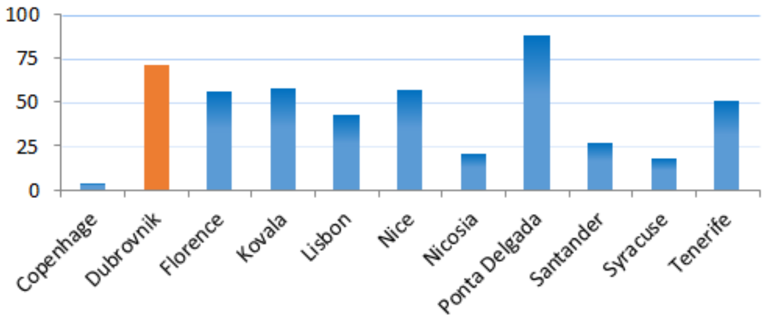

Fig. 2. Waste workers agreeing that tourism influences waste management
Source: [11]

According to data proposed by Nikola Matak [12] in 2015 tourists produced 2 862 tons of solid waste yearly, total disposed solid waste in city of Dubrovnik is 19 035 tons. Thus around 15% of waste is produced by tourist in Dubrovnik region. It is estimated around 2 875 836 m^3/year of wastewater is produced in the city (Table 1).

Table 1. Waste production in city of Dubrovnik

Waste source	**Total**
Solid waste [tones/year]	19 035
Wastewater [m^3/year]	2 875 836

Source: [12]

Waste utilization to produce electricity
Waste such as rubbish and wastewater could be treated as natural energy source. Proper storage conditions allow to produce biogas, that while being burned releases heat, which is utilized to generate energy [13]. The schematic of process is presented below (Fig.3).

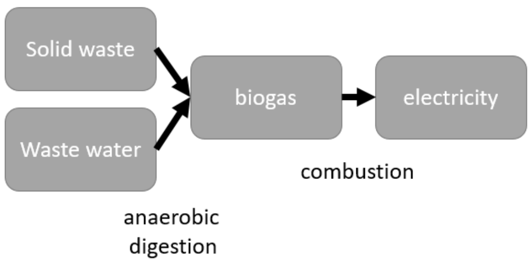

Fig. 3. Schematic of waste utilization be electricity production
Source: [11]

Anaerobic digestion is primary method of utilization products such as plant remains, agricultural products or organic waste. It is natural processes by which microorganisms break down biodegradable material in the absence of oxygen – the amount of organic matter is reduced by extraction of gases. The process intensifies at elevated temperatures, thus external heat source is advantageous. The product of anaerobic digestion is biogas, which in up to 65% consists of methane and other non-flammable ingredients (carbon dioxide, water).

The biogas potential of solid waste depends on the amount of volatile solid. During anaerobic digestion around 0.42m^3 of biogas is obtained by processing 1kg of biodegradable solid [14]. When the content of biodegradable ingredients in waste is 50%, the yield of biogas is reduced to 0.21m^3 per kg. Each 1m^3 of sewage contains around 0.5kg of sludge [8]. Digestion of 1 kg of sewage sludge produces approximately 0.7m^3 of biogas [15]. Biogas extracted during anaerobic digestion of both solid waste and sewage sludge can be used as partial or complete fossil fuel for internal combustion engines and as such, is considered as potential source a renewable energy source.

Combustion is conducted in reciprocating engines or turbines. Thermal energy changes to mechanical power which next is transferred to generator [16]. Turbines have more significant overall efficiency with high output of heat. In reciprocating engines higher share of total production is transformed into electricity.

The potential of anaerobic digestion to produce biogas is presented by Houdková [17] – authors present biogas production in laboratory and next comment potential of biogas utilization and in biogas production for vehicles. Matuszewska et al. [18] evaluated the biological methane potential of various feedstock for the production of biogas to supply engines in agricultural tractors. Otherwise, biogas can feed generators producing electricity in stationary local power plants. Some researchers focus on such waste management – Željko et al. [7] propose energy recovery from waste by creation of waste management centers in regions of Croatia.

Waste digestate is utilized, incinerated or landfilled [15]. Pyrolysis of digestate is one of the utilization methods. Opatokun et al. [19] assessed the energy potential of food waste energy harvesting system. The authors concluded that transitional energy base products (biogas and bio-oil) are generated through the energy harvesting system of food waste, while energy rich solid fuels can be produced through pyrolysis at 500°C. In [20] author propose approaches based on anaerobic digestion and pyrolysis of sewage management.

Assumption of biogas production in city of Dubrovnik

Residents in Dubrovnik produce sewage and solid waste, the utilization of which is a potential biogas source. Paragraph assesses energy production with biogas sources. The two biogas sources are taken into account: solid waste and wastewater (Table 1). Calculation below assesses the maximal biogas availability. In selected applications usage is reduced by the quality of biomaterial and other technics of management.

In the previous paragraph authors assumed that utilization of 1 kg of solid waste has the potential of 0.21 m^3 of waste. Thus the potential biogas production from solid waste produced in Dubrovnik oscillates around 3 807 000 m^3. At the same time 1 m^3 of sewage might be transformed to 0.35 m^3. Therefore potential yearly biogas production from waste water produced in the city oscillates around 1 006 000 m^3.

Energy production correlates with the content of methane in biogas. It can range from 50-75% depending on the substrate and digestion process. Energy content of pure methane is about 9.97 kWh [21]. It is assumed that 1m^3 of waste biogas has a content of 55% of methane that has an energy value of about 5.5kWh [22]. When lower heating value (LHV) of methane is 50.05 MJ/kg the LHV of biogas containing 55% of methane is around 27.52 MJ/kg [23].

Therefore, it can be assumed that yearly estimated total biogas potential is 4 813 000 m^3. Assuming stable electricity supply biogas supply will vary around 0.15 m^3/s. Concluding that energy potential of 1 m^3 biogas is around 5.5 kWh the electricity yield from biogas in Dubrovnik region is around 24.27 GWh per year. It corresponds to 2.77 MW of absorbed energy in the combustion installation. Table 2 summarizes the calculations above.

Table 2. Estimation of energy obtained from waste in city of Dubrovnik

	Solid Waste	**Wastewater**
Yearly waste production	19 035 [t]	2 875 836 [m^3]
Yearly utilization of biogas [m^3]	3 807 000	1 006 000
Estimated biogas potential [m^3]	**4 813 000**	
Potential energy yield [GWh]	**24.27**	
Energy absorption [MW]	**2.77**	

Source: calculation on the basis of [12]

The values above present maximal energetic potential of municipal waste. Authors took all available waste into consideration omitting better techniques of management of selected materials. Another fact is that a certain share of electricity would be spent for the purposes of the preparatory phases, such as energy consuming waste preparation and ashes purification. Authors propose combined installation of biogas combustion – two cycles potentially increase the gain of electricity.

Biogas combustion and electricity generation

Authors propose combined-cycle electricity generation. Firstly, electricity is produced during combustion of biogas in thermodynamic Brayton cycle. In compressor air is compressed, afterword mixed with biogas (fuel) and combusted in combustion chamber. Mechanical work is transformed to generator, exhaust gases power second power cycle. Fig. 4a presents the basic example of biogas Brayton system. To promote electricity generation an additional thermodynamic cycle with its own generator is installed. Heat of exhaust gases causes vaporization of working fluid, which onwards drives turbine. Principle of operation of second cycle is based on vapor Rankine thermodynamic transformations. Figure 4b shows basic example of Rankine turbine. Model consists of evaporator, expander, condenser and pump.

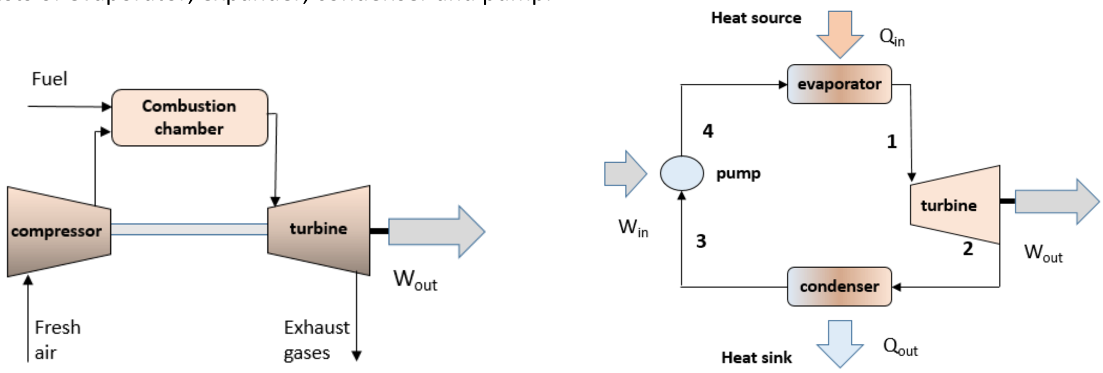

Fig. 4. Schematic of a) biogas turbine in Brayton open cycle b) vapor turbine in Rankine cycle
Source: Authors'

To improve overall efficiency of the system authors propose second cycle with organic working fluid, which may be a mixture of hydrocarbons used in an ORC or an ammonia-water solution used in a Kalina cycle. In the ORC cycle organic low boiling temperature of such working fluid increases ability to transfer heat even from low temperature sources [24]. Kalina cycle bases on mixture of water and ammonia (each of which has a different boiling point) and after evaporator liquid and vapor phases are separated in the separator unit [25]. Basic ORC cycle is simple, on the other side Kalina cycle has better performance and change in the ammonia concentration allows to control by variating the concentration of ammonia [26]. Thus in the simulation Kalina cycle is used, various condensation of ammonia is analyzed in that non-conventional Rankine model.

Simulative implementation

Schematic of biogas combustion installation is presented below (Fig. 5). The model provides a combined-cycle process, that increases share of electricity production in total generation. Firstly biogas is mixed with ambient air compressed by compressor, which is driven by gas turbine connected to generator. Heat recovery vapor generator (HRVG) is a link between the gas turbine and organic cycle. Second cycle is based on Kalina cycle that consists of HRVG as evaporator, turbine with generator, condenser with absorber, pump, recuperator and ammonia separator. Last cycle contains cooling water that condensates organic fluid and which is next relieved outside the system. Table 3 presents the preset values of selected parameters.

Table 3. Values of parameters preset in simulation

Temperature	Value	Apparatus
Biogas flow influent	0.15 m^3/s	4
Biogas LHV	30.03 MJ/kg	4
Combustor equilibrium temperature	1100 °C	5
Isentropic efficiency of turbines	0.8	6, 10
Generators efficiency	0.98	6, 10
Temperature of water/ammonia leaving the HRVG	80 °C	7
Content of ammonia in the cycle	**Defined later**	14
Temperature of cooling water and ambient temperature	15 °C	20

Source: Authors'

https://doi.org/10.32933/ActaInnovations.28.5 • 2300-5599 •

According to calculation above the estimated gross potential of waste production in Dubrovnik is 24.27 GWh which translates to 2.77 MW of power transported with the fuel.

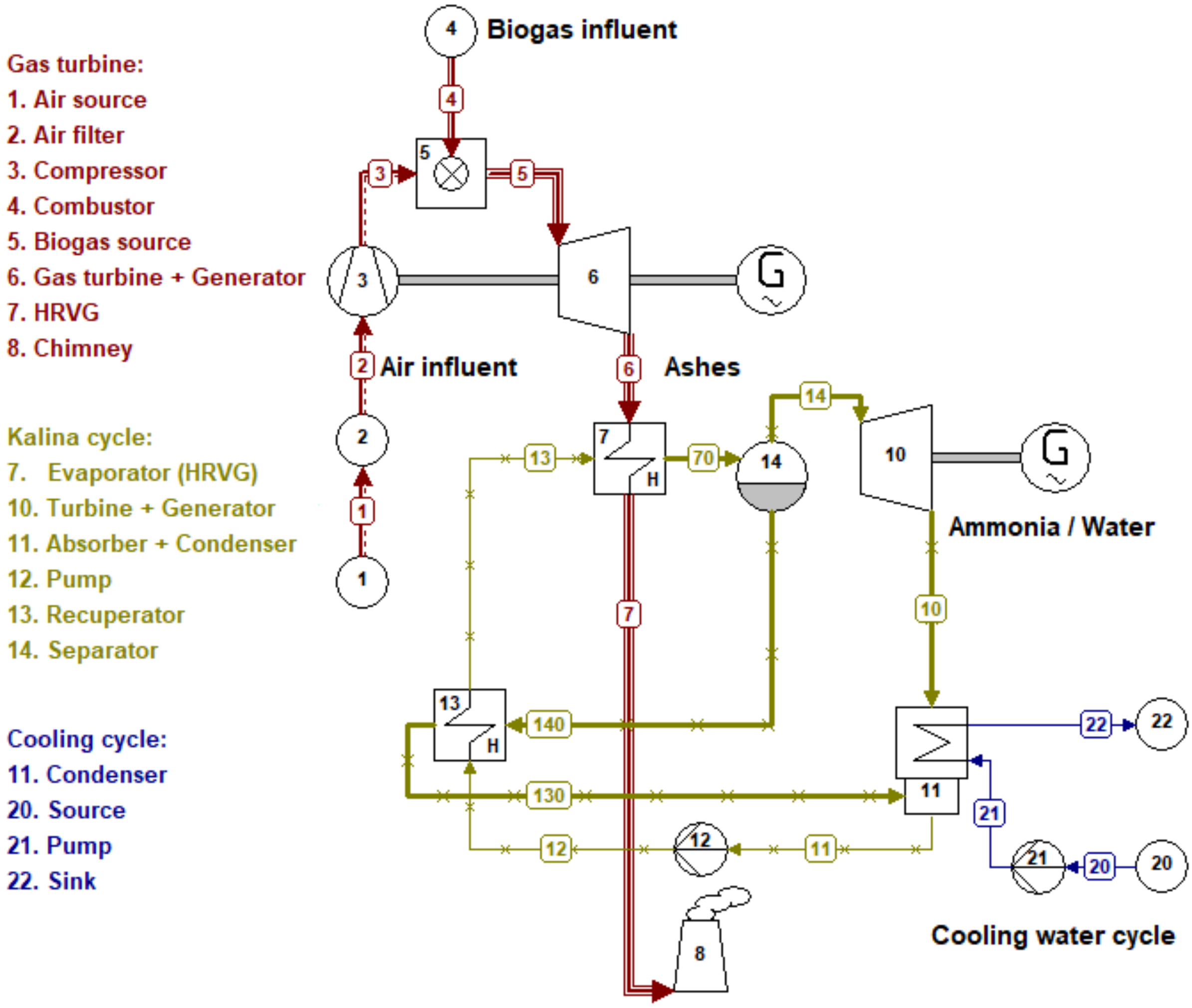

Fig. 5. Model of installation
Source: Authors' model of simulation in Cycle-Tempo

To detect the effectively best efficiency of the system the Kalina cycle was assumed with different amount of ammonia in working fluid. On the basis of Rama Usvika et al. [27] in this analysis authors propose mass content ammonia in working solution between 65% and 75%.

Table 4. State of the model depending on the content of ammonia in Kalina cycle

Cycle	**Parameter**	**The content of ammonia in Kalina cycle**		
		65%	**70%**	**75%**
Main Brayton cycle	Energy delivered with fuel [kW]	2765.52	2765.52	2765.52
	Power recovered by generator 1 [kW]	427.70	427.70	427.70
	Power consumed by compressor [kW]	1582.88	1582.88	1582.88
Kalina cycle	Power recovered by generator 2 [kW]	192.45	280.62	351.07
	Power consumed by pump 12 [kW]	21.58	18.00	15.71
Cooling	Power consumed by pump 21 [kW]	88.01	84.96	82.53
TOTAL	**Gross efficiency [%]**	**22.42**	**25.61**	**28.16**
	Net efficiency [%]	**18.46**	**21.89**	**25.61**

Source: Authors'

The Table 4 presents the results of simulations. Achieved net efficiencies vary between 18.46% - 25.61%. Comparing the simulative results the higher content of ammonia the higher efficiency of the system. The simulative results point that mass flow through air turbine is constant. On the other hand along with increase of ammonia the mass flow in Kalina cycle is lower and less cooling water is expected.

For the analysis the most effective simulation is taken into consideration – with 75% of ammonia in Kalina cycle. Figure below contains Sankey diagram presenting the distribution of energy during the combustion (Fig. 6). The analysis of presented energy balance flow diagram points that the presence of second generator rapidly increases the electricity gain in the installation. Unfortunately, on the other hand Kalina cycle in installation increases the complexity of the system (additional pump uses part of available energy).

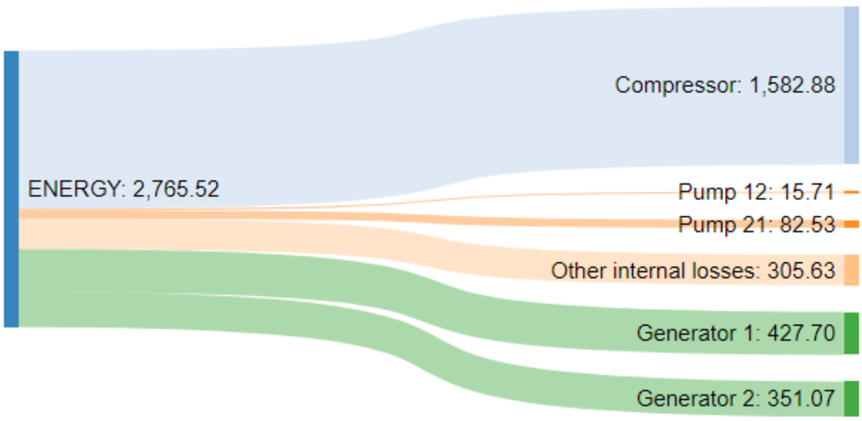

Fig. 6. Energy balance flow Sankey diagram for model with higher efficiency – with 75% of ammonia
Source: Authors'

Sewage processing is energy consuming, so usable energetic yield with installation is reduced by waste preparation and exhaust gases purification. It is worth to add that, some other utilization techniques may be better for selected sorts of waste.

Summary and conclusions

In the touristic cities like Dubrovnik proper waste management is especially worth consideration. Assessments indicate the noticeable impact of tourism on the waste production. The proper environmental politic saves charm of city for both inhabitants and tourists. In the paper the energetic potential of waste produced in the touristic areas like Dubrovnik is considered.

Authors take sewage sludge and solid waste as potential source of electricity. Anaerobic digestion is utilizable way to extract biogas from waste matter. The biogas combustion is proposed to handle with the biogas produced in digesters. The schematic of two stage combined-cycle process fulfilling the expectations is reviewed. Paper introduces to gaseous cycle and Rankine based – ORC and Kalina cycles.

On the basis of available data the assessment of biogas potential is presented – exceeds 4 million m^3 per year. Literature study presents that over 24 GWh of biogas can be achieved. The simulation in Cycle-Tempo estimates the energetic potential of combined-cycle installation – in presented case 2.77 MW of power transported with the fuel allows to generate 0.778 MW of electricity. The calculated value translates to over 28% of energetic gross efficiency. It is worth to add that energetic yield must be reduced by the costs of waste processing necessary to prepare the biogas. On the other hand heat obtained during process might be used in anaerobic digestion tanks.

Acknowledgements

Data from "ESEIA Summer School 2017" in Dubrovnik prepared by Nikola Matak.

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BIOTECHNOLOGICAL RESEARCH IN UKRAINE FOR SOLVING ENERGY, MEDICAL-BIOLOGICAL AND MEDICAL-ECOLOGICAL PROBLEMS IN 2009-2015 TAKING INTO ACCOUNT THE IMPLEMENTATION OF THE ASSOCIATION AGREEMENT WITH THE EU

Abstract
This article summarizes the main results of the biotechnological research of the National Academy of Sciences of Ukraine aimed at solving energy, medical-biological and medical-ecological problems during the period from 2009 to 2015. The prospective bioresources and directions of implementation of the latest technologies of bioenergy conversion for the production of liquid biofuels and expansion of their use for biodiesel were determined. The latest medical and biological and bioengineering technologies for human health and the national economy, biologically active substances for human health, ecological and economic mechanisms of rational use, protection and monitoring of natural resources, new technologies for the efficient use of energy resources were presented in the article. The authors systematized the results of the current research of the National Academy of Science of Ukraine aimed at the development of modern methods for the prevention and diagnosis of diseases in humans and animals, modern methods of cell biotechnology and metabolic engineering for the creation of superproducts of biologically active substances, new forms of plants and microorganisms, the genetic design of improved microorganisms and lines of plant and animal cells for the development of medical and agricultural biotechnology. The authors proved that these directions of research fully correspond to the world-wide trends in research in biomedicine.

Key words: biotechnology, biofuels, medical and biological technologies, medical and environmental technologies, cell biotechnologies

1. Introduction
Biotechnology is one of the priority areas among the wide range of innovative sectors of any developed national economy. Expansion of the practical significance of industry is driven by the social and economic needs of society. Such pressing problems that faced mankind at the beginning of the XXI century, such as a deficit of water and nutrients (especially proteins), environmental pollution, scarcity of raw materials and energy resources, the necessity to generate new environmentally-friendly materials and the development of new methods of diagnostics and therapies, cannot be solved by traditional methods. That is why biotechnological research with the aim of overcoming the energy problem (first of all through the creation and improvement of various biofuels) and the solving of medical, biological and environmental problems are of key importance in the present-day fight against global challenges. The scientific tasks of using biotechnology to solve global problems were studied by Sartakova, O. [1], McCormick, K., Kautto, N. [4], Kudriavtseva, O., Yakovlieva, K. [7], DaSilva, E.J. [8], Voynov, M., Volova, T., Zobova, N. [9], Matyushenko, I., Buntov, I., Moiseienko, Yu., Khaustova, V. etc. [10-18] and other Ukrainian and foreign researchers [2, 3, 5, 6].

2. Methodology
Content analysis and bibliographic retrieval have been used as the main methods of research, which have enabled the making of a meaningful analysis of classic papers and the works of modern economists-

practitioners devoted to the Ukrainian trends in the scientific research of biotechnologies. General scientific methods make up the methodological foundation of the research. They include: description, comparison, statistics review, system analysis and others, which help to characterise the development of this phenomenon in a more comprehensive way. We also apply the methods of dialectic cognition, structural analysis and logic principles that allow the making of authentic conclusions as regards the investigated topic.
Official statistical data of the state institutions and international organizations, publications of reference character, analytical monographs, annual statistical bulletins, World and Ukrainian institutions and university reports serve as the information basis for our research.

3. Results and Discussion

3.1. The perspective of Ukraine's research into biofuel production and application

The process of looking for new ways to use the energy resources of renewable energy accumulated by the living substance through photosynthesis, a biofuel, is of high importance nowadays. Soon, approximately 10% of total energy consumption may be covered by means of the products of photosynthesis. On the other hand, the modern Ukrainian energetics is significantly based on the import of energy commodities – oil and gas, and prices for these are constantly increasing [17].

The leader in solving this problem is Brazil: in this country, the annual production of bioethanol from sugar cane, for example, in 2006, exceeded 150 mln hl. The same amount of bioethanol was produced from maize in 2006 in the USA, but in 2012 the country raised production to about 284 mln hl. Simultaneously developing the manufacture of biodiesel fuel, i.e. biodiesel from rape and soya.

In Europe, the production of biodiesel mainly from rapeseed and soybean oil, and bioethanol from maize and other cereals is ramped up. This is due to certain directives that, on the one hand, contain regulations regarding the mandatory usage of additives to ethanol and biodiesel, while, on the other hand, create the economic conditions favouring the production of these energy sources. In the short term, it is thought that the biofuel share of total fuel consumption will amount to 10% with the further expansion of capacity. Different ways of biofuel generation are being examined. Ethanol generated from cereals is in first position, because average yields of maize, wheat and triticale exceed 80 dt per ha, the second position belongs to ethanol from sugar beet, and third position – to biodiesel from rapeseed. For instance, in France it is planned to triple biofuel production from its primary source in the years ahead and bring it up to 1 mln. 300 thousand tons in prospect. European countries differ in their priorities concerning biofuel production: France prefers maize, wheat, sugar beet; Germany is focused far more on biodiesel from rapeseed.

Sources for biofuel production such as agricultural, food, and forest waste (straw, maize stalks, stems and sunflower husks, sawdust, etc.) are beginning to be used today. Although they are not considered as a top priority, they could become quite an important source of raw materials in the future. Application of raw materials generated from specially modified fast-growing poplar varieties, and new species, particularly, miscanthus, as feedstock for biofuels is gaining in significance. Special emphasis on the use of fast-growing trees is being placed in China.

Taking into account soil and climate conditions in Ukraine, sources of biofuels can be placed in the following order: maize, triticale, wheat, different types of sorghum and millet, sugar beet, sunflower, rapeseed, agricultural and forest waste, miscanthus, poplar, sunflower husk and stalk. Of course, the leader of energy storage per hectare in the Ukrainian conditions is potato, but the problems of storing it until it is processed are not fully solved yet. In Ukraine it is not expedient to use agricultural waste as a feedstock for biofuel so far, because there is a growing deficit of organic matter in soils, and it is better to leave straw, maize stalks, maize and soya tops afield (except sunflower haulm). But in some cases with an excessive presence of waste, it can be processed into biofuels and chemicals.

In addition, until 2007, scientists of the National Academy of Sciences of Ukraine (NASU) already had a portfolio for the improvement and expansion of the raw materials base, the advancement of conventional technologies and the development of their own biofuels based on regional and technological particularities and the creation and enhancement of additives to commercial fuels. Meanwhile, the existing biofuel production in Ukraine is based on outdated and relatively expensive technologies that provide neither adequate costs, nor quantity [13, 18].

Taking into account the necessity of Ukraine to achieve energy self-sufficiency including a significant expansion of alternative fuel application, scientists from the Chemical and Biological sciences Section of the NASU prepared the Concept of the target comprehensive program for scientific research “Biomass as a fuel material” (“Biofuels”) - as provided by the Law of Ukraine “About alternative types of liquid and gas fuels” under the date of 14 January, 2000, № 1391-XIV (1391-14) and in the execution of cl. 4.2 of the NASU Presidium Resolution dated to 12 July, 2006, № 213 (v0213550-06).

According to the Resolution of the NASU Presidium dated 28 February, 2007, № 56, the NASU target comprehensive program for scientific research “Biomass as a fuel material” (“Biofuels”) was approved [19]. This concept indicates that up to 2007, NASU scientists had already performed the groundwork on the improvement and expansion of the raw materials base, advancement of traditional technologies and development of their own technologies on biofuel production based on regional and technological features, the creation and enhancement of additives to the commodity fuels, etc. However, current biofuel production in Ukraine is based on outdated and comparatively expensive technologies that provide neither realistic costs, nor quantity. Thus, the main purpose of the target comprehensive programme for scientific research “Biomass as a fuel material” (“Biofuels”) is to define the priorities in addressing the significant increase in various biofuel production efficiency by expanding the resource base, applying new non-traditional crops and improving the traditional ones by means of breeding and using genomics and biotechnology advances, creating and improving the technologies of biofuels and protein concentrate generation from different cultures and remnants of agricultural and forestry products.

The primary strategic priorities of the programme were: (1) identification of the most promising biofuel sources in Ukraine including non-traditional ones (poplar, willow, miscanthus and other new species); (2) development of production technologies and the main application areas of alternative bioenergy crops as a highly renewable source of energy. Providing consistently high yields of absolutely dry mass (10-20 tonnes per ha which is suitable for the generation of solid biofuels) and technical oil of high quality (900-1100 kg per ha as a source for biodiesel); (3) application of biotechnology and plant genetic engineering to increase production of biofuel raw materials from an area unit with minimal energy consumption and high content of nutrients, and also creation of plant-producers of oils; (4) improvement of technologies for biofuels (biodiesel and bioethanol) and protein concentrates generation out of vegetable feedstock with searching and genetic design of appropriate microbial strains; (5) development of methods for obtaining carbohydrates from dry waste biomass and searching for methods of ethylene generation from biomass (chemical and enzymatic processes); (6) biofeedstock application technologies for biofuel generation together with the creation of technologies for obtaining related organic chemicals (polilaktat, lactic acid, hydroxybutyric acid, glutamic acid, furfurol and furfurol-based products); (7) looking for ways to use the waste and by-products of biofuel production [19].

The most significant results of the programme mentioned above during the years 2007-2012 are included in Table. A.1 of Appendix A [20-24].

The NASU target comprehensive programme for scientific research “Biological resources and the newest bioconversion technologies” for 2013-2017 became a continuance of the research programme on Ukrainian biofuel generation. The concept of the programme was approved by the NASU Presidium instruction dated 20 March, 2013, № 189 [28; 29]. The most crucial results of the programme during 2013-2015 are included in Table. A.2 of Appendix A [25-27].

The mentioned comprehensive programme in case of its implementation will have the following results:

- Involvement of prospective biological resources, development and implementation of the newest bioconversion technologies for liquid biofuel production and expansion of their application;
- initiation of application of the most effective sources of raw materials including unconventional and alternative sources for biofuel production;
- generation of high-quality feedstock from energy-valuable plants including improvement of productivity indicators and alcohol and oil outcome;
- enhancement of quality and quantity content of energy-valuable substances (starch, sugar, oil, etc.) in biofeedstock for liquid biofuel production;
- creating new strains of microorganisms, fungi and algae, as well as expansion of their genetic resource base for the purpose of generation of liquid biofuels;

- improvement and development of the latest chemical technologies and application of new approaches to bioenergy conversion;
- development of the technologies of fatty acid chemical transformation into oils to produce biodiesel;
- improvement of existing and the development of alternative technologies for the generation of the fuel components necessary for biofuel production;
- utilization of agricultural, forestry, food processing and household waste as raw materials for biofuels;
- practical use of biofuel production by-products and waste;
- comparative analysis of different sources of bioenergy feedstock by taking into account their cost, environmental safety, and the possibility of obtaining additional useful products.

The reform and modernization of the energy sector in Ukraine is a challenge of the highest priority for both economic and geopolitical reasons. In the Agreement on the Association of Ukraine with the EU, two separate sections are devoted to energy issues: one section deals with trade issues, and the other concerns enhanced partnership in the field of energy policy. In both,, reference is made to the Treaty establishing the Energy Community, which Ukraine joined as a full member in 2011 after the accession of Moldova in 2010. This Agreement provides for cooperation general terms, in essence, on the whole range of energy policy issues, including policy-making strategies, crisis management mechanisms, modernization of infrastructure, energy security, energy efficiency and energy conservation, as well as support for the development of renewable energy sources. Annex XXVII of the Agreement lists a large number of legislative acts of the EU and timetables for their "gradual adoption" by Ukraine. They cover the main provisions of the Treaty establishing the Energy Community, the deferral of which is not allowed. For other laws, the implementation period varies from two to eight years [37].

The Draft Energy Strategy of Ukraine, that was developed within the framework of the implementation of the Association Agreement, explains the energy intensity of the country's economy by a significant proportion of energy-intensive industries within the structure of GDP, the low energy efficiency of energy-transport sectors (for example, thermal energy generation, transportation and distribution of energy) and high energy consumption by households for heating and hot water. The average annual energy consumption in the residential sector is 250-270 kWh / m2, which is almost twice as high as in European countries with similar climatic conditions. According to the Energy Strategy, and in order to reduce energy intensity by 20%, Ukraine will reduce overall primary energy supply by 10% by 2020 (assuming GDP growth will resume from 2017). This should preferably be achieved by reducing gas consumption by 22%. By 2035, the share of renewable energy of the total primary energy supply is expected to reach 20% due to the replacement of coal and natural gas with biomass and bioenergy. It is anticipated that the energy intensity of GDP will fall to the level of 0.12 kg of conventional fuel for every $ 1 of GDP.

In the years 2014-15, radical measures were taken in Ukraine to reform the energy sector, a factor which was a combination of the conditions established by the IMF with regard to providing macroeconomic financial assistance and legal obligations under the EU agreement and the Treaty establishing the Energy Community. As for renewable energy, Ukraine has a comprehensive framework for promoting renewable energy, but they are not yet fully aligned with the obligations under the Treaty. The government has abolished the discriminatory "local component", corrected the legal definition of "biomass" and introduced a number of incentives for the development of alternative heat supply and bioenergy in the country. At the same time, the regulator has reduced the "green" tariff, which led to the emergence of a certain number of lawsuits regarding the claims of investors.

3.2. The main research into the development of biotechnology in Ukraine for the solution of medical-biological and medical-ecological problems

Studies aimed at solving medical and biological problems, as well as problems of interaction between the environment and human health were studied long ago and were presented by several comprehensive research programs at the National Academy of Sciences of Ukraine. For example, within the last 10 years since 2001, a complex scientific research programmer at the National Academy of Sciences of Ukraine "The latest medical and biological problems and the environment of a person" has been carried out and its implementation was completed in 2010 [30-32]. The aims of the implementation of the programmer were: (1) development of the latest medical, biological and bioengineering technologies for human health and the national economy; (2) biologically active substances for human health; (3) human environmental problems. The most significant results of the implementation of scientific projects within the framework of this program for resolving global problems in 2007-2009 are given in Table B.1 of Appendix B [15, p. 448-452; 20-22].

During the continuation of these studies, the Resolution of the Presidium of the National Academy of Sciences of Ukraine dated 07.07.2010, № 222, launched the Target Complex Interdisciplinary Programme of Scientific Research of the National Academy of Sciences of Ukraine "the Fundamental Foundations of Molecular and Cell Biotechnology" for 2010-2014 [33]. Within the framework of the approved Concept of this programme, research was carried out into the areas of modern biology as: (1) a study of the features and mechanisms of the biomacromolecules, supramolecular complexes, subcellular and membrane structures functioning in health and pathology; (2) the development of the fundamentals of molecular and cell technologies for the diagnosis, prevention and treatment of diseases and the genetic improvement of living organisms; (3) the structural, functional and comparative genomics of humans, animals, plants and microorganisms; (4) the creation of biologically active preparations, new forms of plants and microorganisms. The most significant results of the 2010-2014 implementation of this programme for solving global problems are given in Table B.2 of Appendix B [15, p. 437-440; 23-26].

In 2015, the implementation of the new Target Complex Interdisciplinary Programme "Molecular and Cell Biotechnology for the needs of Medicine, Industry and Agriculture for 2015-2019" was launched. The main areas of research in this programme are: (1) studying the features of the transcript, proteome, immune, interactome and metabolome of humans in health and pathology for the needs of personalized medicine and the development of modern methods for the prevention and diagnosis of human and animal diseases; (2) the elaboration and development of modern methods of cellular biotechnology and metabolic engineering for the creation of supporproducers of biologically active substances, new forms of plants, microorganisms for the requirements of medicine and the national economy (particularly for cell and tissue engineering); (3) a target-oriented search for new or modified biologically active substances, the routes and means of their controlled delivery for the creation of the latest therapeutic agents; (4) molecular and genetic aspects of the study of the structural and functional organization of plants' and microorganism genomes as a fundamental component of molecular biotechnology; (5) a genetic basis for the construction of improved strains of microorganisms and lines of plant and animal cells for the development of medical and agricultural biotechnology [34]. The results of the implementation of the programme for solving global problems in 2015 are given in Table B.3 of Appendix B [15, p. 441-442; 27].

The research into medical and environmental problems has been actively carried out over the past ten years by the Division of Chemical and Biological Sciences at the National Academy of Sciences of Ukraine in cooperation with other departments of NASU and organizations of the Academy of Medical Sciences of Ukraine and the Ukrainian Agrarian Academy of Sciences, as a result certain progress has been made in solving interdisciplinary problems [10; 11].

An example of a state programme aimed at solving these problems is the Target Comprehensive Interdisciplinary Scientific Research Programme of the National Academy of Sciences of Ukraine on the problems of sustainable development, the rational use of natural resources and the preservation of the environment for 2010-2014, approved by the Presidium of the NAS of Ukraine dated February 3, 2010 № 31 [35; 36]. The results of the implementation of this programme are: (1) the development and submission to the authorities of the draft Concept and Strategy of the Sustainable Development of Ukraine and the relevant National Action Plan; (2) the development of effective ecological and economic mechanisms of the rational use, protection and monitoring of natural resources; (3) the development of new technologies for the efficient use of energy resources; (4) further development of new and effective functioning of existing facilities of the natural reserve fund, including biosphere reserves.

The Section of the EU-Ukraine Association Agreement on Environmental Protection is extremely ambitious and obliges Ukraine to cooperate on a wide range of issues related to state environmental policy. Ukraine has agreed to gradually synchronise its legislation to EU legislation in the two to ten years period, in accordance with Annex XXIX of the Agreement, which lists the 35 EU directives. They represent the bulk of EU nature conservation legislation and policies, including environmental management practices, air and water quality, waste management, industrial pollution and hazard, nature protection, the use of GMOs (genetically modified organisms) in agriculture and climate change.

In 2015, the Cabinet of Ministers of Ukraine approved 21 Plans for the implementation of 26 environmental directives and regulations of the EU, which define the measures for ministries and departments for timely implementation of EU environmental legislation. These plans are essential for ensuring transparency and effective monitoring of civil society and business representatives' implementation. Thus, administrative planning has advanced fairly, which is the first step of a long process [37].

The Directive on Environmental Impact Assessment Over the past few years, several bills have been registered in Parliament with a view to implementing this directive, but none of them has been agreed for several reasons, mainly because of the resistance of business lobbyists and civil servants who are interested in maintaining the status quo.

The Directive on industrial emissions. Despite the fact that the national legislation of Ukraine partly complies with the requirements of this Directive (2010/75 / EC), much work has to be done to develop the required by-laws and regulations, which are partly covered by technical assistance projects. According to the implementation plan, which was approved by the Cabinet of Ministers in 2016, most of these measures should be implemented during the years 2015-2017.

The Framework Directive on atmospheric air quality. The national legislation of Ukraine is currently partly in line with the provisions of the Air Quality Directive (2008/50 / EC). Nevertheless, the air quality monitoring system needs some improvement, since it was launched more than 20 years ago. The main legislative and institutional measures identified in the Implementation Plan must be completed by 2017. Nevertheless, the technical re-equipping of existing air quality monitoring stations and the development of air quality improvement plans are scheduled for 2016-2019 through the implementation of technical assistance projects.

The Framework Directive on Water Resources. In accordance with the Transposition Plan of the Water Framework Directive (2000/60 / EC), the national legislation of Ukraine should be completed by 2017. Important steps have already been taken with the creation of an interdepartmental working group by the State Agency for Water Resources in 2015. The draft law introducing changes to the text on integrated approaches to water management issues was registered by the Parliament on December 9, 2015, and was approved at the first reading on May 19, 2016.

4. Conclusions

The authors found that implementation of biotechnology in Ukraine results from the urgent need to solve the energy problems and the related medical, biological and environmental problems. The intensive development of biotechnological research is due to the need to increase the competitiveness of domestic commodity producers in the external and internal markets under conditions of deep integration of Ukraine with European countries and implementation of the Association Agreement between Ukraine and the EU.

The authors also found that during the implementation of the integrated programmes "Biomass as a fuel material" ("Biofuels") and "Biological resources and the newest bioconversion technologies" in 2007-2015, scientific institutions of the National Academy of Sciences of Ukraine in order to expand the use of alternative fuels by the use of biofuel continued to work on the involvement of prospective bio-resources, the development and implementation of the latest bioconversion technologies for the production of liquid biofuels and the expansion of their use, improvement and development of the latest chemical technologies for the production of biodiesel, utilization of agricultural, forestry, food processing and household waste as raw materials for bio-fuels.

As for renewable energy, Ukraine has a comprehensive framework for promoting renewable energy, but they are not yet fully aligned with the obligations under the Treaty. The government has abolished the discriminatory "local component", corrected the legal definition of "biomass" and introduced a number of incentives for the development of an alternative heat supply and bioenergy in the country. At the same time, the regulator reduced the "green" tariff, which led to the emergence of a certain number of lawsuits on the claims of investors.

The authors demonstrated that during the implementation of the interdisciplinary programmes of the National Academy of Sciences "Recent medical and biological problems and the human environment" and "Programmes on sustainable development, the rational use of nature and environmental preservation" in 2001-2014, the latest medical, biological and bioengineering technologies for human health and the national economy, biologically active substances for human health, ecological and economic mechanisms of rational use, protection and monitoring of natural resources and new energy-efficient technologies for energy resources were developed.

It was established that during the years 2008-2015 in Ukraine, within the framework of the interdisciplinary programmes of the NASU "Fundamental Foundations of Molecular and Cell Biotechnology" and "Molecular and Cell Biotechnology for the needs of Medicine, Industry and Agriculture", the main research was focused on the development of modern methods of human and animal disease prevention and diagnoses, modern methods of cellular biotechnology and metabolic engineering for the creation of the superproducts of biologically active substances, new plant forms and microorganisms, genetic design of improved microorganism strains and lines of plant and animal cells for the development of medical and agricultural biotechnologies. The indicated directions of research completely correspond to global trends into research in biomedicine.

In 2015, the Cabinet of Ministers of Ukraine approved 21 Plans for the implementation of 26 environmental directives and regulations of the EU, which define measures for ministries and departments for timely implementation of the EU environmental legislation. Thus, administrative planning has advanced fairly, which is the first step of a long process.

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Appendix A

Table A.1. The most significant results of the NASU target comprehensive programme for scientific research "Biomass as a fuel material" ("Biofuels") during 2007-2012

Year	Sector of the programme	The most significant result	Practical utility
1	2	3	4
2007	Sources of biofuel generation and increase in feedstock efficiency	High-yielding varieties of sorghum, sorice (rice and sorghum hybrid), korakan, artichoke, sunflower artichoke with estimated ethanol outcome from 150-200 dal/ha to 450-900 dal/ha were defined	Genetic pool of plants with high oilness and lipid outcome was made up
		The screening of cellulosolytic activity of a wide range of microorganisms strains was conducted, the most prospective ethanol strains-producers were selected	Prospective strains-producers of ethanol were selected
	Chemical technologi-es of biofuels and the generation their by-products	Polymeric membranes that can operate at a temperature of up to 6000C and pressure to 10,0 MPa are manufactured and studied	Polymeric membranes that can operate at high temperature and pressure
		New nanoporous carbon material with uniquely high marginal adsorption capacity as to absorbing benzol pair and reactive isocyanate-acrylate oligomers out of vegetable oils were derived	New materials for generating polymeric materials
		A number of biodiesel samples were synthetized, basic operation parameters for them and a range of new surface-active agents were defined	New samples of biofuels and new substances that are additives to grease
		Parameters of cheap coal-containing high-porous adsorbents out of synthetic resins and fruit pits were optimized, their prototypes were studied	Creation of heterogeneous catalysts for biodiesel synthesis
	Technologies of biofuel production and application	Technical requirements and design documentation on a research plant to produce liquid biofuels and homogenizer-heat-generator were developed; a laboratory-scale plant scheme for biogas outcome and content estimation with co-digestion of various substrates was designed, basic elements of technology and equipment for biogas transport and fundamental construction of vortex burner for simultaneous and separate combustion of biogas and natural gas were developed; technological schemes of electric and thermal power production by gas reciprocating engines on the biogas basis were created	Documentation on a research plant to produce liquid biofuels; elements of laboratory equipment for production, transportation and combustion of biogas; schemes of electric and thermal power production on the biogas basis
		Prototrophic meiotic segregants with higher thermotolerance were generated; they produce 15-20% of ethanol more than output strains and industrial yeasts do	New more productive strains of industrial yeasts
2008	Sources of biofuel generation and increase in feedstock efficiency	13 crop varieties were obtained and their expert examination as bioethanol sources was made	Looking for new varieties-sources of bioethanol
		Highly stress-resistant varieties of non-traditional crops as to Ukraine for biodiesel production, three of them are registered in the State Commission on crop variety testing	Three new crop varieties for biodiesel production
		8 transgenic plants of potato of "Lugivska" variety and 39 lines of high productivity rape were obtained	Plants of high productivity
	Chemical technologies of biofuels and their by-products generation	Microbial strains that are active digestion tanks of carbohydrates (mono- and disaccharides including cellobiose) were discovered among yeast fungi of the Ukrainian collection of microorganisms; yeast promoters induced by ethanol were selected.	Recombinant constructions and strains for application within positive selection of yeast overproducers
		A range of additives of anti-friction purpose for oil lubricants production was synthesized	Rape-oil-based lubricants

Year	Sector of the programme	The most significant result	Practical utility
		Factors that influence structuring active catalyst centres of biofuel synthesis on the basis of smectite-like laminated metasilicates, double mixed oxides, zeolites, and mesostructured silica	Biofuel synthesis
	Technologies of biofuels production and application	A pilot plant for biodiesel production on a continuous basis by means of ethanol reesterification of rape oil on heterogeneous acid and base catalysts was constructed	Pilot plant for biodiesel production
		Rheological charactetistics of a range of fuel blends were determined	Characteristics of fuel blends
		Research into co-combustion in sawdust stream with pulverous anthracite of increased ash content (24-28%) as a natural gas substitute in a steam-generator furnace was conducted	Natural gas substitute in a steam-generating unit
		Two variants of experimental furnace devices for continuous combustion of full straw bales were developed and constructed	Firebox devices for straw bales burning
		Legal and financial tools for stimulation of bioenergy development in the EU and the US were analyzed, the expediency of their implementation in Ukraine was considered. It was defined that the best prospects of biofuel production in Ukraine could be based on lignocellulosic feedstock and technologies of the 2nd generation	Defining the best prospects for biofuel production in Ukraine
2009	Sources of biofuels generation and an increase in feedstock efficiency	One of the biggest Ukrainian collections of power plants was created, it includes 352 taxones (139 oil-bearing, 71 – sugar crops, and 142 – commodity crops for biofuel and biogas production)	Collection of power plants
		A collection of microalgae strains – prospective lipid producers was formed, their molecular and genetic analysis was conducted	Collection of microalgae strains – lipid producers
	Chemical technologies of biofuels and the generation of by-products	The “cytokininoxidase” gen of korakan was identified, it is responsible for higher biomass growth; mutant maize hybrids on the waxy gen basis with changed starch content in seeds for bioethanol production were generated	Genetically modified mutant maize hybrids with a high starch concentration
	Technologies of biofuel production and application	Pilot plant module for biodiesel generation on the solid catalyst basis in periodic and continuous modes was designed and tested	Pilot plant module for biodiesel generation
		Methods of generation of catalyst mixtures nanoclusters inside nanopores of activated anthracite were optimized and recommended for biomass gasification in high-performance membrane reactor	Best practices for biomass gasification
		Biogasoline formulation was developed; a research party of biogasoline E 10, E 80 and E 85 was created on the basis of commodity straight run gasoline, motor petrol A-76, bioethanol and technological agents complying with the State Standards of Ukraine and ISO	Formulation and manufacturing of experimental biogasoline party
		Original diesel fuel was tried with the use of a tractor diesel engine; the fuel was synthesized using the technology of ethanol reesterificatin of rape oil, in mixtures with traditional diesel fuel, its energy and ecological advantages in comparison to oil diesel fuel of premium quality (Euro) were identified	Original diesel oil synthesized from rape oil and mixed with traditional diesel oil

Year	Sector of the programme	The most significant result	Practical utility
		Technological scheme of the biodiesel production enterprises a with capacity of between 8 and 128 thousand tonnes per year	Scheme of the biodiesel production enterprises
		Tyre rubber modificators on the basis of vegetable oil hydrazides were created	Increasing dynamic parameters of tyre rubber
2010	Sources of biofuel generation and an increase in feedstock efficiency	Overview of introduction resources of non-traditional spring and winter crops with a high oil content was conducted	Overview of non-traditional crops with a high oil content
		The most favourable varieties and forms of miscanthus and switch grass for bioethanol production were selected; their genetic pool was created	The most favourable plants for bioethanol production
	Chemical technologies of biofuels and the generation of by-products	Fermentation and the butanol generating process by means of oleic acid that significantly increased yield, volume productivity and the concentration of butanol were optimized	Increase in outcome, volume productivity and the concentration of butanol
		The technology of homogenous-catalytic ethanol reesterification of rape oil for reducing glycerine content and mono- and diglycerides in the mixture of ethyl esters of fatty acids (biodiesel fuel) was improved. The produced fuel overcomes the parameters of petroleum-derived diesel fuel and does not need special adaptation of the diesel engine's fuel system	The obtained diesel fuel can be used on working diesel equipment in a wide range of combinations with petrodiesel
	Technologies of biofuel production and application	Research into the regime of production of liquid motor and power fuels with vegetable-based bio-components was conducted. Samples of biofuel mixtures of traditional motor and power fuels (diesel fuel, residual fuel oil) with bio-components (vegetable oils, biodiesel, bioethanol) were produced.	Biofuel mixtures of traditional motor and power fuels with bio-components
		A laboratory plant of fast pyrolysis for liquid fuel production from biomass was constructed, adjusted and launched	Plant for liquid fuel production from biomass
2011	Sources of biofuel generation and an increase in feedstock efficiency	New varieties of miscanthus and switch grass as sources of bioethanol were created	New crops varieties as a source of bioethanol
		As a result of microalgae molecular and genetic analysis, 7 of the most favourable microalgae strain-producers of biomass were defined	Prospective microalgae strain-producers of biomass
	Chemical technologies of biofuels and the generation of by-products	It was defined that oligomers on the basis of epoxidized oil and trichloracetic acid are self-extinguishing and can be used for the development of self-extinguishing coatings and sealing compositions	Substances for the development of self-extinguishing coatings and sealing compositions
		Improved technology for biodiesel fuel generation on the basis of renewable raw materials base was proposed and the research plant was adapted	Technology and equipment for biodiesel fuel generation
		Technical specifications and provisional technological regulations for the application of *Phospholidin* agent (one of the best polyfunctional additives to lubricating materials) were developed	Technology of the application of *Phospholidin* agent to lubricating materials
		Thermophysical properties of processing under liquid biofuel mixture production based on diesel fuel, petrol, vegetable	Properties of biofuel mixture production

Year	Sector of the programme	The most significant result	Practical utility
		oils, biodiesel, and ethanol	
	Technologies of biofuel production and application	A laboratory plant with a hydrodynamic cavitator for benzoethanol production was constructed. According to estimates, savings of the benzoethanol application for vehicles with spark ignition and electronic control could be 15-40% of operating costs	Plant for benzoethanol production
		The formulation of motor biofuel E 85 was optimized, its research party was made, motor tests were conducted	Research party of motor biofuel E 85
		Effectiveness of co-digestion of humus and ensilage in terms of periodic standing process at a temperature of 35±10C was studied. Biogas outcome and its content under the conditions of digestion of test mixtures with different proportion of organic matter were defined	Technology of biogas generation within co-digestion of humus and ensilage
		The model of biogas extraction with an individual hole and a group of holes was improved, a system of biogas collection taking into account the physical conditions of one of the Ukrainian field test sites was developed	System of biogas collection taking into account the real physical conditions of a field test site
		A mobile test installation was created and experimental research on the limited system of biogas collection was conducted	Research on the limited system of biogas collection
2012	Sources of biofuel generation and an increase in feedstock efficiency	Suitable crops for biodiesel manufacturing and the technology for their cultivation over an area of about 3,000 ha, miscanthus and switch grass varieties for biofuel production in Ukraine positioned on an area of about 180 ha were implemented	Implementation of suitable crops for biodiesel manufacturing
	Chemical technologies of biofuels and the generation of by-products	Method of generation of *Desmodesmus* microalgae biomass	Method of microalgae biomass generation
		Recombinant *Saccharomyces cerevisiae* yeast strains characterized by enhancement of the efficiency of alcohol fermentation were created	New recombinant yeast strains
	Technolo-gies of biofuel production and application	A construction was developed and a laboratory plant for the co-digestion of firm food waste with biofuel generation was arranged. Technological plant of biodiesel fuel generation by homogeneous-catalytic reesterification of oil by ethanol was constructed and approximately 900 kg of the product were produced. The synthesized products have not only ecological indicators, but also energy ones in contrast with the diesel fuel made in Ukraine according to the current State Standard of Ukraine #3868-99	Plants for co-digestion of firm food waste and for homogeneous-catalytic reesterification of oil by ethanol with biofuel generation
		The construction documentation for scientific and technical work "Status of biofuel mixture preparation" with productivity of 1000 kg/hour was created. Construction documentation for a new disk-cylindrical disperser-homogeniser was developed, it is the main working node of the developed plant.The opportunity for launching the scientific and technical work into serial production was provided	Status of biofuel mixture cooking was implemented at "Il-Prom" Ltd. and PJSC Research and Production Enterprise "Bolshevik"
		The first Ukrainian plant for fast pyrolysis of biomass was constructed and pyro-fuel (bio-oil) samples were generated. Recommendations for the engineering of an ablative	Plant for fast pyrolysis of biomass was constructed at the state enterprise

Year	**Sector of the programme**	**The most significant result**	**Practical utility**
		biomass pyrolysis pilot facility were developed	"GreenEnegro"
		Formulation of the biofuel E 85 was optimized, its research part was made, and its motor tests were conducted. It was defined that within engine operation on the basis of E 85, fuel toxicity of used gases significantly comes down in comparison to gasoline. Also it was found that engine efficiency at all the operating modes working on bioethanol motor fuel E 85 is higher than on gasoline	New biofuel E 85 that reduces the toxicity of used gases and increases engine efficiency at all the operating modes

Composed by: [20-24].

Table A.2. The most significant results of the NASU target comprehensive program for scientific research "Biological resources and the newest bioconversion technologies" for 2013-2017 during 2013-2015

Year	Sector of the programme	The most significant result	Practical utility
1	2	3	4
2013	Biological resources and the technological basis for their primary processing	Screening of 87 strains of green algae, potential biodiesel producers, was carried out. Suitability of butanol producers within alternative substrates application was defined, the most effective strain-producer of butanol, C.acetobutylicum IFBG C6H, was deposited	The most effective strain-producer of butanol was defined
	Chemical aspects of the newest bioenergy-conversion technologies	Energy- and resource-saving method of two-stage transformation of triglycerides by means of ethanolysis with the following sulphidizing of higher fatty acid ethyl esters was created. It allows a decrease in the temperature and duration of the process, excludes emissions of hydrogen sulphide and the use of methanol. The synthesized products are toxicological and ecological safe	Designed materials increase friction characteristics and protection properties of lubricants as to ferrous and non-ferrous metals without using corrosion inhibitors
		An effective and stable catalyser ($Cu/Al_2O_3-Cr_2O_3$) for hydrogenation of ethanol-glycerine mixture into propylene glycol was developed. The opportunity of the selective obtaining of glycerine 2,24-trimethyl 1,3-dioxane according to the front-side split conversion scheme is demonstrated	Generation of the high-octane component of gasoline
		It was found with the help of bed tests of ethyl flax-seed oil acids esters on a commercial tractor engine that mixtured fuels (20-60% volume esters) overcome petroleum-derived diesel fuel in terms of exhaust gases and combustion efficiency according to adopted energy-efficient indicators of engine operation	High efficiency fuel mixtures with the use of esters of flax-seed oil acids
	Technical basis for the newest bioenergy-conversion technologies	A pilot facility for liquid pyro-fuel generation by biomass pyrolysis was designed and manufactured. The first series of experiments on fast pyrolysis of crushed wood biomass (sawdust) with bio-oil generation was conducted. The created facility has a productivity of up to 4,65 kg/hour as to feedstock processing with bio-oil output up to 51,3% of the processed biomass weight	Equipment for liquid pyro-fuel (bio-oil) generation

Continued Table A.2

1	2	3	4
		With the help of an advanced and verified thermophysical model, the parameters of biogas generation, filtration, and collection were calculated. A schematic design of the low cost reconstruction of Bortnitska aeration station was developed for the purpose of simultaneous biogas and natural gas burning and enlargement of biogas income to a boiler-house owing to reduction of losses in methane-tanks and gas-bags	Reconstructi-on of the existing aeration plant with simultaneous burning of biogas and natural gas
2014	Biological resources and the technological basis for their primary processing	New genotypes of winter and spring cabbage crops (typhon, rocket cress, camelina, mustard) were created	Genotypes of cabbage crops
		A research short-rotary plantation of fast-growing poplars was developed and prospective varieties for short-rotary plantations were identified	Prospective plants for short-rotary plantations
		New varieties of power plants (forage sorghum, perennial sorghum, switch grass, camelina sativa, winter rocket cress, typhon) and the technologies of their cultivation and application in various fields were implemented in Ukraine	New varieties of power plants
	Chemical aspects of the latest bioenergy-conversion technolo-gies	Laboratory plant equipped with the node of a sharp decrease of operation pressure to the atmospheric one was made; it allows the study of the process of explosive autohydrolysis of vegetable biomass at a wide range of temperatures and pressures.	Research on the process of explosive autohydrolysis of vegetable biomass
		The influence of benzoethanol content on the operational characteristics of a transport engine was discovered. The method of adaptation of an engine to benzoethanol was developed	The most effective engine operation on the base of different mixtures
		It was found with the help of bed tests of ethyl esters of maize oil acids that mixtures of fuels (20-60% volume esters) overcome petroleum-derived diesel fuel in terms of exhaust gas content (content of CO, CO_2, NOX, CH, smokiness) and combustion efficiency	New mixtures of fuel on the basis of maize oil
	Technical basis for the latest bioenergy-conversion technologies	A pilot facility was modernized and a series of tests on the research of fast pyrolysis of sawdust were carried out. The process of pyro-fuel generation from sawdust by ablative pyrolysis in a reactor with a cone-shaped screw was worked out	Process of pyro-fuel generation from sawdust
		A stand for research on biogas and natural gas burning was developed and constructed, the influence of conditions of biogas and natural gas ray mutual bracing was defined. Elements of swirl and hearth burners of simultaneous biogas and natural gas burning for typical boilers were developed	Burners of simultaneous biogas and natural gas burning
2015	Biological resources and technological basis for their primary processing	New varieties with high oil content and hybrids with improved draught, cold and frost resistance, and high crop yield of above-ground mass were created for enhancement of the outcome indicators of biodiesel oil feedstock. Cluster analysis of SSR-locuses of Camelina was conducted, methodical approaches to application of them as molecular-genetic markers for further selection were developed	New varieties with high oil content and hybrids with improved properties

Continued Table A.2

1	2	3	4
2015	Chemical aspects of the latest bioenergy-conversion technologies	Ethyl esters of mustard oil were synthesized with the use of a main homogenous catalyzer, bed tests of the mixtures with oil diesel fuel based on a diesel tractor engine were conducted	New mixtures of biodiesel and petrodiesel
	Chemical aspects of the latest bioenergy-conversion technologies	Optimum temperature and pressure for explosive autohydrolysis of vegetable biomass (maize cobs, switch grass, drooping birch bark, low- and highland peat) were selected in vitro	Optimum temperature and pressure conditions for explosive autohydrolysis of vegetable biomass
	Technical basis for the latest bioenergy-conversion technologies	Technologies of the production of composition granulated peat fuel were developed, allowing an increase in calorific capacity of granulas to 25%, density – to 22%, and a decrease of energy consumption of granulation. Modes of heat processing and composition content of peat and biomass mixture were developed for peat fuel generation with a calorific value of 4800-5000 kcal/kg. A process of pyro-fuel generation out of sawdust by ablative pyrolysis in a reactor wih a cone-shaped screw was worked out	Technologies of production of composition granulated peat fuel of higher calorific capacity and density
	Technical basis for the latest bioenergy-conversion technologies	An automated machine for current definition of benzoethanol content was constructed, allowing an increase in the efficiency of biofuel application in automobile transport, broadening a range of bio-oil mixtures for motor power and reducing the rate of polluting emissions through used gases	Increasing efficiency of biofuel application in automobile transport and a decrease in the rate polluting emissions
		Technical projects on installing two hearth burners to the boiler of Bortnitska aeration station were developed, a working project of the existing burners' reconstruction was implemented	Installation of new burners and reconstruction of existing ones

Composed by: [25-27].

Appendix B

Table B.1. The most significant results of the implementation of the NASU comprehensive program for scientific research "Recent medical and biological problems and the human environment" during 2007-2009

Year	**Sector of the programme**	**The most significant result**	**Practical utility**	**Branch**	**The global problem**
1	2	3	4	5	6
2007	The latest biomedical and bioengineering technologies	The features of changes in the activity of different classes of calcium channels in the primary nociceptive neurons in pain syndromes were determined by the experimental models of the nervous pathology	Features of changes in the activity of calcium channels in pain syndromes	Medicine	Depopulation and the ageing of the population
		The high potential of methylphosphonate derivatives of the 2,814,20 tetraacialix[4]arene as an effective inhibitor of metal-dependent alkaline phosphatase was demonstrated for the first time	Inhibitors of metal-dependent alkaline phosphatase	-«-	-«-

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
		A new diasoxide analog was synthesized and tested	Treatment of cardiovascular diseases	-«-	-«-
		Immunoglobulin against toxoplasma was created and its activity is 1700 international units, that does not change over a period of 6 months	Sustained high-level immunoglobulin against toxoplasma	-«-	-«-
	Biologically active substances	A number of varieties of wheat were identified and they are resistant to the action of the local populations of brown rust, powdery mildew and septoriosis	Disease-resistant varieties of wheat	Agriculture	Food shortage
	Human environment	Floating carriers for the manufacturing of photo-catalysed sorbents with pre-set floatation were created	Purification of natural reservoirs and sewage	Environmental protection	Pollution of the environment
2008	The latest biomedical and bioengineering technologies	Clinical studies of the cardioprotective effect of Epatol preparation in patients with coronary heart disease and detection of an improvement in their condition during the second week of medication administration	Cardioprotective effects of Epatol	Medicine	Depopulation and ageing of population
		A method of synthesis of new segmented polyurethanes that do not cause aortic inflammation was developed	Cardiovascular surgery	-«-	-«-
2008	The latest biomedical and bioengineering technologies	A significant increase in the expression of Ruk/CIN85 in the papillary cancers of the human thyroid gland was revealed.	Makes it possible to consider this adaptor protein one of the markers of tumor growth	-«-	-«-
		The State Pharmacological Center of the Ukrainian Ministry of Health approved the analytical and normative documentation for a substance based on 5-aminolevulinic acid hydrochloride	Photodynamic cleaning of bone marrow autotransplants from leukemic cells	-«-	-«-
		The medication "Diazocid" was obtained and patented, which shows a hypotensive effect without the onset of arrhythmia	Hypotension medication	-«-	-«-
		Composite sorbents of various composition based on the peloid were synthesized and a series of absorption of heavy metals was obtained for them	Composite sorbents	-«-	-«-
		The technology of synthesis of semi-products for separate derivatives of in-dolohinoxaline and naphthalamide has been developed to study them as inducers of interferon and antiviral agents.	Inductors for interferon and antiviral agents	-«-	-«-
		The pre-clinical study of the medication "Metovitan" was completed, the technology of production was transferred to the chemical and pharmaceutical company CJSC "Technolog" (Uman)	Production technology of the medication "Metovitan"	-«-	-«-

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
		A patent for nanobiotechnology for obtaining a bactericidal composition containing marine biopolymers and ultrasound particles of silver was obtained	Nanobiotechnology for the production of bactericidal composition	-«-	-«-
		A test-evaluation of the level of immuno-depression in oncological diseases with the use of native interleukin 12 was developed.	Test-evaluation of the level of immuno/depression in oncology	-«-	-«-
		The technology of production of the ointment Teobon-dithiomycocide was developed and patented	Ointment Teobon-dithiomycocide	-«-	-«-
		Methods for the synthesis of oligoetherbisalicylates and oligoetheres that bind uranium and transuranium elements were proposed	Substances that bind these types of elements	-«-	-«-
		It was demonstrated that a pharmaceutically valuable human α2b interferon can coexist in N.excelsior plants in the context of transient expression	Accumulation of human interferon in plants	-«-	-«-
		The regularities and mechanism of macrocyclic inhibitors' effect of calix[4]arene and tacaliks[4]arene-tylphosphonic acids on the activity of Zn-dependent alkaline phosphatase from shrimp and other sources were investigated	Properties of macrocyclic inhibitors	-«-	-«-
		The effectiveness of antioxidant and antiradical action of a number of medicinal plants extracts under UV irradiation was investigated	Antioxidant and antiradical effects of medicinal plants	-«-	-«-
	Biologically active substances	As a result of selection tests, high protein wheat (up to 17,4% protein in grain) were selected, and they can serve as the source material for the creation of high-quality starins	High-protein wheat lines as a source material for new strains	Agriculture	Food shortage
	The Human environment	An original construction of the electro dialysis concentrator-separator for deep concentration of saline solutions was constructed	Provides efficient treatment of the concentrates of wastewater salts	Environmental protection	Pollution of the environment
		Composite materials based on natural zeolites with high bactericidal and fungicidal activity were suggested	Composite materials with bactericidal and fungicidal characteristics	-«-	-«-
		The efficiency of the purification of rivers and soils from oil contamination with new preparations "Kelan" and "Rod oil", which were created on the basis of active strains of hydrocarbon destroyers, was investigated.	Preparations for the purification of river water, soils	-«-	-«-
2009	The latest biomedical and bioengineering	Genetic constructions were created and they make it possible to express recombinant proteins (TB, human somatotropin hormone, interferon) and separate them from all other components of the herbal extract	Ability to purify protein in one stage	Medicine	Depopulation and ageing of population

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Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
	technologies	For the first time, a visionary sorption matrix for the creation of application composites within immobilized biologically- active complex of Nano silver with an alginate lining based on an activated carbon fibrous sorbent in the form of a material possessing powerful bactericidal properties was developed	Technical specifications for "Silver Carbon Tie Bonding" and "Fibrous Carbon Materials for Bandaging" were developed	-«-	-«-
		A new fluorine-containing analogue of Diazoxid, which acts on heart performance, vascular tone and hemodynamic parameters, was developed.	Low-toxic medicinal product	-«-	-«-
		The semi-industrial technology for obtaining the finished form of "Calmed" and "Calmed M" preparations for the treatment of bone marrow diseases with high specific activity in the normalization of vitamin D, mineral, lipid metabolism and structural and functional activity of bone tissue in alimentary osteoporosis was developed and designed.	The technology of obtaining the finished form of the drugs "Calmed" and "Calmed M" for the treatment of bone tissue diseases	-«-	-«-
		The standard specific immunoglobulin against toxoplasma and specific immunoglobulin against the anti-viral worm virus were developed and tested, and the stability parameters of the standard specific immunoglobulins were identified	Standard specific immunoglobulins against toxoplasma and tertiary sclerosis virus	-«-	-«-
	Biologically - active substances	For the first time, the effectiveness of a biologically active lipid N-stearoylethanolamine (NSE) as an antitumor agent that is capable of inhibiting the growth of the primary tumor individually was proved	Biologically active lipid, which inhibits tumor growth	-«-	-«-
	Human environment	It was found that a stay at a height of 2100 m (Elbrus area) is accompanied by positive changes in the lipid plasma spectrum of blood, a decrease in glucose content, a tendency to normalize metabolic shifts and a decrease in pathological manifestations of volunteers	A beneficial effect on the human body from staying at a height above sea-level of over 2000 meters	-«-	-«-

Composed by: [20-22].

Table B.2. The most significant results of the Target Complex Interdisciplinary Programme "Fundamental Foundations of Molecular and Cell Biotechnology" for 2010-2014.

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
1	2	3	4	5	6
2011	Features of biomacromolecules complexes	The search for inhibitors which will become the basis for the creation of new antibacterial drugs with selective action against pathogenic bacteria were carried out	Antibacterial drugs against tuberculosis and enterococcal infections of a	Medicine	Depopulation and ageing of population

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
			person		
	Molecular and cellular technologies	Prototypes of test systems for DNA-diagnostics of the most common monogeneous hereditary diseases in Ukraine and the genetic factors of hereditary predisposition to stroke development were created	DNA-diagnostics of hereditary diseases	-«-	-«-
	Genomics	Vectors containing the genes of herbicide resistance were constructed	Receiving of herbicide-resistant plants	Agriculture	Food shortage
	Biologically active substances	The laboratory technology for the production of biologically active substances rich in biogenic stimulants from marine raw materials was developed	Biologically active supplements for nutrition and as components of medical preparations	Agriculture Medicine	Food shortage Depopulation and ageing of population
2012	Features of biomacromolecule complexes	Scientific principles for the development of advanced test systems for the diagnosis and treatment of human hereditary diseases, effective delivery systems for targeted therapeutic genes in cells and organs were created	Gene therapy, therapeutic use of stem cells	Medicine	Depopulation and ageing of population
		The research on the improvement of the methods of the target-oriented search of selective biologically active substances has been carried out	Selective biologically active substances	-«-	-«-
	Molecular and cellular technologies	The scientific aspects of new strains of microorganisms and plants producers of drugs were studied	New strains producers of drugs	Medicine	Depopulation and ageing of population
		The work on the creation of the latest biotechnologies in order to increase the productivity of agricultural plants and their resistance to the action of biotic and abiotic factors are carried out	Increase in productivity and sustainability of agricultural plants	Agriculture	Food shortage
	Genomics	The scientific principles of the comparative genomics of plants and animals (including rare and endangered species) were developed	Saving the gene pool and finding new genes	Agriculture Medicine	Food shortage Depopulation and ageing of population
	Biologically active substances	Research into the molecular mechanisms of action of biologically active substances, growth regulators and plant protection products was conducted	Creation of insecticides, fungicides, herbicides	Agriculture	Food shortage
2013	Features of biomacromolecule complexes	A highly expressive producer of recombinant scFv antibodies specific to human protein C has been obtained. Work was carried out to obtain monoclonal antibody-specific human C	Development of the immunoassay method for determining the	Medicine	Depopulation and ageing of population

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
		proteins	concentration of protein C in human plasma		
		The differentiation and integration of neutral stem cells transplanted in the modeling of cerebral ischemic injury in vitro and in vivo were investigated. According to the results of cerebral ischemia modeling, these cells are able to restore the functions of the damaged tissue of the hypocalumand to form synaptic terminals	Use of stem cells to restore the function of the damaged tissue of the hypocalm	-«-	-«-
		Transcriptional studies of proteinurin expression from the PKD1 and PKD2 family in malignant tumors of the stomach were conducted. It was discovered that the level of PKD2 expression in malignant tumors of the stomach correlates with the prevalence and stage of the tumor process, in particular, with the presence of metastases. A test system was developed for differential determination of the level of expression of human mRNA protein kinases using real-time CPCR	Development of a test system for the diagnosis of malignant tumors of the stomach	-«-	-«-
2013	Molecular and cellular technologies	Prototypes of test systems for the determination of the hereditary predisposition to the development of ischemic stroke and the prognosis of the effectiveness of anti-aggregate therapy in specialised health care establishments were established	Development of a prototype test system for the diagnosis of ischemic stroke	-«-	-«-
	Genomics	The use of "vector cells" as a multipurpose tool for changing the microenvironment was investigated	Use of stem cells	-«-	-«-
		Three species of trichinella were identified in wildlife of Ukraine: Trichinella britovi, Trichinella native, Trichinella spiralis.	The first DNA library in Ukraine was formed Trichinella	Agriculture Medicine	Food shortage Depopulation and ageing of population
	Biologically- active substances	The study of the molecular genetic polymorphism of varieties and lines of winter soft wheat was conducted to determine the influence of the Glu-Blal allele on the parameters of baking quality	The ability to quickly differentiate breeding samples of wheat	Agriculture	Food shortage
2014	Features of biomacromolecules complexes	The method of determination of sial-containing receptors on the surface of the influenza virus, herpes types 1 and 2, hepatitis C and HIV in the human and animal organism was developed.	A test system for the diagnosis and treatment of viral infections using	Medicine	Depopulation and ageing of population

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
			molecular forms of sialo-specific lectins as immunosorbents		
	Molecular and cellular technologies	Animal models of brain tumors have been created using cellular lines of glial and non-glial origin.	Ability to use for testing anticancer drugs in vivo to create new drugs	-«-	-«-
	Biologically active substances	The methodology of cultivating the roots of endangered and rare plants, which are used in medical practice was developed. A collection of cultures of isolated and transformed roots of different types of plants was created and analysed	The use of these plants as a potential source of compounds with biological activity	Agriculture Medicine	Food shortage Depopulation and ageing of the population
	Biotechnology	The methodology of cultivating the roots of endangered and rare plants, which are used in medical practice was developed. A collection of cultures of isolated and transformed roots of different types of plants was created and analysed	The use of these plants as a potential source of compounds with biological activity	Agriculture Medicine	Food shortage Depopulation and ageing of population
		The biotechnology of the accelerated production of new forms of wheat was developed for the first time	Wheat with a high-resistance to ophiopoil root rot and water scarcity	Agriculture	Food shortage
		An effective wheat supply system was developed and introduced into production	A power system which provides a grain production increase of 10-15%	-«-	-«-

Composed by: [23-26].

Table B.3. The most significant results of the implementation of the target complex interdisciplinary programme for scientific research "Molecular and Cell Biotechnology for the needs of Medicine, Industry and Agriculture for 2015-2019" for 2015

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
1	2	3	4	5	6
2015	Features of biomacromolecules complexes	A model of perinatal hypoxic-ischemic injury of the brain of animals in combination with inflammation was created	Usage of perinatal pathology of the central nervous system in further studies	Medicine	Depopulation and ageing of population
	Molecular and cellular technologies	Selection of immunophenotypical cell markers was performed	The ability to determine the initial stages of leukemization	-«-	-«-

Year	Sector of the programme	The most significant result	Practical utility	Branch	The global problem
			of bone marrow by various forms of β-cell lymph		
		Considering the presence and nature of the expression of the different diagnostic immunodeficiency chemical markers	Allows you to identify rare cases of leukemia	-«-	-«-
	Genomics	A base of the clinical data of patients diagnosed with chronic viral hepatitis C was created. The diagnostic methods of polymorphism analysis of certain genes were developed and tested	This methods will become the basis of the pharmaco-genetic testing of this disease	-«-	-«-
	Biologically active substances	Modification of the method of determination of cytokillins in micellar biomass of basidial fungi was carried out and data on the content of these hormones in 6 types of fungi were obtained. The most productive strains were determined and the method of drying the mushroom material was introduced	A possible preparation of drugs with high biological activity	-«-	-«-
	Biotechnology	The crossing of winter wheat of the Kuyalnik strain (as a source of extra baking quality of flour) was carried out. The seeds of the second generation and the first backcross generation were obtained	Creation of selective breeding populations	Agriculture	Food shortage
		The method of stepped cell selection yielded callus lines and regenerants of soft wheat of Khutoryanka strain	Wheat varieties resistant to the simulated water scarcity	-«-	-«-
		The prospective strains of grain cereal crops for further selection with a high level of accumulation of valuable human microelements (iron, zinc, manganese, selenium) are determined	New strains of cereals with a high level of trace elements for human	-«-	-«-
		Doses of acute irradiation of medicinal plants' seeds that stimulate the accumulation of biomass and the synthesis of secondary metabolites are determined. Methods of growing these plants, as well as selection and determination of secondary metabolites in medicinal raw materials were developed	Methods of cultivating medicinal plants that cause the synthesis of secondary metabolites	-«-	-«-

Composed by: [23-26].

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METHODS FOR REGENERATION AND STORAGE OF CERAMIC MEMBRANES

Abstract
Ceramic membranes are among one of the most promising candidates for membrane applications, owing to their excellent resistance to mechanical, chemical, and thermal stresses. These advantages make them an attractive filter material. An additional benefit which is extremely important for the industry, is their possibility of continuous operation at high efficiency while maintaining constant transmembrane pressure. Due to the inorganic material from which they are made, ceramic membranes have the possibility of being cleaned by steam sterilization and are resistant to micro-organisms. Although, due to low production costs, ceramic membranes are one of the most cost-effective membrane filtration technologies they are prone to substantial fouling. When used, a layer of contaminants is formed on the active surface, often reducing or completely filling the membrane pores resulting in fouling and concentration polarization. These phenomena cause a decreased efficiency of the process, which leads to the need for the membrane to be replaced with a new one. However, ceramic membranes have the possibility of being regenerated through a series of activities and the use of various chemical agents. The use of regenerated membranes would provide the opportunity to reduce exploitation costs. Although membrane regeneration does not guarantee a return to the initial parameters, it does allow for the recovery of high permeation flow. The aim of the research was to compare operating parameters of the ceramic membranes after multiple use and longtime storage with different condition of storage.

Key words
ceramic membranes, fouling, membranes regeneration

Introduction
Development of separation techniques are extremely important for industries using membranes. Chemical engineering scientists are working on increasing the conditions and parameters of the process. These separation techniques are well adapted to the use of ceramic membranes, which thanks to its features fulfil current needs and are distinguished in the use of available methods. Ceramic membranes remain one of the most promising technologies among membrane processes. This technology has many applications such as specialized wastewater treatment processes or enriching uranium. Ceramic membranes have also been adopted in the food industry to separate proteins and fats in milk and to concentrate fruit juices. Other applications include biotechnology, the pharmaceutical industry, petrochemistry, metallurgy and energy generation [1,2]. Ceramic membranes have many advantages, including durability, chemical stability and resistance to high temperatures. They are used in processes with specific technological requirements where the use of polymeric membranes is impossible [3]. Ceramic membranes allow operations at high flow rates while maintaining constant transmembrane pressure. This technology makes it possible to carry out the process in a continuous mode with high separation ability. Ceramic membranes enable microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) with pores diameters from 0,5 nm to 5 µm [4,5].

Ceramic membranes have a porous, asymmetrical structure. They usually consist of two or three layers of different porosity called the support and active layers. The active layer determines the separation properties of the membrane and is a selective barrier to mass transport. Usually, this layer is covered by aluminum oxide, titanium, zirconium and silicon. Each oxide has a different surface charge, which reacts with other substances. The active layer is applied by dipping the ceramic support elements in a suspension of the above compounds, which are then dried and fired [7]. The support layer is only a carrier that does not affect the separation capacity and is made of ceramic powder that can be pressed and then dried and baked. Ceramic membranes are produced in the form of flat plates or in a single or multi-channel tubular form with a circular or hexagonal cross-section, as shown in Fig. 1. In industry, multi-channel membranes are most commonly used due to their increased effective exchange surface.

https://doi.org/10.32933/ActaInnovations.28.7 • 2300-5599 •

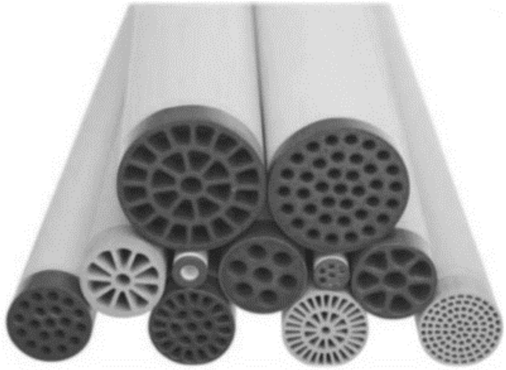

Fig. 1. Examples of single and multi-channel tubular ceramic membranes
Source: [6]

Most often, ceramic membranes are used for filtration in the cross flow mode. This technology is based on a parallel stream feed (tangent to the surface of the membrane), which is separated into a filtrate flowing through the pores (permeate) and a retentate consisting of retained particles. The driving force of the process is the differential pressure placed on the membrane (transmembrane pressure). Ceramic membranes can be used in high-temperature processes (up to 300°C) having extreme acidity or alkalinity. They are more stable than polymeric membranes and their lifetime is much longer [8]. However, their cost is much higher than polymeric membranes. Ceramic membranes are also characterized by high microbiological resistance. Their unquestionable advantage is the possibility of sterilization by means of steam and backwashing. There are two main ceramic membranes commercially available in Europe: Membralox GP (graded permeability) manufactured by Pall Corporation and Isoflux produced by Tami Industries [9].

Unfortunately, as mentioned, the primary challenge for using ceramic membranes is fouling. This results in a decrease in the permeate flow and an increase in the process resistance dependent on the duration of filtration. Fouling consists in the deposition of colloids, salts and particles in the pores and on the surface of the membrane. This can be caused by several factors, including among others, blocking and narrowing the pores (filtration cake), adsorption of filtered substances and concentration polarization [10]. In order to prevent the negative effects of fouling of ceramic membranes, it is recommended maintaining high cross-flow velocities and low transmembrane pressures [11]. In addition, when the filtration flux drops significantly, it is necessary to clean the membrane so that as much as possible, it regains its original parameters. This can be done in many ways, e.g. backwashing or chemical washing.

Therefore, presented difficulties associated with the application of ceramic membranes it was decided to examine the effect of the method of storing. Membrane was use before and has some fouling load caused by previous process. Optimization of membranes storage parameters can increase their industry adaptation, and above all at low costs, improve the operational parameters of the operation. In the experiment, it was use a hydrogen peroxide solution as an oxidant for contaminants caused by foultants, added to the distilled water during storage.

Ceramic membrane fouling and regeneration

The performance of ceramic membranes decreases with the duration of the process after each filtration. This problem is most often associated with fouling, which significantly limits the permeability and increases flow resistance. As a result, it is necessary to either replace the membrane or regenerate it. In the case of ceramic membranes, it is possible to remove part of contamination from the pores by regeneration, however initial efficiency cannot be restored [12-14]. Fouling can cause adsorption of components on the surface of the membrane and inside the pores, deformation of the membrane, reaction of molecules with membrane material, reduction of the diffusivity of particles in the pores as well as bacterial growth. The symptoms of this phenomenon are a decrease of the permeate flux during the duration of the process while maintaining a constant pressure or an increase of pressure over time at constant filtration rate conditions. Initially, separated components of a size smaller than those of the membrane's pores become partially deposited on the pore walls leading to a reduction in pore size. This results in a significant reduction of the cross-section and the surface available for filtration. Also, larger particles are adsorbed at the pore entrances, causing significant decrease of the flow and clogging of the pores. Both cases lead to the accumulation of retained particles on the surface of the membrane, increasing its resistance.

The phenomenon of fouling has been described by the classic blocking laws of filtration as first described by Hemans and Bredėe in 1935 [15], and then modified by Grace (1956) [16], Shirato et al. (1979) [17] and by Hermia (1982) [18]. Initially, this referred to the traditional filtration of liquids under constant pressure, however, currently they are used to describe the phenomena of permeate flux decline in membrane microfiltration and ultrafiltration. The model of blocking consists of four different filtration blocking mechanisms: total blocking, indirect blocking, standard blocking and the filtration cake (Fig.2). The first two phenomena describe the surface clogging of pores and refer to fouling by particles larger than the membrane pores. Standard blocking refers to the accumulation of contaminants in the pore walls, which leads to a reduction in their diameter. The mechanism of creating a filter cake is focused on the increase of the thickness of film consisting of accumulated particles on the surface of the membrane. The models assume that the pores in the membrane are parallel and have the same geometry (diameter and length) [10].

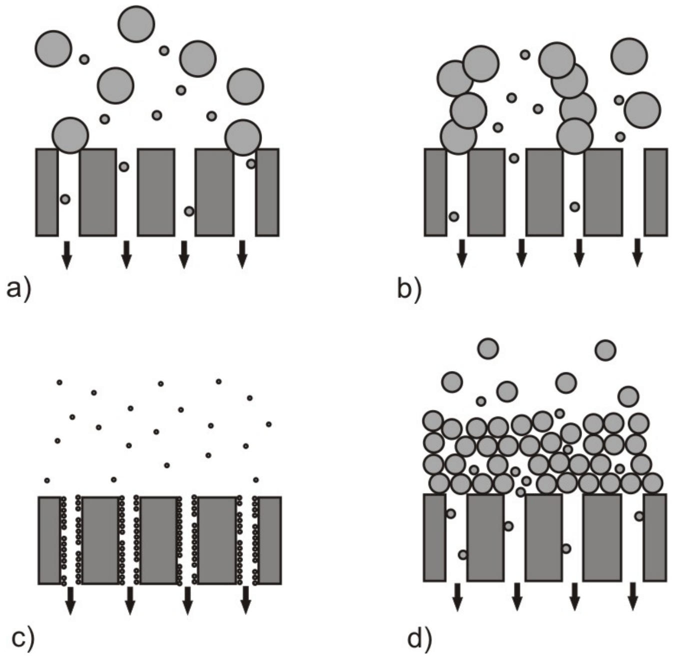

Fig. 2. Blocking filtration mechanisms: a) total blocking model, b) indirect blocking model, c) standard blocking model, d) filtration cake
Source: [10]

Fouling is unavoidable during filtration and essentially limits the ability to purify the membrane system. It is necessary to develop an innovative method of fouling reduction in order to minimize operational costs related to the maintenance of membrane filtration [8]. So far, many methods of regeneration have been invented, however, research into the discovery of a process of the highest efficiency is still in progress.

Currently, back washing is the most popular method of fighting against fouling. This method involves washing the membrane in the opposite direction than the normal membrane permeate flux. Unfortunately, this technique brings with it a high risk of damaging the active surface and structures of the membrane [19]. Destruction of the membrane causes a significant increase in installation costs. Although ceramic membranes can be regenerated using various chemical agents. A short view of the substances used is presented in Table 3. Yin and Xing (2013) investigated the fouling and cleaning of ceramic membranes after wastewater desulphurization. They found that the most effective membrane cleaning solution was 1% NaOH mixed with 0.5% NaClO [20]. Li et al. (2018) led in the process of ultrafiltration of limed sugarcane juice by ceramic membranes. To oppose fouling, membranes are washed in distillated water, followed by a mixture of 1.0% NaOH and 0.5% NaClO (similar to above) and a 0.5% HNO_3 solution. This process produces a repetitive permeate flux recovery at a level of 96.6% [21].

One of the latest methods used in water treatment technology is the combination of filtration using ceramic membranes and aeration by Air nano Bubbles [10]. Air Nano Bubbles are spherical air bubbles, 10-20 nm high and 50-100 nm wide [22]. So far, they have been used in wastewater treatment processes: for coagulation and aeration aimed at increasing the activity of aerobic microorganisms and water disinfection [23]. The membrane filtration technology with nano air bubbles effectively prevents and reduces the blocking of membrane pores, breaking the film of contaminants accumulated on the surface. Air nano Bubbles exhibit degrading properties of organic matter, which makes them an ideal solution for filtration of humic acids and proteins, e.g. BSA (Bovine Serum Albumin). Nano air bubbles remove contaminants with minimal observed side effects. Using this technology allows extension of membrane's life and reduces process costs.

Table 1. Common chemical cleaning agents used for chemical cleaning of ceramic membranes

Family	**Examples**	**General functions**
Acids	Strong: HCl, HNO_3 Weak: H_3PO_4	pH regulation, dissolution of inorganic precipitates, acidic hydrolysis of certain macromolecules
Alkalis	Strong: NaOH, KOH Weak: Na_2CO_3	pH regulation, alteration of surface charges, alkaline hydrolysis of proteins, catalyzing saponification of fats
Oxidants	NaClO, H_2O_2	Oxidation of organics; disinfection
Surfactants	Anionic: SDS Cationic: CTAB Nonionic: Tween 20	Dispersion/suspension of deposits
Chelates	EDTA	Complexion with metals, removal of mineral deposits.
Enzymes	Proteases, lipases	Catalysis of specific substrates (e.g., proteins, lipids)

Source: [24]

Materials and methods

The measurements were carried out in a laboratory-scale installation working in a cross flow mode with module for one membrane, made by Intermasz company. In industrial equipment is possibility of multi stream flow wit application of many membranes module to increase efficiency. Tubular, microfiltration ceramic membrane produced by Tami Industries was used in the research . The main parameters of the investigated membrane are shown in Table 2.

Table 2. Characteristics of tubular ceramic membrane use in tests

Active layer	**TiO_2**
Average pores [μm]	0,2
Diameter inside/outside [mm]	6/10
Length [mm]	600
Filtration area [m^2]	0,011
Number of channel	1
Operating pressure [MPa]	< 1 MPa
Operating temperature [°C]	< 300°C

Source: [25]

The experimental equipment consisted of a 10 dm^3 supply tank, a pressure circulating pump and a membrane module prepared for the used membrane. The installation is equipped with manometers from the feed and permeate to determine the transmembrane pressure. The stream temperature was thermostatically controlled by cooling water. The value of the flow rate depends on the transmembrane pressure. The membrane tested was already used for the microfiltration of milk and then for 2 months stored in distilled water. The membrane would be clogged by fats and large proteins. The aim of the study was to investigate operating parameters of the ceramic membranes after multiple use and longtime storage. The membrane hydrodynamics are determined by the following parameters:

- water permeate flux - J_v

$$J_v = \frac{V}{t * A} \quad \left[\frac{m^3}{m^2 * h}\right] \tag{1}$$

V - measured permeate volume $[m^3]$ in time t [h]
A- active filtration area $[m^2]$

- membrane resistance- R_m

$$R_m = \frac{\Delta P}{J_v * \eta} \ [m^{-1}] \qquad (2)$$

ΔP - transmembrane pressure [Pa]
η - dynamic water viscosity [Pa·s]

The experiment was carried out on the hydrodynamic of the membrane stored for 2 months in distilled water. These tests showed low permeate flux. Therefore the storage in 0.5% V/V H_2O_2 solution for 2 weeks was tested. The solution was prepared by mixing 80 ml of 30% H_2O_2 from the POCH manufacturer with 5 dm^3 of distilled water. The idea of adding hydrogen peroxide to distilled water during storage has been taken from the membrane operating instructions [6,25]. It has been suggested there to use H_2O_2 in the case of heavy contaminants on the membrane. Hydrogen peroxide is a popular oxidant, has a bactericidal effect and is cheap and easily available. The concentration proposed in the data sheet is 0.2% V/V. The experiment decided to try a higher concentration due to several tests without satisfactory results. The investigations of hydrodynamics were performed at temperatures of 25°C, 50°C and 80°C with transmembrane pressure equal to values between 0,2-0,5 MPa.

Results

The tests began with rinsing with distilled water. The hydrodynamics (the permeat flux for different transmembrane pressure for water stream) of the processes were investigated. The results of membrane permeability of distilled water is presented in Table 3. The viscosity of water was taken in accordance with literature data [26].

Table 3. Membrane permeability for water after storage in distillated water

T [°C]	η [Pa*s]	Δp [Pa]	V [cm^3]	$t_{śr}$ [s]	Jv [$m^3/s*m^2$]	Jv [$m^3/h*m^2$]	Rm [m^{-1}]
25	8,91E-04	200000	10	50,01	1,82E-05	0,065	1,23E+13
		250000	10	37,21	2,44E-05	0,088	1,15E+13
		300000	10	29,72	3,06E-05	0,110	1,10E+13
		350000	10	25,26	3,60E-05	0,130	1,09E+13
		400000	10	20,14	4,51E-05	0,162	9,95E+12
		450000	10	17,74	5,12E-05	0,184	9,86E+12
		500000	10	16,03	5,67E-05	0,204	9,90E+12
50	5,52E-04	200000	20	42,66	4,26E-05	0,153	8,50E+12
		250000	20	32,61	5,58E-05	0,201	8,12E+12
		300000	20	27,85	6,53E-05	0,235	8,33E+12
		350000	20	23,66	7,68E-05	0,277	8,25E+12
		400000	20	20,21	9,00E-05	0,324	8,06E+12
		450000	20	17,54	1,04E-04	0,373	7,87E+12
		500000	20	15,29	1,19E-04	0,428	7,62E+12
80	3,56E-04	200000	20	28,80	6,31E-05	0,227	8,90E+12
		250000	20	23,22	7,83E-05	0,282	8,97E+12
		300000	20	20,09	9,05E-05	0,326	9,32E+12
		350000	20	18,02	1,01E-04	0,363	9,75E+12
		400000	20	16,74	1,09E-04	0,391	1,04E+13
		450000	20	14,69	1,24E-04	0,446	1,02E+13
		500000	20	13,33	1,36E-04	0,491	1,03E+13

Source: Author's

The driving force behind the microfiltration process is the pressure difference, therefore along with an increase in transmembrane pressure, the permeate flow also increases. Figure 3 shows that the hydrodynamics of the membrane exhibits a linear relationship, and the stream values increase with increased feed temperature which is connected with viscosity of the water and was included in the calculations.

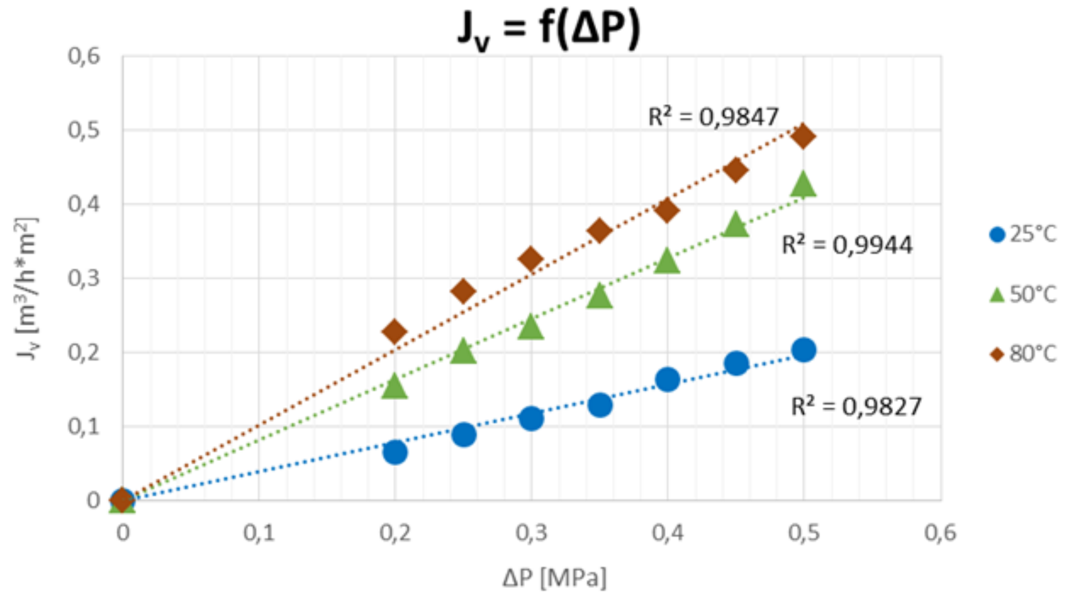

Fig. 3. Effect of transmembrane pressure on permeate volume flux for a membrane stored in distilled water
Source: Author's

Figure 4 shows the tendency of membrane resistance measured for different values of transmembrane pressure. It can be noticed that as the temperature of the media increases the membrane resistance decreases. However, at a temperature of 80 °C, the trend of membrane resistance increases. The tests of permeate flux and membrane resistance were made during one session. There is a possibility that previous experiment made elimination of the foulants at membrane surface which could expose pores of membrane and the particles from the surface could clog and decrease pores of membrane. As a result, the membrane pores have been reduced and resistance would increase.

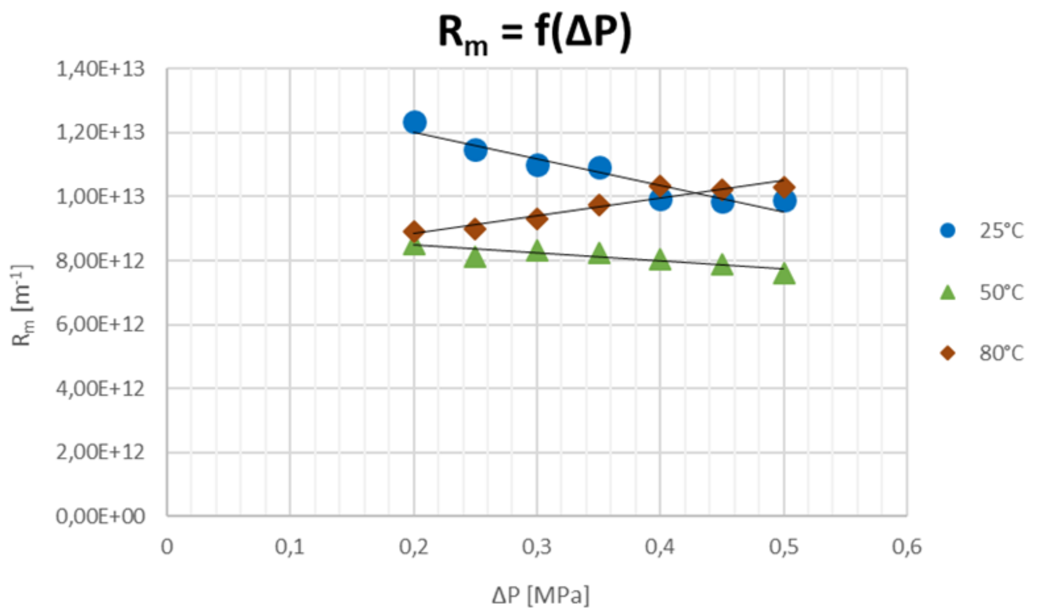

Fig. 4. Effect of transmembrane pressure on membrane resistance for a membrane stored in distilled water
Source: Author's

Despite multiple regeneration performed in accordance with recommendations (Table 4) the ceramic membrane showed results below expectation. The values of the permeate flux were too low, therefore the storage method was changed. The membrane was stored in a 0.5% solution of hydrogen peroxide for 2 weeks, after which tests were repeated. The results are shown in Table 5.

Table 4. The sequence of membrane installation rinsing according to instructions.

cleaning agent	temperature [°C]	rinsing time [min]
H_2O	25	20
NaOH 0,1M	80	40
H_2O	25	10
H_3PO_4 1%	50	20
H_2O	25	20

Source: [27]

Table 5. Membrane permeability of water after storage in 0,5% H_2O_2 solution.

T [°C]	η [Pas]	ΔP [Pa]	V [cm³]	tśr [s]	Jv [m³/s*m²]	Jv [m³/h*m²]	Rm [m⁻¹]
25	8,91E-04	100000	10	4,53	2,01E-04	0,723	5,59E+11
		150000	10	2,78	3,28E-04	1,179	5,14E+11
		200000	10	2,18	4,18E-04	1,505	5,37E+11
		250000	20	3,40	5,35E-04	1,925	5,25E+11
		300000	20	2,93	6,22E-04	2,238	5,42E+11
		350000	30	3,73	7,32E-04	2,636	5,37E+11
		400000	30	3,33	8,20E-04	2,953	5,47E+11
		450000	30	2,75	9,92E-04	3,570	5,09E+11
		500000	50	4,15	1,10E-03	3,943	5,12E+11
50	5,52E-04	100000	20	5,98	3,04E-04	1,095	5,95E+11
		150000	20	3,83	4,75E-04	1,711	5,72E+11
		200000	20	2,75	6,61E-04	2,380	5,48E+11
		250000	50	5,50	8,26E-04	2,975	5,48E+11
		300000	50	3,94	1,15E-03	4,153	4,71E+11
		350000	50	3,69	1,23E-03	4,435	5,15E+11
		400000	50	3,06	1,49E-03	5,348	4,88E+11
80	3,56E-04	100000	50	8,41	5,40E-04	1,946	5,20E+11
		150000	50	6,08	7,48E-04	2,691	5,64E+11
		200000	50	4,65	9,78E-04	3,519	5,75E+11
		250000	50	3,79	1,20E-03	4,318	5,86E+11
		300000	50	3,14	1,45E-03	5,211	5,82E+11
		350000	50	2,74	1,66E-03	5,972	5,93E+11
		400000	50	2,40	1,89E-03	6,818	5,94E+11

Source: Author's

Figure 5 shows the hydrodynamics of the examined membrane stored in 0.5% H_2O_2 solutions. The permeate fluxes presented similar relationships as membranes stored in distilled water. Furthermore, Figure 6 shows the membrane resistance for various transmembrane pressure. The values at each temperature oscillated at a similar level.

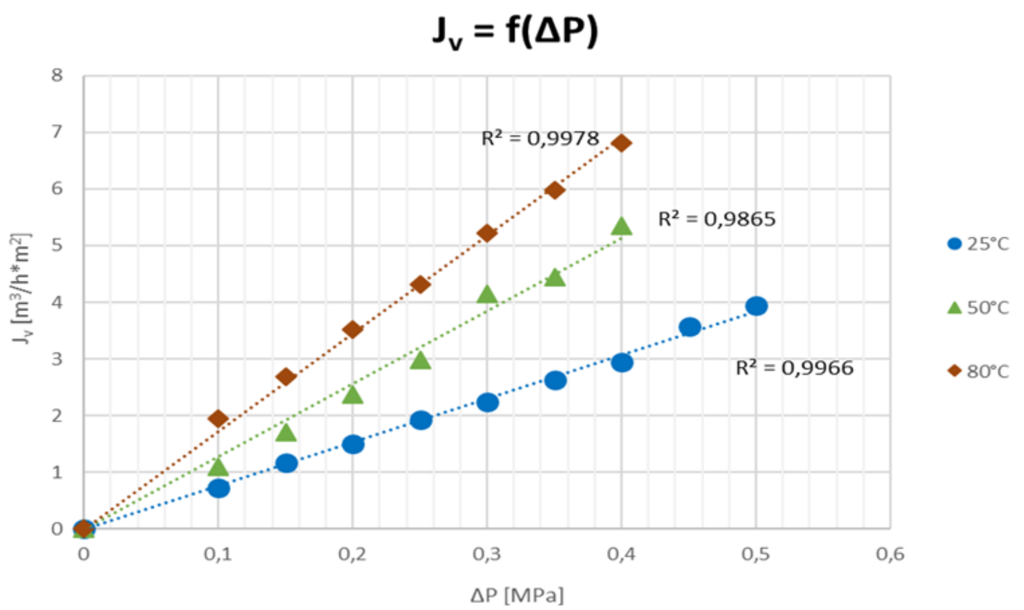

Fig. 5. Effect of transmembrane pressure on permeate volume flux for a membrane stored in 0.5% H_2O_2 solution

Source: Author's

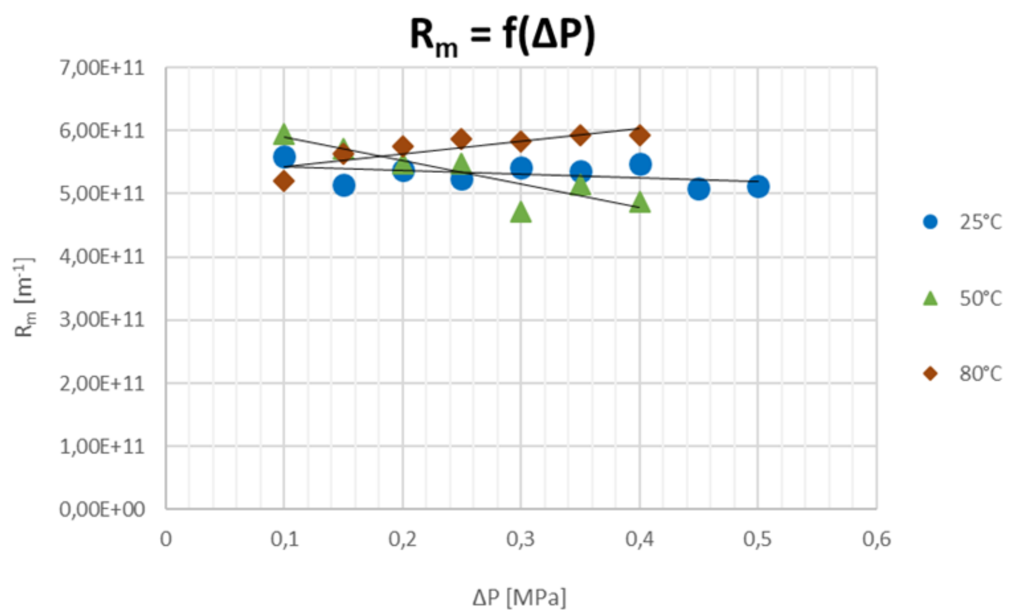

Fig. 6. Effect of transmembrane pressure on membrane resistance for a membrane stored in 0,5% H_2O_2 solution

Source: Author's

As expected, the permeate flux values for membranes stored in 0.5% H_2O_2 solutions were higher than for membranes stored in distilled water. Corresponding values of membrane resistance were lower than before. The comparison of values at a temperature of 25°C is shown in Figures 7 and 8.

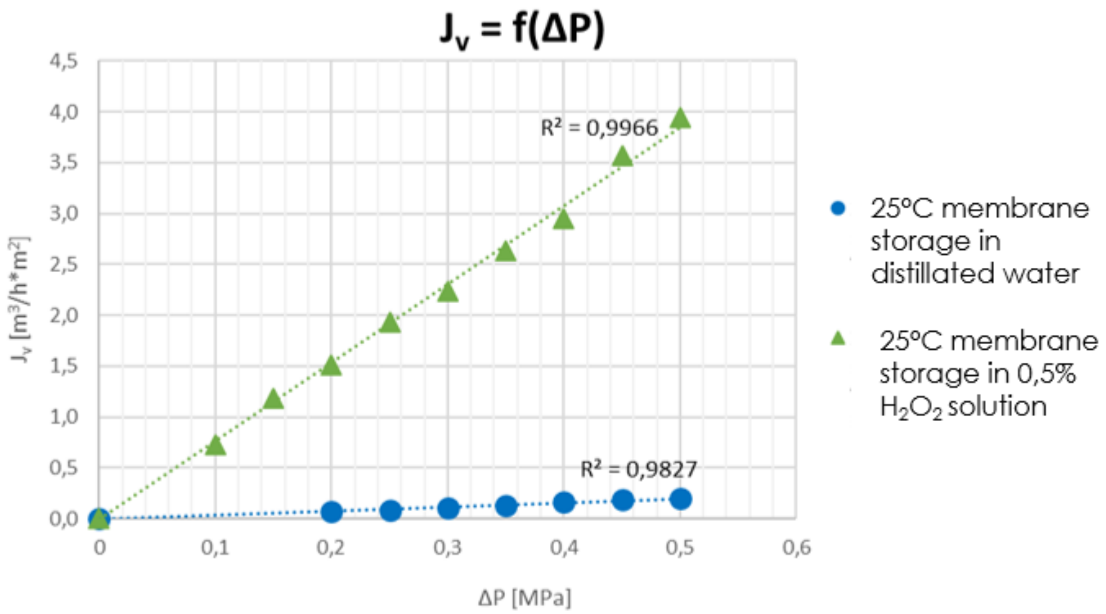

Fig. 7. Comparison of effect of transmembrane pressure on permeate volume fluxes
Source: Author's

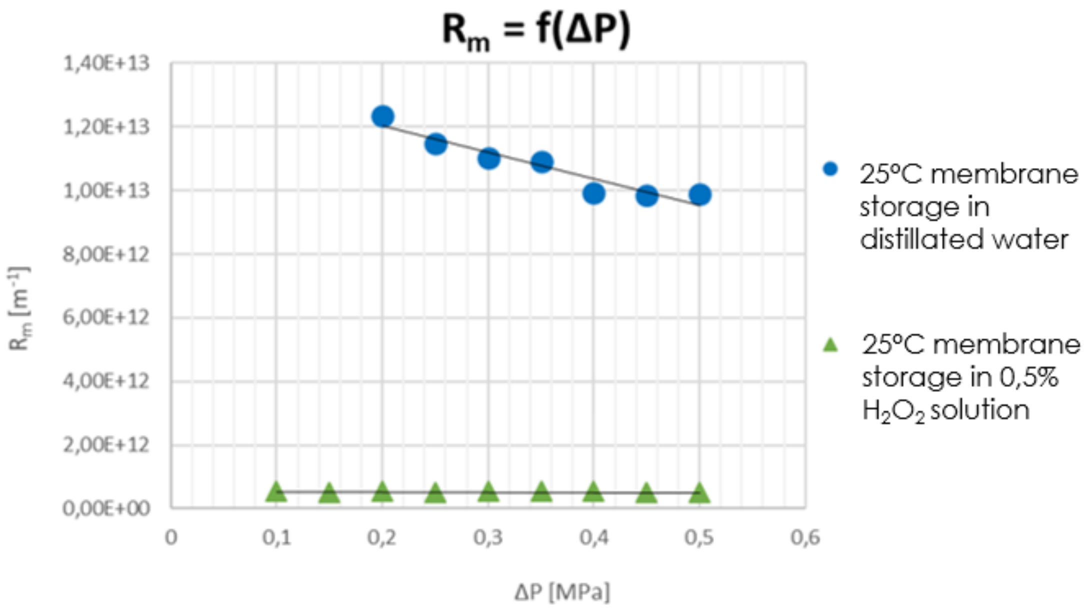

Fig. 8. Comparison of effect of transmembrane pressure on membrane resistance
Source: Author's

The research has shown that the value of the permeate flux increased about twenty times, also the resistance of the membrane decreased significantly.

Summary and conclusions

Ceramic membranes are a technology increasingly being used in industries. However, fouling remains an inherent problem, as it significantly reduces the efficiency of the process that requires the fouled membrane to be replaced with a new one. An undoubted advantage of ceramic membranes is the possibility of regeneration. Depending on the medium–filtered, the regeneration can be realized in many ways to recover the highest possible permeate flow. This study investigated the effect of membrane storage on its regeneration. It was shown that the hydrogen peroxide solution positively influenced the renewal of the membrane filtration capacity, when the fouled membranes were stored in 0.5% V/V solution for a period of two weeks which released a significant increase in the permeate flux (about 20 times), with the decrease in flow resistance.

Hydrogen peroxide is an oxidant, which removes mainly organic pollutants and was found to be more effective in this study, as compare to treatments with NaOH and ortho-phosphoric acid solutions. As the regeneration of the fouled membranes was found to be better by using hydrogen peroxide solution the same could be used for similar applications involving other processes.

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OVERVIEW OF THE EXISTING HEAT STORAGE TECHNOLOGIES: SENSIBLE HEAT

Abstract
Over the past several decades, much attention has been given to the development of technologies utilizing solar energy to generate inexpensive and clean heat for heating purposes of buildings and even for electricity generation in the concentrating solar thermal power (CSTP) plants. However, unlike conventional heat-generating technologies consuming coal, natural gas, and oil, heat produced by solar energy is intermittent because it is significantly affected by daily (day-night) and seasonal fluctuations in solar insolation. This fact issues a considerable challenge to the adoption of solar energy as one of the main renewable heat sources in the future. Therefore, along with the development of the different solar technologies, the heat storage technologies have also been the focus of attention. Use of the storage devices, able to accumulate heat, enables not only enhance the performance of the heating systems based on solar energy but also make them more reliable.

This paper gives an overview of the various sensible heat storage technologies used in tandem with the fluctuating solar heat sources.

Key words: heat storage, sensible heat, solar energy.

Abbreviations:
ATES – aquifer thermal energy storage,
BTES – borehole thermal energy storage,
CHP – combined heat and power,
COP – coefficient of performance,
CSTP – concentrating solar thermal power,
GWTES – gravel-water thermal energy storage,
HDPE – high-density polyethylene,
HT – high-temperature,
HTF – heat transfer fluid,
HWTES – hot water thermal energy storage,
n/a – not available,
NREL – National Renewable Energy Laboratory,
R&D – research and development,
TES – thermal energy storage,
TFS – thermocline-filler storage,
UHP – ultra high performance.

Nomenclature:
c – heat capacity, $\frac{J}{K}$,
c_P – isobaric specific heat, $\frac{J}{kg \cdot K}$,

dQ – infinitesimal amount of heat, J,
dT – infinitesimal change of temperature, K,
k_f – hydraulic conductivity, m/s,
T_C – absolute temperature of the cold reservoir, K,
T_f – final temperature, K,
T_H – absolute temperature of the hot reservoir, K,
T_i – initial temperature, K,
Δh – change in specific enthalpy, J,
η_t – thermal efficiency.

Introduction

Waste heat from combined heat and power (CHP) units in biogas plants and solar collectors are examples of the renewable heat sources, which can be used more efficiently when the heat storage is applied [1-4]. For example, the engine-based CHP unit has a total efficiency of up to 90%, producing about 35% of electricity and 65% of heat including around 10% of irreversible heat losses. In most biogas plants, a smaller fraction (20-40%) of the generated heat is needed for the digester heating, but the larger portion (60-80%) is considered as waste heat, which is often not used for further useful purposes and as a result wasted. As shown in [5], one of the possible solutions could be the use of the heat storage technology in biogas plants.

In the case of solar collectors installed in regions with relatively low value of solar irradiance such as Europe, use of the insulated hot water storage tanks in conjunction with the solar collectors enables to store enough hot water to cover all of the hot water requirements for several overcast days in summer until the collectors are capable to renew the major heat supply [1-2]. Moreover, there is more attractive and challenging heat supply concept when heat generated from solar collectors is retained for long period of time in heat storage reservoirs in summer for its further use for heating purposes in winter, which is also referred to as seasonal or long-term heat storage [1-3].

In both cases, the significant energy savings and consequently reduction of the CO_2 emission into the atmosphere are the logical results of the heat storage implementation. That's why the heat storage can be the best solution not only from the technical but also environmental and economical points of view [1-4].

Classification of the heat storage methods

It is well known that every energy system is composed of a primary energy source (e.g. solar energy or biogas), a transformer (e.g. solar collector or CHP unit) to transform primary energy into useful form of energy, and a final energy user-appliance (e.g. a heating system, a hot water supply system or some industrial process). However in some systems, especially with renewables, so-called spatiotemporal disagreements between the energy supply and energy consumption may arise. Therefore, the primary intent of the heat storage is to minimize or totally prevent these disagreements by means of shifting the supply of thermal energy in time. Obviously, a thermal flask is an example of the simplest and most widely used conventional heat storage device in the world.

The heat storage system usually consists of:

- storage tank, which is usually heat-insulated,
- working substance, which is also known as the storage material,
- facilities for charging and discharging. In general, for charging and discharging some special heat exchangers are used,
- and some auxiliary facilities, for instance: pumps, sensors, controllers etc., to transfer heat from, e.g. solar collectors, to the storage substance, and control the charging and discharging process.

In general, two criteria define the technology and material applied to store heat: (i) the heat storage period, and (ii) needed temperature level. Regarding the heat storage period, the storage technology can be used for [1-4]:

- seasonal or long-term heat storage, when storage period is about several months,
- medium-term heat storage, when storage period is about a week,
- and short-term heat storage, when storage period is up to 24 hours.

https://doi.org/10.32933/ActaInnovations.28.8 • 2300-5599 •

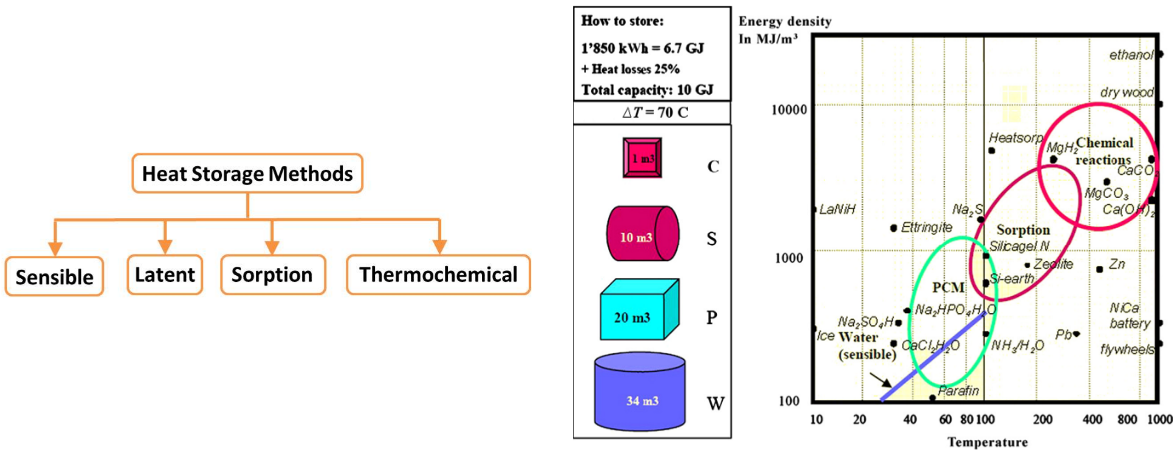
Concerning needed temperature level, the heat storage technology can be exploited for [1-4]:

- High-temperature (HT) heat storage, when the temperature of the stored heat is above 200 °C. In this case, the stored heat has the greatest energy potential and can be used as a backup heat source to support power generation in the concentrating solar thermal power plants and even some industrial processes, e.g. plastic molding, rubber and polymer vulcanization, industrial pasteurization and sterilization etc.
- Middle-temperature heat storage, when the temperature of the stored heat is above 40 °C. Such temperature level of the stored heat is particularly suitable for district heating and domestic hot water preparation.
- And for cooling applications, when the temperature of the stored heat is below 20 °C, to support air conditioning systems, refrigerators, transplants in medicine etc.

According to the system design the heat storage systems are classified as [6]:

- Direct, where the storage substance and the heat transfer fluid (HTF) are the same fluid pumped through the solar absorber and heated up on its way to the heat storage reservoir;
- Indirect, where the storage substance is located in a separate storage reservoir and another fluid transfers the solar heat from solar absorber to the storage substance by means of a heat exchanger;
- And the hybrid concept, which is a combination of direct and indirect system designs to increase flexibility and performance of the renewable energy system.

In terms of thermodynamics, heat can be stored by means of the several ways (Fig. 1, a).



(a) Source: Author's

(b)

(c) Source: [7, 8]

Fig. 1. Heat storage technologies:
(a) classification of the heat storage methods;
(b) comparison of the different heat storage technologies represented in energy cubes;
(c) energy density versus working temperature ranges of the various heat storage materials.

First, sensible heat storage, when the storage substance is heated or cooled. In this case, the technology is based on the use of the specific heat of a heat storage medium. Commonly known sensible heat storage technology is an insulated hot water storage reservoir.

The phase change or phase transition of a storage substance, e.g. melting/crystallization of paraffin, consumes/release a large amount of heat without temperature change. Therefore, in this case, the heat required to melt substance is called latent. The latent heat storage technology can provide higher storage capacity than the sensible heat storage at practically constant charging-discharging temperature.

Heat can also be stored by reversible chemical reactions and sorption physicochemical processes. Both of the storage methods can achieve the highest storage capacities compared with the sensible and latent heat storage, and they also are able to absorb and release heat at constant charging-discharging temperatures, depending on the thermochemical reaction or sorption physicochemical process.

Fig. 1 (b) illustrates a comparison of the different heat storage technologies, especially: sensible, latent, sorption and thermochemical heat storages, represented in the energy cubes. From this picture, it can be seen that in order to store 10 GJ of heat, generated by e.g. solar collectors, 34 cubic meter hot water reservoir is necessary. On the other hand, if a phase change material, e.g. paraffin, is used instead of water only 20 cubic meters of the storage material is required to store the same heat amount. And finally, if the sorption or thermochemical heat storage technologies are applied the volumes of the heat storage substances can be reduced up to 10 and 1 cubic meter respectively. That is to say, that in terms of theoretical values of the heat storage capacities as well as material consumption and the space needed for the storage reservoir the thermochemical heat storage promises the storage of the future. At the same time, as shown in Fig. 1 (c), the four heat storage technologies mentioned above are usually applied at different working temperature ranges. Thus, for low-temperature heat storage of up to 100 °C, water, and phase change materials are exploited. Sorption heat storage is appropriate to store medium heat. And finally, for HT heat storage, e.g. in CSTP plants, reversible chemical reactions are the most suitable.

Thermodynamics of the sensible heat storage

Sensible heat storage is based on the use of the heat capacity of a storage substance to retain the thermal energy. The heat capacity c is defined as a ratio of the infinitesimal amount of heat dQ, which is added to the substance, to the infinitesimal increase of temperature dT:

$$c = \frac{dQ}{dT}. \quad (1)$$

The heat capacity indicates how much thermal energy dQ a storage substance can accumulate in a temperature change dT.

According to the first law of thermodynamics, in the isobaric process the specific heat quantity, which can be accumulated in the mass unit of a storage substance, can be calculated as follows:

$$q = \Delta h = \int_{T_i}^{T_f} c_p \cdot dT, \quad (2)$$

where Δh – change in specific enthalpy of a storage substance, T_i – initial temperature, T_f – final temperature, c_p – isobaric specific heat.

If the specific heat is constant, then specific heat quantity is just multiplication of the average isobaric specific heat c_P and temperature change ($T_f - T_i$):

$$q = \Delta h = c_p \cdot \left(T_f - T_i\right). \quad (3)$$

Hot water storage

Table 1 shows thermophysical properties of some of the common materials/substances, which are currently used or can be potentially applied for sensible heat storage.

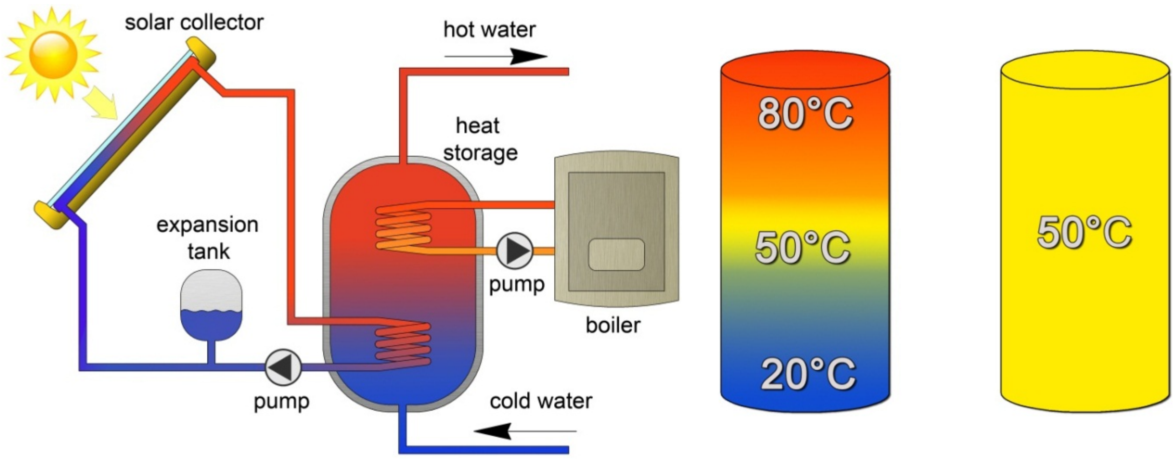
The table shows that among conventional storage media, water has the highest value of the specific heat of app. 4182 $\frac{J}{kg \cdot K}$ at 20 °C, what is more than 4 times higher than for other materials. This positive feature helps to make the heat storage system based on the water more compact. Moreover, water possesses high fluidity, which enables to use it along with the conventional pumps and heat exchangers both as a heat storage substance and HTF. Additionally, in the economic point of view, water is the most inexpensive substance to store the low-temperature heat of up to 100 °C, which is particularly suitable for domestic applications. Therefore, as shown in [9], the heat storage market is largely ruled by the hot water storage technology.

Table 1. Thermophysical properties of some of the common used sensible heat storage media at 20 °C

Material	Specific heat, $\frac{J}{kg \cdot K}$	Density, $\frac{kg}{m^3}$	Heat Conductivity, $\frac{W}{m \cdot K}$	Source
Water	4182	998.2	0.602	[10, 11]
Soil (wet)	2093	1700	2.51	[14]
Soil (dry)	795	1260-1300	0.25-0.3	[14, 15]
Clay	860-880	1500-2300	0.7-1.5	[15]
Sand	754-796	1700	0.35	[12, 16]
Granite	600-950	2640-2760	1.73 to 3.98	[12, 14, 15]
Marble	800-883	2600-2840	2.07 to 3.2	[12, 15]
Limestone	741-921	2500-2760	1.26-2.2	[12, 13, 14]
Sandstone	694-950	2200-2600	1.7-2.9	[13, 15]
Lime-and-sand brick	837-879	1800	0.7	[12, 16]
Brick magnesia	1130-1150	3000	5.0-5.1	[15]
Silica fire brick	1000	1800	1.5	[15]
Slag	840	2700	0.6	[15]
Graphite	401-610	2200-2300	122-155	[15]
Cast iron	465-837	7200-7900	29.3-73.0	[14]

Source: Author's

To sustain heating and hot water supply system, insulated hot water storage vessels are the most applicable. Fig. 2 (a) illustrates the solar hot water supply system where the solar loop filled with antifreeze is separated by a heat exchanger from the storage medium (water) within the storage reservoir. Here, a pump conveys the antifreeze through the solar collector, where it is heated and then the solar heat is transferred to the water by means of the heat exchanger. If solar insolation is not high enough, the conventional boiler is triggered to heat up water up to the appropriate temperature level. The system can also be used to provide not only hot water but also heating. The heat exchanger of the solar loop is usually installed at the bottom of the hot water storage reservoir, while the heat exchanger of the boiler at the top. This arrangement allows sustaining the temperature stratification within the tank.



(a) *Source: Author's*

(b) *Source: [17]*

Fig. 2. Solar hot water supply system:
(a) scheme of the solar hot water supply system with a hot water storage tank;
(b) two types of the thermal stratification within the tank with the same amount of stored heat: left – fully stratified hot water storage tank, right – unstratified fully mixed hot water storage tank.

According to Henninger S. [16], currently, modern hot water storage vessels combine several specific features, which improve the overall efficiency of storing solar heat, including:

- the small number of thermal bridges around the storage vessel, in order to reduce the heat losses,
- enhanced heat insulation for example by using vacuum insulation,
- siphon introductions of pipes to avoid natural convection losses,
- stratification enhancers to increase the exergy value of the content of the store,

- internal devices to reduce the speed of inlet water not to disturb stratification inside the storage vessel,
- and, large heat exchangers or mantle heat exchangers.

As shown in [18-22], since the end of the 1960ies, enhancement of the thermal stratification within the solar hot water storage tanks was the focus of the R&D attention. The vertical thermal stratification is a natural process occurring over time in an undisturbed hot water tank due to the heat losses through the external walls, which in turn initiate dynamics of water due to the density difference between cold and hot water regions.

Fig. 2 (b) illustrates two types of the vertical thermal stratification within the hot water storage tanks with the same amount of stored heat.

In thermodynamics point of view, the thermal stratification increases considerably the thermal efficiency of the hot water storage tank as given by the Carnot's formula:

$$\eta_t = 1 - \frac{T_C}{T_H}, \quad (4)$$

where η_t – thermal efficiency; T_C – the absolute temperature of the cold reservoir; T_H – the absolute temperature of the hot reservoir.

Thus, the higher temperature difference between hotter and colder water regions within the hot water storage tank, the higher the thermal efficiency of the heat stored is. Moreover, compared to some conventional media, such as bricks, glass, and soil, the not disturbed water is relatively poor heat conductor.

According to Gang Li et al. [23], based on a comparison between the fully stratified water tank and fully mixed water tank (Fig. 2, b) employed in many solar systems, the energy storage efficiency and the whole system efficiency of the former one may increase up to 6% and 20% respectively. For the seasonal TES, the average net energy and exergy efficiencies can even be improved by 60%.

Moreover, as shown in [17], thermal stratification within the storage tank results in longer operation hours of the solar collectors and thus their significantly larger utilization and thereby reduction in the use and cost of auxiliary energy.

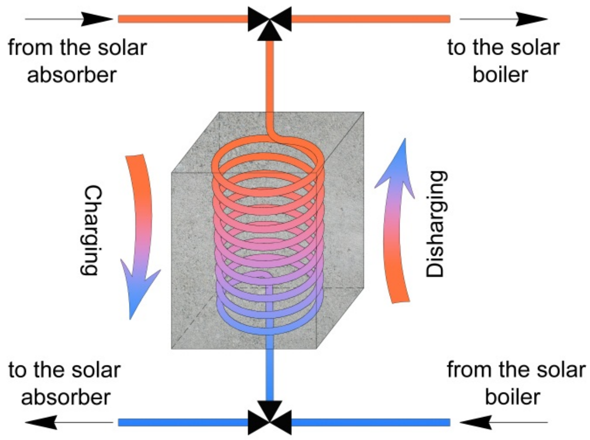
High-temperature heat storage with solid materials and molten salts

Despite some positive features of water as the sensible heat storage substance, it has an upper-temperature limit of around 100 °C only, which makes the HT heat storage for CSTP or industrial applications with water impossible. Therefore, among other sensible heat storage substances, various types of molten salts and rocks including concrete, castable ceramics and bricks are employed.

At the first blush, concrete is a very durable material. However, as shown in [24] typical structural concrete explodes violently in the temperature range between 200 °C and 300 °C. Therefore, different types of concrete and castable ceramics with improved properties were developed to allow a heat storage system operate in HT range of 500 °C-565 °C suitable for CSTP plants, industrial waste heat recovery, thermal management of decentralized CHP systems and other HT processes [25].

There are two basic concepts established to store HT heat in solid materials such as concrete, castable ceramics and natural rocks. First one is so-called passive storage concept where heat exchangers are embedded inside modular blocks of concrete or ceramics and HT fluid, usually thermal oil, molten salt or air, is pumped through them to transfer HT heat to and from the solid medium. Fig. 3 (a) illustrates the conceptual design of concrete heat storage and Fig. 3 (b) shows an actual example of the passive concept application represented with HT concrete storage in CSTP plant.

The wide range of possible operational temperatures (up to 600 °C), the modular structure of the store and environmental friendliness of the technology are obvious advantages what will enable the concrete heat storage to be the storage technology of the future, especially for CSTP plants.



(a)

Source: Author's

(b)

Source: [26]

Fig. 3. Illustration of the HT heat storage in concrete and castable ceramics:
(a) Passive HT heat storage concept in concrete;
(b) Example of the passive HT heat storage concept applied at Plataforma Solar de Almería (Spain).

Table 2 shows a list of operational CSTP plants and those, which are under construction, with the concrete and ceramic materials applied to store HT heat.

Table 2. List of CSTP plants with the concrete and ceramics heat storage

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
Zhangjiakou 50MW CSG Fresnel project, China	Linear Fresnel reflector	Water/Steam	n/a	n/a	Solid state formulated concrete	14
Zhangbei 50MW CSG Fresnel CSP project, China	Linear Fresnel reflector	Water/Steam	n/a	n/a	Solid state formulated concrete	14
Jülich 1.5 MW Solar Tower, Germany	Power tower	Air	n/a	680	Ceramic heat sink	1.5

Source: [27]

The main issue of the passive storage concept is that metallic materials usually applied to manufacture the heat exchangers have higher average value of the thermal expansion coefficient compared to concrete or ceramics, for instance $17.5 \cdot 10^{-6}$ 1/°C for 316 stainless steel [28] versus $11.8 \cdot 10^{-6}$ 1/°C and $9.3 \cdot 10^{-6}$ 1/°C for castable ceramics and HT concrete at 350 °C respectively [26]. Thus, if a material for the heat exchanger design is incorrectly selected, this will induce an intensive cracking in solid concrete blocks when heated due to the temperature stresses at the interface between the concrete material and heat exchanger. Ultimately, this will lead to the reduction of the heat storage performance. As shown in [29, 30], possible solution of this problem could be an incorporation of a soft material such as Teflon tape between concrete and tubes of the heat exchanger, which reduces considerably the stresses at the interface preventing cracking of the concrete blocks and allowing heat transfer between heat exchanger and the concrete media.

Thermo-physical properties of the different types of concrete and ceramics are presented in Table 3. In contrast to the passive concept, so-called thermocline TES system has shown good ability to store HT heat.

There are several concepts of the thermocline TES developed in recent years, such as the single tank with floating barrier [31], single tank with embedded heat exchanger [32], and the thermocline-filler storage (TFS). However, among these three concepts, the thermocline-filler storage (TFS) developed by Sandia National Laboratories [33, 34] is the most promising since it allows to use inexpensive and durable solid filler material, such as concrete, sand or natural rocks, replacing about 50-75% of the costly molten salt. Moreover, in this type of the thermocline TES system, hot air can be applied instead of molten salt as HTF.

Table 3. Thermophysical properties of concrete and castable ceramics for HT heat storage

Material	Density, $\frac{kg}{m^3}$	Heat Conductivity at 20 °C, $\frac{W}{m \cdot K}$	Specific heat at 20 °C, $\frac{J}{kg \cdot K}$	Source
HT concrete	2800	1.0	916	[15]
UHP concrete	2100-2300	1.65-2.52	800-950	[24]
High alumina concrete	2400	0.2	980	[15]
Reinforced concrete	2200	1.5	850	[15]
Castable ceramics	3500	1.4	866	[15]
Alumina ceramics	3800-4000	18.0-33.0	755-880	[15]
Silicon carbide ceramics	3200	120.0	750	[15]

Source: Author's

Here (Fig. 4, a), the system operates similarly to the stratified hot water storage reservoir but instead of water HT fluid is used as HTF being in direct contact with the solid filler [34-41]. This allows: (i) to dispense with costly stainless steel heat exchanger because HTF is in direct contact with the filler, (ii) to increase heat transfer rate since molten salt or air transfers heat directly to the solid material eliminating use of the heat exchanger, (iii) to create vertical thermal stratification within the storage container and thus increase the exergy value of the content of the store, (iv) use one container only instead of two containers, which significantly reduces cost of the storage system. It was also estimated by Sandia, that the cost reduction potential is to be about 20-37% [33, 34].

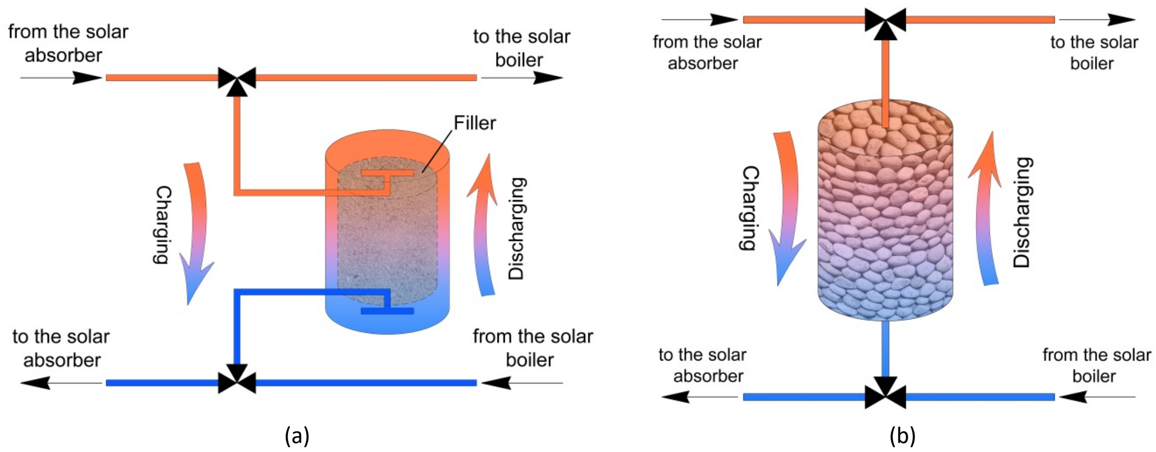


Fig. 4. Illustration of the thermocline HT heat storage concepts:
(a) thermocline heat storage concept with molten salt and UHP concrete filler;
(b) thermocline heat storage concept with molten salt or hot air and natural rock filler.

Source: Author's

However, the main problem of the thermocline HT heat storage is that filler stays always in direct contact with the corrosive hot molten salt mixture, which makes a demand to the chemical resistivity of the solid filler. Therefore, currently, many R&D efforts are made with the purpose to develop the filler, which will satisfy the requirements for chemical resistivity. One of the examples is so-called ultra-high performance (UHP) concrete able to be used in the corrosive environment and at high temperatures [24].

Recent studies [15] also showed that some natural rocks such as dolerite, granodiorite, hornfels, gabbro and quartzitic sandstone can be used as very promising and inexpensive storage materials for large-scale air-based CSTP systems equipped with packed rock bed heat storage containers.

Thermo-physical properties of these promising natural rocks are presented in Table 4.

Table 4. Thermophysical properties of the promising natural rocks suitable for HT heat storage

Material	**Density, $\frac{kg}{m^3}$**	**Heat Conductivity at 20 °C, $\frac{W}{m \cdot K}$**	**Specific heat at 20 °C, $\frac{J}{kg \cdot K}$**
Granodiorite	2700	2.1-2.6	650-1020
Gabbro	2900-3000	1.5-2.6	600-1000
Hornfels	2700	1.5-3.0	820
Quartzitic sandstone	2600	5.0-5.2	652
Dolerite	2700-2900	2.2-3.0	870-900

Source: [15]

As shown in [15, 42-51], HT heat storage in packed rock bed employed in air-based CSTP plants has some technical and economic advantages over other HT heat storage technologies: (i) low investment cost, (ii) high heat transfer rate because of the direct contact between HTF and rocks, (iii) higher efficiency because costly heat exchanger separating solar loop filled with HTF from storage container in not needed, (iii) simple and compact storage unit. Principal scheme of the packed rock bed is illustrated in Fig. 4 (b).

Table 5 shows a list of operational CSTP plants with the packed rock bed heat storage system. However, since it is the relatively new concept design for HT heat storage, which is still under development, we have found only one CSTP plant with TES system based on TFS in NREL database [27].

Table 5. List of CSTP plants based on the packed rock bed heat storage

Name of the CSTP Project, Country	**Type of Technology Applied**	**Type of the Heat-Transfer Fluid**	**Solar-Field Inlet Temperature, °C**	**Solar-Field Outlet Temperature, °C**	**Type of Rock**	**Storage Capacity, hours**
Airlight Energy Ait-Baha 3 MW Pilot Plant, Morocco	Parabolic trough	Air at ambient pressure	270	570	n/a	5

Source: [27]

Despite some benefits of the solid materials as the HT heat storage media, molten salts are widely used for large-scale HT heat storage in CSTP plants. Molten salts compared to other HT heat storage media have some benefits including excellent thermal stability at HT, low vapor pressure, low viscosity, high thermal conductivity, non-flammability, and non-toxicity. Moreover, molten salts can be designed in various chemical formulations to allow not only efficient HT heat storage at suitable temperature level but also heat transfer from the solar absorber to the storage tank and boiler.

Among different salt mixtures so-called Solar Salt, Hitec, and Hitec XL are the most widely used molten salts as the heat storage media. Thermal properties of these molten salt mixtures are represented in Table 6.

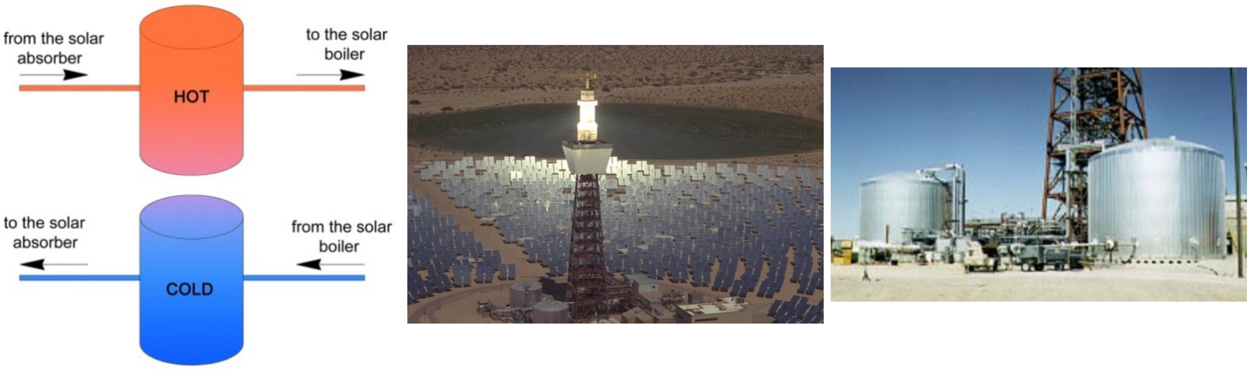
Actually, there are two concepts applied to the HT heat storage with molten salts in CSTP plants: direct and indirect. Direct storage systems (Fig. 5, a) are systems where the molten salt serves as HTF and heat storage media, hence the costly heat exchangers to transfer heat from HTF to the heat storage substance are not needed. The system consists of two molten salt storage reservoirs: one to retain enough hot molten salt after being heated in solar receiver to provide heat for water-steam cycle during cloudy periods (or even at night) when solar energy is not sufficient for steam generation by concentrating solar system; another tank to retain cold molten salt until the sun will be able to heat it up. The hot and cold molten salt storage reservoirs are installed in series to molten salt circulation in the solar cycle, before and after solar boiler respectively (see Fig. 5, a).

Table 6. Thermophysical properties of the eutectic molten salt mixtures suitable for HT heat storage

Molten Salt	**Composition, w%**	**Melting point**	**Maximum operation temperature**	**Specific heat at 300 °C, $\frac{J}{kg\cdot K}$**	**Density at 300 °C, $\frac{kg}{m^3}$**	**Viscosity at 300 °C, cp**
Solar salt	60% $NaNO_3$ + 40% KNO_3	220	585	1495	1899	3.26
Hitec	7% $NaNO_3$ + 53% KNO_3 + 40% $NaNO_2$	142	450-538	1560	1860	3.16
Hitec XL	45% KNO_3 + 7% $NaNO_2$ + 48% $Ca(NaNO_3)_2$	120	480-505	1447	1992	6.37

Source: [52]

Fig. 5, b illustrates an example of the CSTP plant with the two-tank direct heat storage applied to provide three full hours of the HT heat storage.



(a) *Source: Author's*

(b) *Source: [53, 54]*

Fig. 5. Illustration of the direct concept applied for HT heat storage with molten salt in CSTP plant:
(a) Two-tank direct heat storage concept;
(b) The two-tank direct molten-salt TES system at the Solar Two CSTP plant.

Table 7 shows a list of CSTP plants with HT heat storage systems based on the two-tank direct concept.

Table 7. List of CSTP plants with the 2-tank direct heat storage

Name of the CSTP Project, Country	**Type of Technology Applied**	**Type of the Heat-Transfer Fluid**	**Solar-Field Inlet Temperature, °C**	**Solar-Field Outlet Temperature, °C**	**Description**	**Storage Capacity, hours**
Archimede 5MW, Italy	Parabolic trough	Molten salt (60% $NaNO_3$, 40% KNO_3)	290	550	Total of 1,580 tons of molten salt. 60% sodium nitrate, 40% potassium nitrate. Capacity 100 MWh (thermal). Tanks are 6.5 m high and 13.5 m in diameter.	8
ASE 0.35 MW Demo Plant, Italy	Parabolic trough	Molten salt	290	550	molten salt	4.27 MWh-t
Atacama-1	Power	Molten salt	300	550	molten salt	17.5

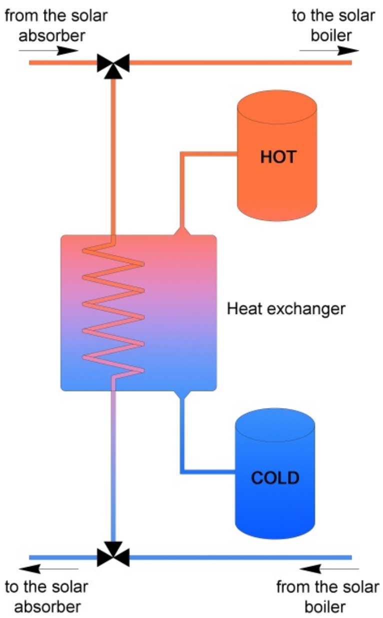
Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
110MW, Chile	tower					
Aurora 150 MW Solar Energy Project, Australia	Power tower	Molten salt	n/a	n/a	molten salt	8
Chabei 64MW Molten Salt Parabolic Trough project, China	Parabolic trough	Molten salt	n/a	n/a	molten salt	16
Copiapó 260 MW, Chile	Power tower	Molten salt	n/a	n/a	molten salt	14
Crescent Dunes 110 MW Solar Energy Project, United States	Power tower	Molten salt	288	566	TES achieved by raising salt temperature from 550 to 1050 F. Thermal storage efficiency is 99%	10
Dacheng Dunhuang 50MW Molten Salt Fresnel project, China	Linear Fresnel reflector	Molten salt	n/a	n/a	molten salt	13
DEWA 100 MW CSP Tower Project, United Arab Emirates	Power tower	Molten salt	n/a	n/a	molten salt	15
Gansu Akesai 50MW Molten Salt Trough project, China	Parabolic trough	Molten salt	n/a	n/a	molten salt	15
Gemasolar Thermosolar 19.9 MW Plant, Spain	Power tower	Molten salts (sodium and potassium nitrates)	290	565	One cold-salts tank (290 °C) from where salts are pumped to the tower receiver and heated up to 565 °C, to be stored in one hot-salts tank (565 °C). Annual equivalent hours = 5,000.	15
Golden Tower 100MW Molten Salt project, China	Power tower	Molten salt	n/a	n/a	molten salt	8
Golmud 200 MW, China	Power tower	Molten salt	n/a	n/a	molten salt	15
Hami 50 MW	Power tower	Molten salt	n/a	n/a	molten salt	8

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
CSP Project, China						
Jemalong 1.1 MW Solar Thermal Station, Australia	Power tower	Liquid sodium	270	560	Liquid sodium	3
Likana 390 MW Solar Energy Project, Chile	Power tower	Molten salt	n/a	n/a	molten salt	13
NOOR III 150 MW, Morocco	Power tower	Molten salt	n/a	n/a	molten salt	7
Qinghai Gonghe 50 MW CSP Plant, China	Power tower	Molten salt	n/a	n/a	molten salt	6
Redstone 100 MW Solar Thermal Power Plant, South Africa	Power tower	Molten salt	288	566	molten salt	12
13.8 MW Solar Electric Generating Station I, United States	Parabolic trough	n/a	n/a	307	Storage system was damaged by fire in 1999 and was not replaced	3
SunCan Dunhuang 10 MW Phase I, China	Power tower	Molten salt	n/a	n/a	molten salt	15
SunCan Dunhuang 100 MW Phase II, China	Power tower	Molten salt	n/a	n/a	molten salt	11
Supcon 50 MW Solar Project, China	Power tower	Molten salt	n/a	n/a	molten salt	6
Tamarugal 450 MW Solar Energy Project, Chile	Power tower	Molten salt	n/a	n/a	molten salt	13
Yumen 100MW Molten Salt	Power tower	Molten salt	n/a	n/a	molten salt	10

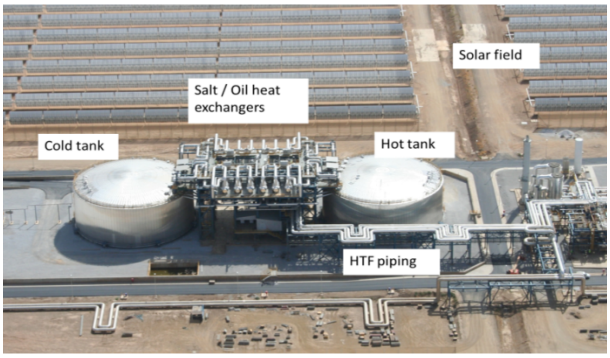
Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
Tower CSP project, China						
Yumen 50MW Molten Salt Tower CSP project, China	Power tower	Molten salt	n/a	n/a	molten salt	9

Source: [27]

Indirect storage systems (Fig. 6, a) consist of two separate storage reservoirs for hot and cold molten salt, which are connected in the parallel scheme to the solar loop. Here, HTF and heat storage media are different fluids. In the charging process, thermal oil, mostly used as HTF, transfers excess solar heat to the molten salt by means of the shell-and-tube heat exchangers, while molten salt is pumped from cold tank to the hot tank. In discharging process, e.g. at night, the hot molten salt returns back the stored heat to the thermal oil to sustain the water-steam cycle when pumped back from the hot to the cold tank.



(a)
Source: Author's



(b)
Source: [55]

Fig. 6. Illustration of the 2-tank indirect heat storage concept:
(a) Two-tank indirect heat storage concept;
(b) Two-tank indirect heat storage applied in CSTP Plant Andasol 3 (Spain).

Table 8 shows a list of the CSTP plants with HT heat storage systems based on the 2-tank molten salt indirect concept.

Table 8. List of CSTP plants with the 2-tank indirect heat storage

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
50 MW Andasol-1, Spain	Parabolic trough	DOWTHERM A *	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Andasol-2, Spain	Parabolic trough	DOWTHERM A *	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Andasol-3, Spain	Parabolic trough	DOWTHERM A *	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Arcosol 50 (Valle 1), Spain	Parabolic trough	Diphenyl/Diphenyl Oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Arenales, Spain	Parabolic trough	Diphyl	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	7.0
110 MW Ashalim, Israel	Parabolic trough	n/a	n/a	n/a	molten salt	4.5
50 MW Aste 1A, Spain	Parabolic trough	Dowtherm A *	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	8
50 MW Aste 1B, Spain	Parabolic trough	Dowtherm A *	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	8
50 MW Astexol II, Spain	Parabolic trough	Thermal oil	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	8
55 MW Bokpoort, South Africa	Parabolic trough	Dowtherm A *	293	393	molten salts	9.3 (1300 MWht)
50 MW Casablanca, Spain	Parabolic trough	Diphenyl/Biphenyl oxide	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	7.5
Delingha 50MW Thermal Oil Parabolic Trough project, China	Parabolic trough	Thermal oil	293	393	molten salts	9
DEWA 600	Parabolic	Thermal oil	n/a	n/a	molten salts	10

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
MW CSP Trough Project, United Arab Emirates	trough					
100 MW Diwakar, India	Parabolic trough	Thermal oil	n/a	n/a	molten salts	4 (1010 MWht)
50 MW Extresol-1, Spain	Parabolic trough	Diphenyl/Biphenyl oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
49.9 MW Extresol-2, Spain	Parabolic trough	Diphenyl/Biphenyl oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Extresol-3, Spain	Parabolic trough	Diphenyl/Biphenyl oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
28 MW Gujarat Solar One, India	Parabolic trough	Diphyl	293	393	molten salts	9
Gulang 100MW Thermal Oil Parabolic Trough project, China	Parabolic trough	Thermal oil	n/a	n/a	molten salts	7
Huanghe Qinghai Delingha 135 MW DSG Tower CSP Project, China	Power tower	Water/Steam	n/a	n/a	molten salts	3.7
100 MW Ilanga I, South Africa	Parabolic trough	Thermal oil	293	393	molten salts	4.5
100 MW Kathu Solar Park, South Africa	Parabolic trough	Thermal oil	293	393	molten salts	4.5
100 MW KaXu Solar	Parabolic trough	Thermal oil	n/a	n/a	molten salts	2.5

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
One, South Africa						
100 MW KVK Energy Solar Project, India	Parabolic trough	Synthetic Oil	n/a	n/a	molten salts	4 (1010 MWht)
50 MW La Africana, Spain	Parabolic trough	n/a	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	7.5
49.9 MW La Dehesa, Spain	Parabolic trough	Diphenyl/Biphenyl oxide	298	393	29,000 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW La Florida, Spain	Parabolic trough	Diphenyl/Diphenyl oxide	298	393	29,000 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
49.9 MW Manchasol-1, Spain	Parabolic trough	Diphenyl/Diphenyl oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Manchasol-2, Spain	Parabolic trough	Diphenyl/Diphenyl oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
52 MW MINOS, Greece	Power tower	n/a	n/a	n/a	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	5
160 MW NOOR I, Morocco	Parabolic trough	Dowtherm A *	293	393	molten salts	3
200 MW NOOR II, Morocco	Parabolic trough	Thermal oil	293	393	molten salts	7
Rayspower Yumen 50MW Thermal Oil Trough project, China	Parabolic trough	Thermal oil	n/a	n/a	molten salts	7
50 MW Shagaya CSP Project, Kuwait	Parabolic trough	n/a	n/a	n/a	molten salts	10
Shangyi	Power	Water/Steam	n/a	n/a	molten salts	4

Name of the CSTP Project, Country	Type of Technology Applied	Type of the Heat-Transfer Fluid	Solar-Field Inlet Temperature, °C	Solar-Field Outlet Temperature, °C	Description	Storage Capacity, hours
50MW DSG Tower CSP project, China	tower					
280 MW Solana Generating Station, United States	Parabolic trough	Therminol VP-1/Xceltherm MK1	293	393	molten salts	6
49.9 MW Termesol, Spain	Parabolic trough	Diphenyl/Diphenyl Oxide	293	393	28,500 tons of molten salt (60% of sodium nitrate and 40% of potassium nitrate)	7.5
50 MW Termosol 1, Spain	Parabolic trough	Thermal oil	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	9
50 MW Termosol 2, Spain	Parabolic trough	Thermal oil	293	393	molten salt mixture (60% of sodium nitrate and 40% of potassium nitrate)	9
Urat 50MW Fresnel CSP project, China	Linear Fresnel reflector	Thermal oil	n/a	n/a	molten salts	6
Urat Middle Banner 100MW Thermal Oil Parabolic Trough project, China	Parabolic trough	Thermal oil	n/a	n/a	molten salts	4
100 MW Xina Solar One, South Africa	Parabolic trough	Thermal oil	n/a	n/a	molten salts	5.5
Yumen 50MW Thermal Oil Trough CSP project, China	Parabolic trough	Thermal oil	n/a	n/a	molten salts	7

* DOWTHERM A is a eutectic mixture of two very stable organic compounds, biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$) [56].

Source: [27]

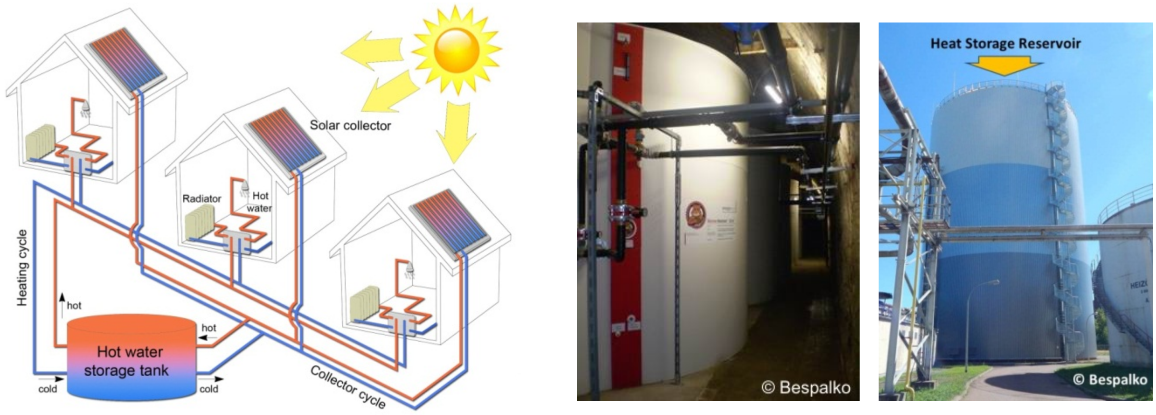
The data presented for CSTP plants (see Tables 2, 5, 7, 8) clearly show that currently, the molten salts are the most applicable for HT heat storage.

Seasonal heat storage with sensible materials
Seasonal heat storage, which is also referred to as the long-term heat storage, is used to accumulate thermal energy, e.g. generated by solar collectors installed on the building roofs (Fig. 7, a), in summer for its further use for heating purposes in winter. Along with the short and medium term heat storage, water (including groundwater) is also the most commonly used conventional heat storage substance to store heat on a seasonal time scale.

Since a bigger size hot water storage tank has the lowest value of the surface to volume ratio, the heat losses through the external walls are much lower. Hence, the seasonal heat storage systems are usually designed as the huge central hot water storage tanks with high storage capacities (Fig. 7 b, c). Moreover, by enlarging the heat storage system size the specific investment costs are reduced drastically. [57]

Generally, for seasonal heat storage, the following technologies are commercially applied: hot water tank, pit also known as gravel-water, borehole, and aquifer TES. Most of them are underground storage systems and therefore hydrogeological conditions of the location chosen for new installation define the use of one or another technology.

Long-term hot water thermal energy storage (HWTES)
Hot water tanks for seasonal heat storage are often made from steel or concrete with/without a stainless steel or plastic liner inside. Along with the advanced heat insulation minimizing the heat losses through the external walls, temperature stratification enhancers are also installed within the tanks to increase the exergy value of the content of the store. Since water has very high value of the specific heat and the power rate for charging and discharging, it is mostly used as a heat storage medium. This type of the seasonal heat storage systems has primarily been implemented in Germany in solar district heating systems with 50% or more of solar fraction [58].



(a) (b) (c)

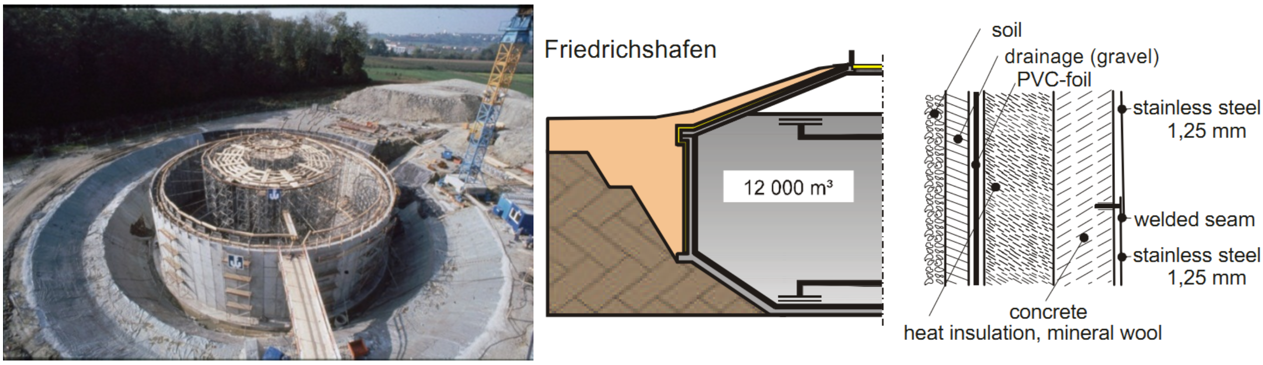
Source: Author's *Source: [59]*

Fig. 7. Solar heating and hot water supply system with central seasonal heat store (left) and examples of the underground and above ground hot water tank installations (right):
(a) functional scheme of the solar community with a central heat storage tank;
(b) 50 m^3 heat insulated hot water tanks installed in the basement of the building for long-term solar heat storage (Dessau-Rosslau, Germany);
(c) above ground 20 000 m^3 hot water storage reservoir in district heating system (Dessau-Rosslau, Germany).

There are two types of the hot water tanks' installations: above-ground and underground. Above-ground tanks are regular heat insulated tanks, which are installed on the surface of the ground as shown in Fig. 7 (c) or in the basement of the building as it can be seen from Fig. 7 (b). In both examples, the storage capacity of the single tank constitutes 20 000 m^3 and 50 m^3 of the hot water respectively.

In contrast to the above ground installations, the underground concept for constructing the hot water storage tanks benefits from the additional insulation of the external walls by natural soil from the ambient air. Since the subsurface temperature is positive and nearly constant throughout the year, the thermal losses are much lower for this type of the store in winter. The example of the underground HWTES is the hot water storage tank constructed in Friedrichshafen–Wiggenhausen (Germany) to support heating and hot water supply for 570 apartments [60].

Fig. 8 (a, b) illustrates the heat storage reservoir in Friedrichshafen–Wiggenhausen under construction and the internal scheme of the heat storage tank respectively.



(a) *Source: [61]* (b) *Source: [62]*

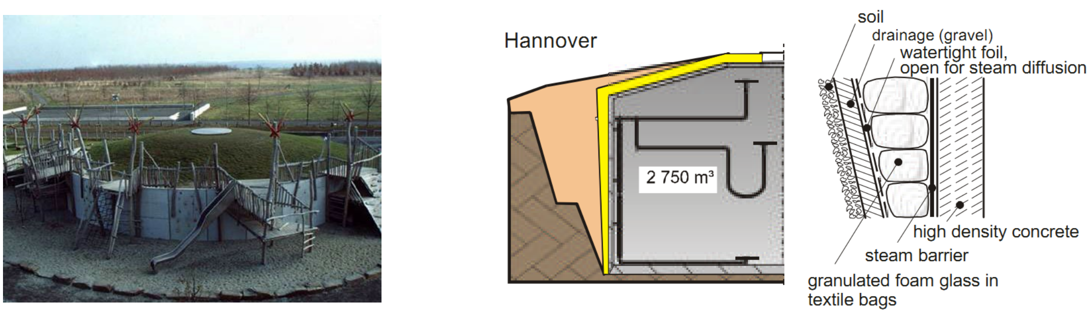
Fig. 8. Heat store in Friedrichshafen–Wiggenhausen (Germany):
(a) construction of the store;
(b) construction of the hot water storage reservoir in Friedrichshafen.

It is obvious that the heat stored in the tanks can only be used without the backing of a heat pump till the storage temperature is higher than the return temperature of the water from the district heating system [63].

The heat storage in Friedrichshafen–Wiggenhausen is in operation since 1996, where the hot water storage tank is partially buried in the ground to keep the heat losses low in winter. The storage was built using reinforced and pre-stressed concrete tank, which is heat insulated only on the roof and at the side walls and lined with 1.2 mm stainless steel sheets inside [60].

However, the cost analysis of the heat storage plant in Friedrichshafen showed that the internal stainless steel liner is a very expensive component of the tank [64]. Therefore, in a new construction concept represented in Hannover-Kronsberg, the liner is avoided by applying high density reinforced concrete [61]. But as high-density concrete is not able to prevent totally the water vapor diffusion through the walls at hot water temperatures, a layer of the vapor barrier is installed between the heat insulation and concrete [65].

Fig. 9 (a, b) illustrates the heat storage reservoir constructed in Hannover-Kronsberg and the internal scheme of the heat storage tank respectively.



(a) *Source: [66]* (b) *Source: [62]*

Fig. 9. Heat store in Hannover-Kronsberg (Germany):
(a) thermal storage tank landscaped as a public area (children's playground);
(b) construction of the hot water storage reservoir in Hannover.

Table 9 represents characteristics of the Friedrichshafen–Wiggenhausen and Hannover-Kronsberg hot water storage plants. In both cases, the planning solar fractions are 47% and 39% of the total heat demand respectively for space heating and domestic hot water preparation. Rest is covered by the fossil energy supply.

Table 9. Characteristics of the hot water storage reservoirs installed in Friedrichshafen–Wiggenhausen and Hannover-Kronsberg (Germany)

Parameter	Friedrichshafen–Wiggenhausen	Hannover-Kronsberg
Solar collector area	5 600 m^2	1 350 m^2
Type of the store	Concrete hot water store with a stainless steel liner inside	Concrete hot water store without internal liner
Volume of the store	12 000 m^3	2 750 m^3
Max. temperature	95 °C	95 °C
Service area	Final stage: 570 apartments in multifamily house	106 apartments in multifamily house
Heated area	39 500 m^2	7 365 m^2
Total heat demand	4 106 MWh/a	694 MWh/a
Solar net energy	1 915 MWh/a	269 MWh/a
Solar fraction (long-term planning)	47%	39%
In operation since	1996	2000

Source: [57, 60, 63]

In the Friedrichshafen-Wiggenhausen storage, a distributed manifold of the vertical stratification enhancer within the tank has only two injectors (Fig. 8, b), located at the top and bottom, for charging and discharging respectively. In contrast, in the Hannover-Kronsberg storage additional injector for charging or discharging was introduced (Fig. 9, b). This injector is placed at one-third of the distance from the top of the storage medium height and provides an optimized flexibility for using different water temperatures at various layers of the stratified hot water storage reservoir. [65]

According to D. Mangold and T. Schmidt [62], the storage capacity of the hot water storage reservoirs is about 60-80 kWh/m^3.

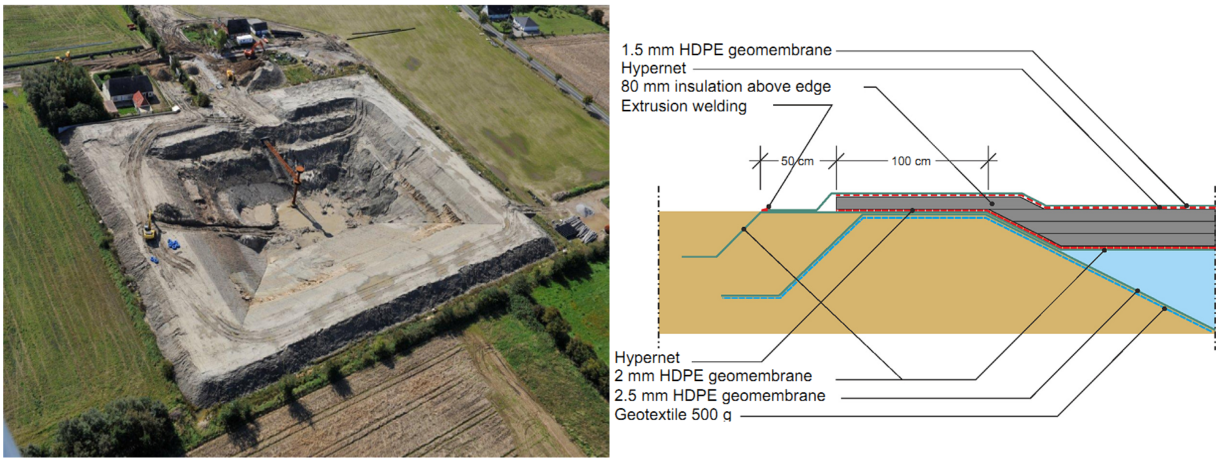
Gravel-water thermal energy storage (GWTES)

Pit thermal energy storage, which is also referred to as a gravel-water, is an underground heat storage technology realized in the form of large basins. In this case, instead of building huge and costly hot water storage tank, an excavated pit with a depth of around 5-15 meters is applied [67]. The pit is typically filled with water as a heat storage medium. Alternatively to water, gravel-water or sand-water mixtures can be used as inexpensive solid fillers with a gravel/sand fraction between 60-70% [67-69]. However, the storage capacity of this type of the storage media is lower than that of water and therefore the storage volume should be by 30-100% larger compared to HWTES technology to store the same heat amount. Nevertheless, as shown in [67], in contrast with the tank heat storage, use of the pit concept allows reducing considerably the specific cost of the store, especially for large-scale projects.

To avoid water leakage through the bottom and sides of the pit, a plastic liner, usually high-density polyethylene (HDPE), is implemented and welded separating the storage medium from the surrounding soil and making the underground storage basin tight. In addition, the pit has heat insulation usually on the sides and top to make heat losses low. Moreover, the heat stratification enhancers are also applied to increase the exergy value of the content of the store as do tank storages. [58]

Extraction and injection of the heat can be realized in an indirect way by means of a heat exchanger embedded in the pit or directly through piping installed at different layers of the store [65]. The pit heat storage operates under no overpressure, and therefore the maximum operating temperature is up to 95 °C only. [70]

The example is the pit heat storage built in New Marstal in southern Denmark with 75 000 m^3 of hot water inside providing approximately 7 500 MWh of solar heat for space heating of buildings with 27% of solar fraction and the lowest specific cost among other projects, which is the largest underground TES project in Europe (Fig. 10).



(a) (b)

Fig. 10. New Marstal pit heat storage with 75,000 m^3 of the hot water (Denmark):
(a) construction of the store;
(b) scheme of the pit heat storage.

Source: [58]

Borehole thermal energy storage (BTES)

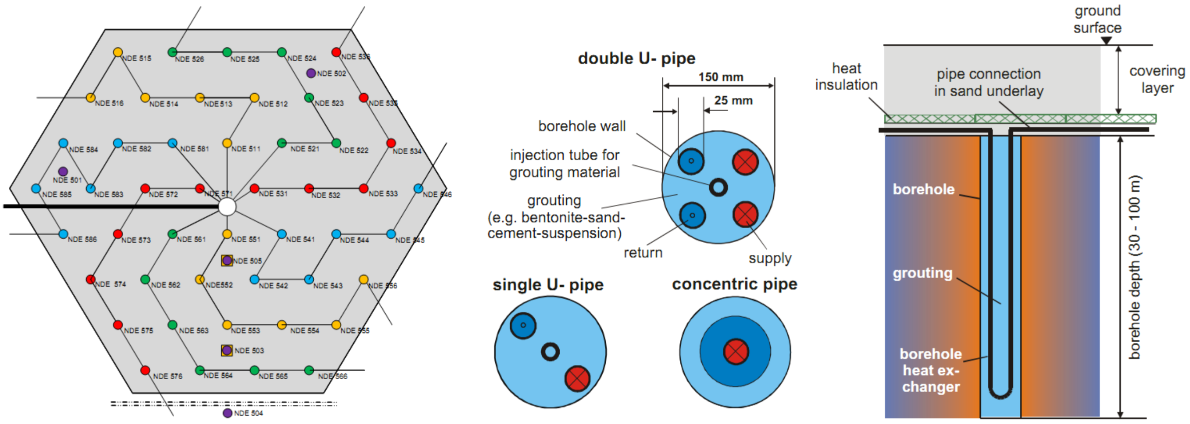
In BTES, soil serves as the heat storage medium. Here, heat is transferred to the soil by means of the ground-coupled heat exchangers installed in a number of the drilled vertical holes with a depth of up to 200 meters [71, 72] and with around 3-4 meter separation from each other [62] as shown in the layout (Fig. 11, a). In this case, the heat exchangers applied are usually in the form of U–shaped or concentric pipes (Fig. 11, b) and made of HDPE to prevent corrosion and consequently increase their lifetime [65]. The vacuous space between the heat exchangers and the surrounding soil is filled with the grouting to be a good thermal conductor between pipes and soil. The pipes of ground-coupled heat exchangers are connected to a central connection well and on the top of the borehole storage, the heat insulation with the ground as a covering layer finalizes the construction (Fig. 11, b) [58]. The thermal capacity of the BTES depends considerably on the water contents in the soil. Therefore, the water-saturated soil is the most suitable for BTES installations. On the other hand, since there is no any heat insulation in the subsurface no natural groundwater flow should be existent in the location where the BTES is planned [62]. The storage capacity of the BTES technology is about 15-30 kWh/m^3 [62].

In summer, the hot HTF is circulated in heat exchangers transferring the surplus heat, from e.g. solar field, to the soil for long-term storage. In winter, the HTF has reverse circulation and transfers the heat stored back to buildings for heating purposes. Water is mostly used as HTF. However, in some cases to prevent possible HTF freezing in winter water-antifreeze mixture is applied.

Fig. 11 (b) illustrates the common types of the ground-coupled heat exchangers and their typical installation scheme.

Depending on the working temperature range, BTES can be applied for low-temperature (0-40 °C) and high-temperature (40-80 °C) heat storage in the subsurface [73]. In the first case, extraction of the low-temperature heat occurs in combination with the heat pump. With the high-temperature store, the heat is extracted and delivered to the consumers directly with the HTF circulation. However, since the subsoil storage volume is not insulated soil overheating at high temperature may cause a moisture flow and drying effect of the soil, which will generate soil cracks and obviously reduce the performance of the underground heat store [65].

Many projects are about the storage of solar heat in summer for space heating of houses in winter. Thus, table 10 shows characteristics of some of the borehole application projects for large-scale heat storage in Europe.



(a) *Source: [58]*

(b) *Source: [62]*

Fig. 11. Borehole TES:
(a) a layout of the drilled boreholes; (b) type of borehole heat exchangers and sample installation.

Table 10. Characteristics of some large BTES projects in Europe

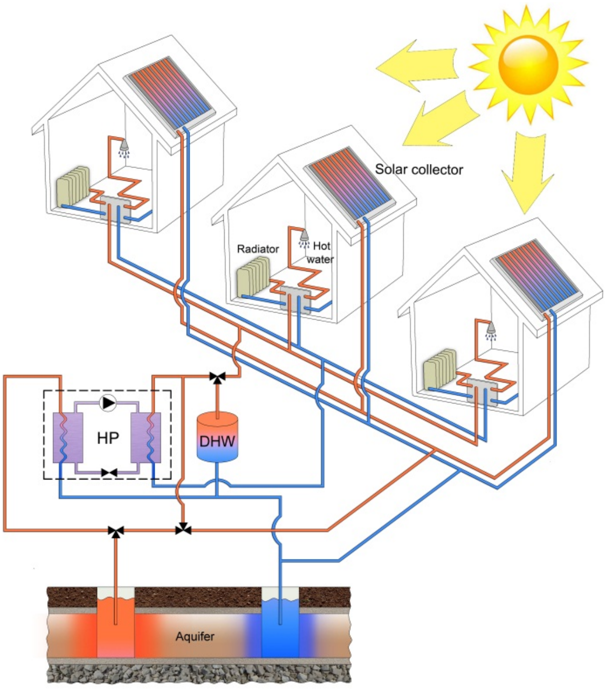
Country	**Plant**	**Year of initial operation**	**Service building**	**Solar collector**	**Borehole storage**	**Load size (MWh/a)**	**Solar fraction (%)**
Italy	Treviglio	1985	Existing residential area	2 727 m^2, roofmounted, flat plate	43 000 m^3	-	70
Sweden	Lidköping	-	New residential area, 40 two family houses	2 500 m^2, roof module	15 000 m^3 clay	980	70
Sweden	Anneberg	2002	50 residential units with about 120 m^2 floor area each	2 400 m^2, roofmounted	60 000 m^3 crystalline rock; 100 65-m-deep boreholes that filled with double U-pipes	550	70 (calculated)
Germany	Neckarsulm	1999	20 000 m^2	5 470 m^2	6 3360 m^3, doubled in U-shape duct of 30-m-deep	1 700	50
Germany	Attenkirchen	2002	6 200m^2, 30 low energy homes	836 m^2	9 350 m^3, 90 borehole double-U-loops heat exchangers with 30 m depth	487	55
Germany	Crailsheim	2007	260 houses, school and gymnasium	7 300 m^2 vacuum tubes collector	37 500 m^3, double U-pipes, 80 boreholes with a depth of 55 m	4 100	50
Netherlands	Groningen	1984	New residential area	2 400 m^2 roof-mounted evacuated	23 000	-	65
Canada	Drake Landing Solar Community (DLCS)	2007	52 detached energy efficient homes	2 293 m^2 flat-plate, roof-mounted	33 657 m^3; 144 boreholes with a depth of 35 m	530	97

Source: [74]

Aquifer thermal energy storage (ATES)

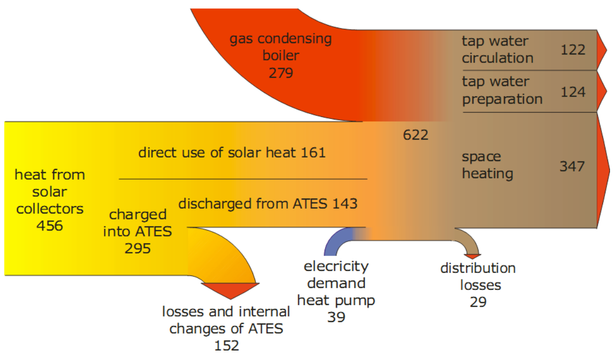
The term "*aquifer*" refers to a permeable and saturated with water underground layer of porous rock or unconsolidated materials such as soil, sand, clay, gravel, loam and etc. [75]. The aquifer can be found in the subsurface where geologic formations are permeable enough to rainwater and able to store large quantities of groundwater [76]. At the same time, the groundwater temperatures stay almost constant at 1-2 °C in the depth between 10 and 30 meters [77] and as a result, in locations where the groundwater is available, the aquifer may serve as a reliable source of low-temperature geothermal energy [76].

An example of the ATES system is a system installed in Rostock-Brinckmanshöhe (Germany) to supply a multifamily house with a heated area of 7 000 m^2 in 108 apartments with space heating and domestic hot water preparation (Fig. 12). According to the heat balance diagram illustrated in Fig. 12 (c), the efficiency of the ATES system constructed in Rostock is closed to 50%.



(a)
Source: Author's

(b)
Source: [78]



(c)
Source: [78]

Fig. 12. Aquifer TES:
(a) functional scheme of the ATES system operation;
(b) multifamily house with ATES system installed in Rostock-Brinckmanshöhe;
(c) energy flow diagram for the year 2003 (numerical values in MWh).

In contrast to the BTES, the ATES is distinguished as an open heat storage system because the groundwater is used both as HTF and heat storage medium.

Injection and recovery of the heat into and from the groundwater is realized by using two or several wells drilled into the aquifer named warm and cold wells. In a charging mode, the groundwater is extracted from the cold well, transported through the heat exchanger where it is heated up directly by utilizing industrial waste heat or solar heat in summer and then is injected back into the aquifer for storage forming so-called a warm well nearby. In a discharging mode, the warm water is extracted from the warm well and recovery of the heat stored occurs by means of a heat pump, and used for space heating or domestic hot water preparation in winter. Due to the changing and discharging flow directions cold and warm wells have to be equipped with pumps, production and injection pipes [78]. Since in the subsurface, there is no any heat insulation between the wells and the surrounding soil the natural groundwater flow should be as low as possible to reduce potential heat losses.

Depending on the temperature level of the heat stored, the ATES systems are classified as: (1) cold storage, (2) heat storage, or (3) combined cold and heat storage systems. [79]

Injection, storage, and extraction of the chilled water in a temperature range between 6-12 °C provide excellent cold storage with high efficiency between 70 and 100 %. This temperature level is appropriate for cooling purposes in summer without the need for a heat pump operation. [76]

Injection, retain and recovery of the heated water allow heat storage in the aquifer. [76] Potentially the temperature of the heated water injected into the subsurface could be up to 95 °C because the groundwater is not heavily pressurized and therefore higher temperatures are impossible to be achieved. At the same time higher temperatures of the heat stored causes high heat losses and as a result efficiency of the heat storage is lower than that for cold storage and varies between 50-80%. Along with this, some countries, such as Germany, have implemented restrictions aimed to protect environment from warming and therefore most of the ATES installations operate at low or moderate temperatures up to 50 °C [63] and therefore heat extraction from the well is realized by heat pump operation to cover heat demand in winter.

Combined ATES systems provide both cold and heat storage. According to Ghaebi et al. [80], the ATES system used both for cooling and heating purposes is the best solution in terms of the high value of COP. Thus, the COP values of about 17.2 and 5 can be achieved for cooling and heating applications respectively.

Table 11 represents characteristics of the ATES system installed in Rostock-Brinckmanshöhe. The planning solar fraction is 62% of the total heat demand including space heating and domestic hot water preparation. The remaining heat load is covered by a gas condensing boiler [78].

Table 11. Characteristics of the aquifer TES system installed in Rostock-Brinckmanshöhe (Germany)

Parameter	**Rostock-Brinckmanshöhe**
Solar collector area	980 m^2
Type of the main store	aquifer TES
Life time for ATES	40 years
Depth of the aquifer	15-30 meters
Number of the wells drilled	2
Distance between wells	55 meters
Max. design ground water flow rate	15 m^3/h
Hydraulic conductivity of the aquifer	k_f=6·10^{-5}-9·10^{-5} m/s
Mean volumetric heat capacity	$2.7 \frac{MJ}{m^3 \cdot K}$
Mean thermal conductivity	$3.2 \frac{W}{m \cdot K}$
Volume of the ATES	20 000 m^3
Max. heat storage temperature	50 °C
Type of the buffer heat store	Insulated hot water tank
Volume of the buffer heat store	30 m^3
Max. temperature of water in the buffer heat store	50 °C
Domestic hot water system	2 central 750-liter tanks
Temperature level used for domestic hot water preparation	65 °C
Type of the heat pump installed	Absorption heat pump
COP of the heat pump	6-7 at the beginning of the discharging period 3.5 at the end of the discharging period
Heat output of the heat pump	100 kW_{th} (thermal power)
Service area	108 apartments in multifamily house
Heated area	7 000 m^2
Total heat demand	497 MWh/a
Solar net energy	307 MWh/a
Solar fraction (long-term planning)	62%
In operation since	2000

Source: [57, 60, 63, 78]

Comparison of the underground TES technologies is presented in Table 12.

Table 12. Comparison of the different seasonal heat storage technologies

Type of the underground TES	HWTES	GWTES	BTES	ATES	Source
Storage medium	Water	Water / Gravel-water	Ground material	Saturated water ground	[62]
Heat capacity, kWh/m^3	60–80	60-80 / 30–50	15–30	30–40	[62]
Storage volume (for 1 m^3 of water equivalent), m^3	1	1.3–2	3–5	2–3	[62]
Operational temperature	up to 95 °C	up to 95 °C	0-40 °C (low temperature applications), 40-80 °C (HT applications)	6-12 °C (cold storage), 13-25 °C (low temperature heat storage), 25-40 °C (moderate temperature heat storage), 40-95 °C (HT heat storage)	[57, 60, 63, 65, 79, 81]
Efficiency	90%	90%	40-60%	70-100% (for cold storage), 50-90% (for heat storage)	[63, 65, 67, 73, 79]
Approximate cost per 1 m^3 of water equivalent * **	160 Euro/m^3	120 Euro/m^3	95 Euro/m^3	40 Euro/m^3	Estimated based on data from [67]
Advantages	- High thermal storage capacity of water, - High charging/discharging power, - Freedom of design (geometry), - Thermal stratification	- Reasonable construction cost, - Medium (for gravel-water mixture) to high (for water) thermal storage capacity, - Nearly unlimited dimensions of the store, - Thermal stratification	- Low construction cost, - Easily extendable just by drilling additional boreholes	- Very low construction cost, - Medium thermal storage capacity	[82]

Table 12. Comparison of the different seasonal heat storage technologies (continued)

Type of the underground TES	HWTES	GWTES	BTES	ATES	Source
Disadvantages	- Limited size (<100 000 m³), - High construction cost	- Sophisticated construction of cover (so called floating cover for water), - Limited freedom of design (especially slope angle of the sides)	- Low thermal capacity, - Low charging/discharging power, - Buffer storage required, - Heat pump recommended, - Limited choice of locations - No thermal insulation at sides and bottom	- Low/medium charging/discharging power, - Heat pump recommended, - Very limited choice of installation, - No thermal insulation	[82]
Geological requirements	- Stable ground conditions, - Preferably no groundwater, - 5–15 m deep	- Stable ground conditions, - Preferably no groundwater, - 5–15 m deep	- Drillable ground, - Groundwater favorable, - High heat capacity, - High thermal conductivity, - Low hydraulic conductivity (k_f<10^{-10} m/s), - Natural ground-water flow <1 m/a, - 30–100 m deep	- Natural aquifer layer with high hydraulic conductivity (k_f>10^{-5} m/s), - Confining layers on top and below, - No or low natural groundwater flow, - Suitable water chemistry at high temperatures, - Aquifer thickness 20–50 m	[62]

* The cost does not include VAT, system cost (e.g. cost of the heat pump if necessary), and maintenance cost.
** The cost was estimated for four reference pilot projects: München (HWTES), Chemnitz (GWTES), Neckarsulm (BTES), and Rostock (ATES).

Source: Author's

The cost estimation of the four different underground TES technologies described, clearly shows that the most expensive way to store heat on a seasonal time scale is HWTES. At the same time, ATES seems to be the most inexpensive technologies among others. The cost was estimated using data from [67] for four reference projects with approximately the same amount of water equivalent storage volume. Generally, as shown in [67], there is a strong tendency in the reduction of the investment cost from 250 Euro to 40 Euro per 1 m^3 of water equivalent with increasing the storage volume.

Summary and conclusions

The scope of this paper was to give an overview of the existing sensible heat storage technologies applied in thermal energy systems based on fluctuating renewable heat sources to overcome the problem of mismatch between the thermal energy supply and consumption.

In the analysis, the general classification and thermodynamics of the heat storage methods were presented and the following sensible heat storage technologies were discussed: hot water storage with thermal stratification, HT heat storage in CSTP plants, and seasonal underground TES technologies, especially: HWTES, GWTES, BTES, and ATES.

Many factors influence the selection of the appropriate heat storage method. First of all, the time scale to store heat, temperature level needed, and estimated heat demand.

If operation temperature is below 100 °C, storage period is short- or medium-term, and the heat demand is only for a single family house then the conventional hot water storage tank is the most suitable technology because it offers the most inexpensive way to store heat. Therefore, this type of technology dominates in the heat storage market. Moreover, hot water tank always benefits from initiation of the temperature stratification within the storage reservoir since the exergy value of the store as well as the solar collector's efficiency increase with enhancing the temperature stratification.

When it comes to implementing the long-term heat storage or heat storage for multifamily houses/solar communities with high heat demand, one of the four underground heat storage technologies, notably: HWTES, GWTES, BTES or ATES, can be employed. Here, the geological conditions of the place chosen for underground installation play a significant role. At the same time, as shown in our analysis, among underground heat storage technologies, ATES is the most inexpensive and relatively efficient way to store heat. However, since the heat is stored at low or moderate temperature level, the heat extraction is impossible without the heat pump operation.

Concerning HT heat storage, crucial for CSTP plants, currently, molten salts are largely used for this purpose in 2-tank direct and indirect schemes. However, these two HT heat storage concepts require huge storage volume because the specific heat of the molten salts is relatively low.

The storage substances applied for sensible heat storage have the following advantages:
- they are low priced, e.g. water, molten salts etc.,
- they are durable since there is no any chemical decomposition during operation and they offer long-term exploitation without performance degradation,
- they are relatively simple in use in terms of realization of the heat and mass transfer, e.g. conventional heat exchangers and pumps can be utilized for transferring heat and conveying the HTF or even storage media (e.g. water or molten salts) respectively.

On the other hand, sensible storage substances have some inherent imperfections:
- only small heat amount can be accumulated compared to other storage technologies such as latent, sorption and thermochemical heat storage, therefore the sensible heat stores should contain a large volume of the storage medium to retain the same heat amount,
- sensible storage substances cannot provide constant temperatures in charging and discharging and therefore to store more heat greater overheat is needed, which results in essential heat losses and reduction of the storage efficiency.

Thus, in the recent years, the results achieved in developing TES systems show that the sensible heat storage technologies are the most technically reliable and economically feasible. As a consequence, nowadays the sensible TES systems are the most applicable storage systems in tandem with the intermittent renewable heat sources. Nevertheless, research is still needed, especially on material and the system design, for the purpose to reduce cost, increase the storage capacity and efficiency.

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